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**ORIGINAL ARTICLE**

# Prevent the Nutrients Release from Polluted Marine Sediments Using Recycled Waste Oyster Shell Powder

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## Abstract

To evaluate the remediation performance of recycled oyster shell powders to control nutrients release from polluted sediments. Different types of recycled oyster shell powder were applied on separated bottom sediments. The first type of oyster shell powder is Calcined Oyster Shell Powder (COSP) and another consist of ultrasonicated oyster shell powder (SOSP) which were composed of calcium peroxide. The recycled oyster shell powders were improving the water quality as slow oxygen releasing compound. The experimental results indicated that the Dissolved Oxygen (DO) in the treated columns were higher than the control column. pH was increased in the both experimental columns due to the hydrolysis of $CaO_2$. Meanwhile, recycled oyster shell powders could prevent the nutrients (nitrogen and phosphorus) release from sediments into the overlying water. In addition, the total nitrogen and total phosphorus concentrations of the COSP applied column were decreased 27% and 20% compared to the control column respectively and the SOSP applied column were decreased 33% and 27% compared to control in the overlying water. It was proved that, COSP and SOSP can effectively adsorb phosphorus from sediments and prevent phosphorus release into overlying water from bottom sediments. In conclusion, COSP and SOSP applications was increased DO in the overlying water and nutrient released controlled effectively from the sediment.

**Key words** : Nutrients release, Nitrification, Eutrophication, Water quality, Oyster shell

## 1. Introduction

Contaminated marine sediments is a serious problem in coastal areas. It is caused mainly inputs high loading of nutrients from industrial wastewater, aquaculture activities, agricultural waste etc. (MOF, 2013; Zhang et al., 2015). Input nutrients containing nitrogen, phosphorus and organic matter accumulated in the sediment which is act as internal pollution source. Under different environmental conditions, nitrogen and phosphorus are released from sediments into overlying water become the main cause of eutrophication (Carpenter et al., 1998). The nutrient release occurred eutrophication causes the excessive

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reduction of oxygen reduction potential level and dissolved oxygen concentration in the coastal areas (Li et al., 2016). Moreover, it is important to reduce nutrient release from the sediments as well as controlling coastal eutrophication. Many methods have been developed at the nutrients decreasing from sediment water interface by using calcium oxide, calcium peroxide, magnesium peroxide, blast furnace slag, granulated coal ash, calcium nitrate etc. (Aelion and Bardley, 1991; Acton and Barker, 1992; Asaoka and Yamamoto, 2010; Nykänen et al., 2012; Yamamoto et al., 2013; Liu et al., 2015). Therefore, finding new materials which is efficient, environment-friendly, and low cost for the remediation of contaminated marine sediments.

Recycling Oyster Shell Powders (OSP) used in this study for preventing nutrients release from sediments to water. The waste oyster shell powder is consisting of 97% calcium carbonate (Boyjoo et al., 2014). It has been used as a construction material, cement clinker, soil conditioner limestones in fertilizer etc. (Cheon and Song, 2003; Kwon et al., 2004; Yang et al., 2005; Yoon et al., 2005). Recycled oyster shell powder ($CaO_2$) is a slowly release oxygen in the water. The released oxygen can promote contaminant's oxidation and enhance in situ aerobic microbial degradation (Hanh et al., 2005; Liu et al., 2006).

The main objectives in this study were to examine the ability of calcined and ultrasonicated waste oyster shell powder to prevent nutrients release from contaminated sediment.

## 2. Materials and Methods

### 2.1. Sample collection and study area

In this study, marine sediment and water were collected in the mariculture sea area of Tongyeong bay, in the southern part of Korea. The sediment sample was collected from 0 to 15 cm below the sediment-water interface using a grab sampler. The collected sediments were packed in airtight polyethylene bags and stored at 4℃. Seawater samples were collected from 0.5-1.0 m depth below the surface water. The sediment samples were strained to remove debris and pebbles, followed by homogenized before column packing and sediment characterization.

### 2.2. Preparation of calcined and ultrasonicated oyster shell powders (COSP and SOSP)

The natural oyster shells are consisting of 97% calcium carbonate (Boyjoo et al., 2014). Natural oyster shell powder dried in a drying oven was ground for fine formation by using mortar. The fine oyster shell powder passed through the 0.85 mm sieve. The fine oyster shell powder was calcined at ambient air condition inside an electric furnace at a constant temperature of 900℃ for 1 hour. After that heat treatment, it is mixed with some calcium carbonate containing $CO_2$ portion and most of crystalline CaO (Boyjoo et al., 2014). The main components were showed that, the waste oyster shell included calcium carbonate ($CaCO_3$) and after calcination it can be almost completely converted to calcium oxide (CaO). The crystalline CaO turned to be a hydrated form of calcite, namely $Ca(OH)_2$. Then calcium hydroxide was reacted with hydrogen peroxide to produce calcium peroxide ($CaO_2$), which is a so-called calcined oyster shell powder (COSP), an oxygen releasing compound. Involved reactions are shown as follows:

$$CaCO_3 \xrightarrow{\text{Calcination}} CaO + CO_2 \quad (1)$$

$$CaO + H_2O \longrightarrow Ca(OH)_2 \quad (2)$$

$$Ca(OH)_2 + H_2O_2 \longrightarrow CaO_2 + 2H_2O \quad (3)$$

One part of shell powder was sonicated with distilled water for 60 min (powder: water(w/w) =1:2) using an ultrasonicator (T18, Ultra-turrax, USA). The dried powder was milled and then oxidized with

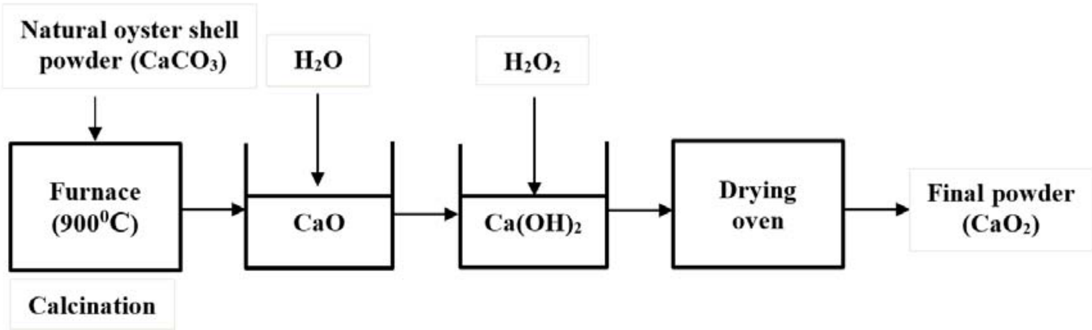


**Fig. 1.** The process of preparing calcined oyster shell powder (COSP).

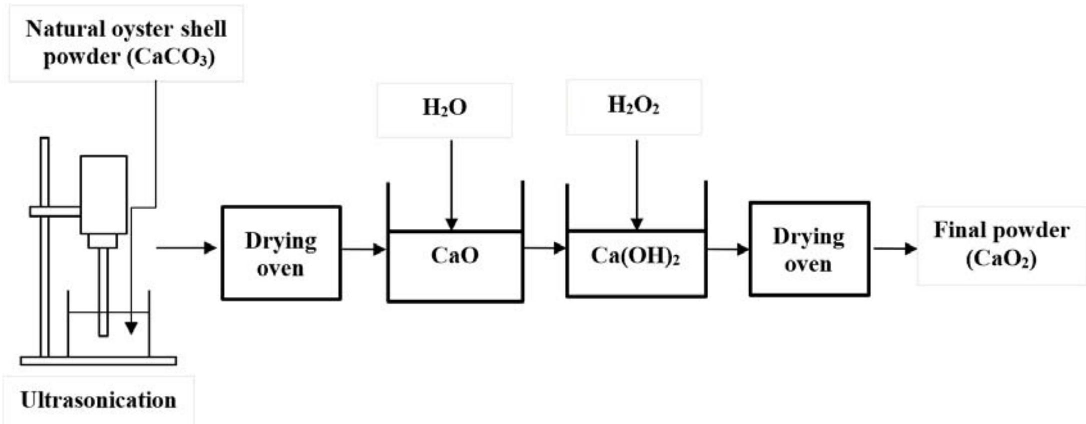


**Fig. 2.** The process of preparing ultrasonicated oyster shell powder (UOSP).

hydrogen peroxide. The re-milled powder was used for experiments, which is called Sonicated Oyster Shell Powder (SOSP), as oxygen releasing compound. The involving chemical reactions are shown in Eqs. (4), (5) and (6).

$$CaCO_3 \xrightarrow{\text{Ultrasonication}} CaO + CO_2 \quad (4)$$

$$CaO + H_2O \longrightarrow Ca(OH)_2 \quad (5)$$

$$Ca(OH)_2 + H_2O_2 \longrightarrow CaO_2 + 2H_2O \quad (6)$$

### 2.3. Experimental incubation

For laboratory-scale experiments was conducted in a 3-L transparent column (100 cm height × 6 cm diameter). 300 gm sediment was added into the column to a height of 20 cm from the bottom. Calcined Oyster Shell Powder (COSP) and Sonicated Oyster Shell Powder (SOSP) were added in the sediment (0.5% w/w) and mixed to be fully homogenized each column. While another column prepared as control by the same quantity of natural sediment. 2-L of filtered seawater was slowly added to the column to avoid resuspension of sediment. The columns were roofed by aluminum foil and stood in room temperature (22℃ ± 2℃). The overlying water samples analysis were conducted on the days of 0, 3, 9, 12, 15 and sediment samples were analyzed before and at the end of the experiments.

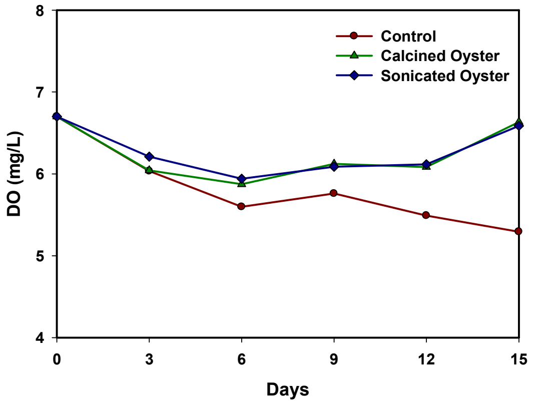


**Fig. 3.** Change of DO in the overlying water by addition of COSP, SOSP (0.5% w/w) and control for 20 d.

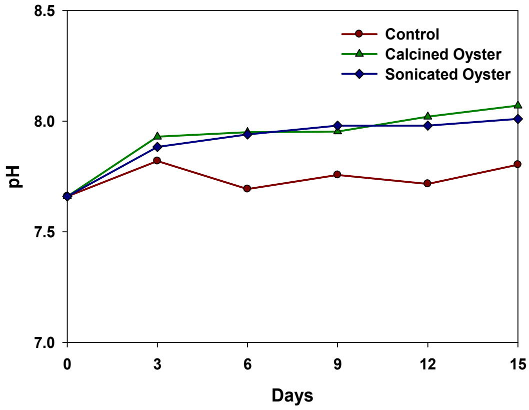


**Fig. 4.** Change of pH in the overlying water by addition of COSP, SOSP (0.5% w/w) and control for 20 d.

### 2.4. Analysis of physicochemical property and chemical analysis

The pH and Oxidation-Reduction Potential (ORP) were measured using a multifunctional meter (Orion 3 star, USA). Dissolved oxygen of the overlying water was measured with a DO meter (YSI 550A, USA). Before analysis, the overlying water samples were filtered by microfiber filter (47 mm, GF/C). The concentration of T-N, $NH_4^+$-N, $NO_2^-$ -N and $NO_3^-$-N in the filtrate were analyzed by potassium persulfate oxidation assays, indophenol blue method, N-(1-naphthyl)-ethylenediamine adsorption spectrophotometry and cadmium-copper column reduction method respectively according to the following previously described (Huh et al., 2016). Total phosphorus (T-P) and phosphate ($PO_4^{3-}$) were measured using the ascorbic acid reduction method. For all experiments, overlying water and sediment were conducted in triplicate and the average result were used.

## 3. Results and Discussion

### 3.1. Changes of pH and DO in the overlying water by adding oyster shell powder

The pH and DO concentration of recycled oyster applied columns were higher than control column in the overlying water. The initial concentration of DO was 6.8 in the all column. The concentration of DO of control column in the overlying water decreased gradually until experimental period (Fig. 3). But, the DO concentration of the calcined and sonicated oyster applied columns were decreased from 0 to 6 days, and then gradually increased in the overlying water. Therefore, recycled oyster shell powder could increase the dissolved oxygen in the overlying water.

The pH value was not visible changed of the control column changes in the overlying water until experimental period (Fig. 4). But the oyster shell applied column pH value were increased gradually. The pH increased in the treated columns were due to the hydrolysis of calcium peroxide from recycled oyster shell powders. Thus, recycled oyster shell powder could increase the pH value in the overlying water.

### 3.2. Effect of recycled oyster shell powder on nitrogen release in the overlying water

Basically, nitrogen forms include $NO_2^-$ -N, $NO_3^-$ -N, $NH_4^+$- N and organic nitrogen in the water. The total nitrogen concentration of the overlying water was increased early and the steadily in the entire process. Besides, the ammonium nitrogen concentrations of the

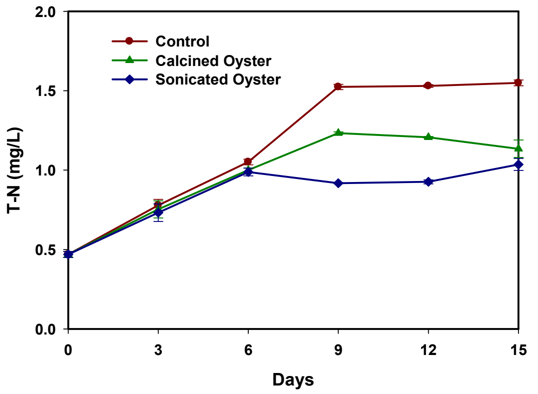


**Fig. 5.** Change of T-N in the overlying water by addition of COSP, SOSP (0.5% w/w) and control for 20 d.

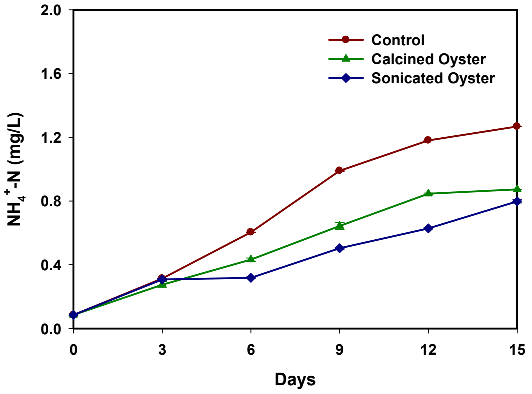


**Fig. 6.** Change of $NH_4^+$-N in the overlying water by addition of COSP, SOSP (0.5% w/w) and control for 20 d.

overlying water were increased as time progressed of all columns. However, the nitrate nitrogen concentrations were decreased in the overlying water of all column as time progressed. The ammonia nitrogen and total nitrogen increasing trends were similar of the all columns in the overlying water. The initial concentration of $NO_3^-$ -N, $NH_4^+$- N and T-N were 0.28, 0.2 and 0.5 mg/L respectively. The concentration of $NH_4^+$- N and T-N were increased gradually of control column in the overlying water, while calcined and ultrasonicated oyster shell powder applied columns $NH_4^+$- N and T-N concentrations increased slowly in the overlying water (Fig. 5, Fig. 6). However, the $NH_4^+$- N and T-N concentrations of the calcined oyster shell powder applied column decreased by 31% and 27% compared to the control on day 15 in the overlying water. On the other hand, the $NH_4^+$- N and T-N concentrations of the ultrasonicated oyster shell powder applied column decreased by 37% and 33% compared to the control in the overlying water on day 15.

The NO3- -N concentration was decreased gradually of the treated column with control in the overlying water. The oyster shell applied columns $NO_3^-$ -N concentration was much higher than control column (Fig. 7). This result indicates that, $NO_3^-$ -N is reduced and produce $NH_4^+$- N in the experimental columns. Because $NH_4^+$- N increase would be possible with dissimilatory nitrate reduction to ammonia (DNRA) by the influence of denitrifying bacteria in the control column. Thus, recycled oyster shell powder could decrease the concentration of $NH_4^+$- N, T-N and increased $NO_3^-$ -N effectively compared to control in the overlying water. This decreased attributed to prevent the nitrogen release from sediment and enhanced assimilation and nitrogen removal by biological action (Khirul et al., 2020).

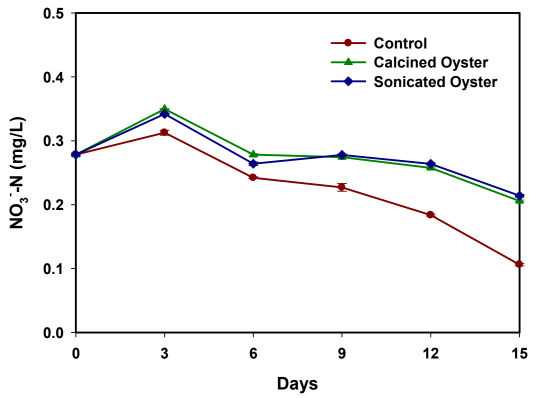


**Fig. 7.** Change of $NO_3^-$-N in the overlying water by addition of COSP, SOSP (0.5% w/w) and control for 20 d.

Low oxidation reduction potential and dissolved oxygen concentrations would enhance nitrogen release from the bottom sediment in the form of ammonia nitrogen (Wang et al., 2019), which would result in a large increased T-N and $NH_4^+$- N in the overlying water. It was observed that, control column sediment ORP was -211.9 mV which could enhance anaerobic condition in the sediment.

The addition of recycled oyster shell powders was increased ORP and DO level in the overlying water with reduce anaerobic condition in the sediment. Consequently, decreased $NH_4^+$- N concentrations released from the sediments and $NH_4^+$- N and T-N concentrations effectively decreased in the oyster shell powder treated columns overlying water compared to control column. Moreover, oyster shell powder treated column could enhance nitrification action in the sediment-water interface, which resulted in higher $NO_3^-$ -N concentration in the treated columns than control column. So, the concentration of $NH_4^+$- N could be reduced from water by the anaerobic ammonia oxidation and biological nitrification action, which was conduct the reduce of $NH_4^+$- N and T-N concentrations in the overlying water.

In general, calcium peroxide could improve the slowly release of nitrogen into water from sediment. Moreover, the biological nitrification and anaerobic ammonium oxidation could help the reduce nitrogen concentration in the overlying water.

### 3.3. Effect of recycled oyster shell powder on phosphorus release in the overlying water

The concentration of TP and $PO_4^{3-}$- P upward were increased of the overlying water in the all experimental columns. The TP and $PO_4^{3-}$- P concentrations of control column was higher than oyster shell applied columns in the overlying water (Fig. 8, Fig. 9). The trends of TP and $PO_4^{3-}$- P concentrations were similar of the all columns in the overlying water. The initial concentration of TP and $PO_4^{3-}$- P were 0.05 and 0.03 mg/L respectively. During the experiments, TP and $PO_4^{3-}$- P concentrations increased gradually of the control column in the overlying water, while calcined and sonicated oyster shell powder applied column TP and $PO_4^{3-}$- P concentrations increased slowly in the overlying water. However, the concentrations of TP and $PO_4^{3-}$- P in the calcined oyster shell powder applied column decreased by 20% and 16% compared to control column on day 15 in the overlying water. Besides, the TP and $PO_4^{3-}$- P concentrations of the overlying water in the ultrasonicated oyster shell powder applied column decreased by 27% and 31% compared to control column on day 15. Thus, recycled oyster shell powder could decrease the concentration of TP and $PO_4^{3-}$- P in the overlying water effectively. This decreased indicated that recycled oyster shell powders could effectively control the P concentration in the overlying water. The P concentration was controlled by recycled oyster shell powders by the prevent of P release from the sediment, improved microbial assimilation process and enhance sediment adsorption capacity. The oxidation reduction potential could affect the P release from sediment. Low oxygen reduction potential and dissolved oxygen concentration would enhance the phosphorus release into overlying water from the sediment (Arshad et al., 2017). Under anoxic condition, organic P would be converted to soluble reactive phosphorus and finally release into overlying water by the diffusion effects (Wang et al., 2016). Whereas, recycled oyster shell powders increased ORP and DO levels in the overlying water, therefore it was effectively prevent the P release into overlying water from sediment.

When the sediment pH value is acidic, organic matter produce by the sediment decomposition, which reduce the insoluble of phosphorus precipitation in the sediment (Istvánovics, 2015) and sediment pH value is neutral, its increase the adsorption capacity by the sediment (Wu et al., 2017). In was observed that, the control column sediments pH value was acidic, which

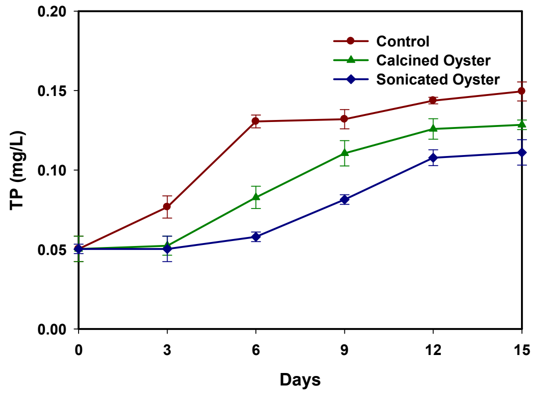


**Fig. 8.** Change of T-P in the overlying water by addition of COSP, SOSP (0.5% w/w) and control for 20 d.

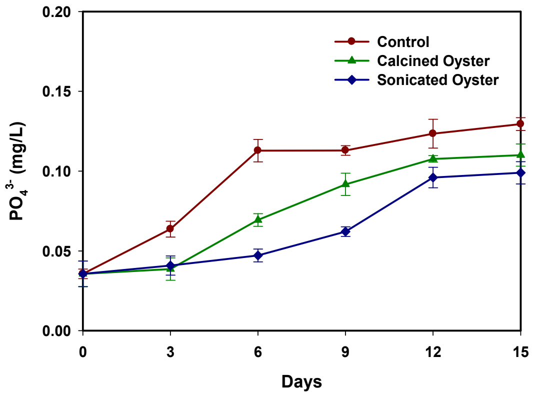


**Fig. 9.** Change of $PO_4^{3-}$-P in the overlying water by addition of COSP, SOSP (0.5% w/w) and control for 20 d.

was alleviate the phosphorus adsorption capacity of sediment. However, oyster shell powders applied columns sediment pH value were alkaline condition, which were enhance phosphorus adsorption capacity in the sediment. Overall, oyster shell powders were enhanced the phosphorus adsorption capacity in the sediment and prevent phosphorus release into the overlying water from the sediment.

## 4. Conclusion

The purpose of the study is to evaluate the remediation efficiency of the two types of recycled oyster shell powders ($CaO_2$) application to polluted coastal sediments in terms of prevent nutrients flux release into overlying water from sediments. The result showed that recycled oyster shell powders could increase DO and ORP level in the overlying water compared to control, which could improve the oxic condition in the sediment water column. It was enhanced the aerobic condition and alleviate anaerobic condition. recycled oyster shell powders were prevented the nitrogen and phosphorus release from sediment and phosphorus adsorption capacity increased in the sediment. Finally the results of column experiments proved that calcined oyster shell powder able to reduce concentrations of T-N, $NH_4^+$–N, T-P, and $PO_4^{3-}$-P in the overlying water were 27%, 31%, 20%, and 16% respectively compared to control column. On the other hand, ultrasonicated oyster shell powder able to reduce concentrations of T-N, $NH_4^+$–N, T-P, and $PO_4^{3-}$-P in the overlying water were 33%, 37%, 27%, and 31% respectively compared to control column.

In summary, recycled oyster shell powders could effectively prevent the nutrient release from the sediment and control nitrogen and phosphorus concentrations of the overlying water with the increase dissolved oxygen concentration. Thus, it is concluded that the application of ultrasonicated oyster shell powder is more effective to remediate polluted coastal sediments.

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