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Recycling waste oyster shells for eutrophication control

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Abstract

Oyster shells are a waste product from mariculture that presents a major disposal problem in coastal regions such as southeast Korea. It was found in the present study that pyrolysis of waste oyster shells under defined conditions (750 °C for 1 h under a nitrogen atmosphere) transforms this material into a sustainable reagent for efficient (up to 98%) removal of phosphates from wastewater. In comparison, raw oyster shells removed almost no phosphate from water, whereas oyster shells heated to 750 °C under an air atmosphere removed a moderate proportion (up to 68%) of phosphates from water. X-ray diffraction (XRD) analysis of pyrolyzed oyster shells showed peaks that were characteristic of calcium oxide, whereas analysis of raw oyster shells showed peaks that were characteristic of calcium carbonate. Surface morphology of pyrolyzed oyster shells also differed from that of raw oyster shells. Preliminary economic feasibility analysis indicates that cost of activated oyster shell is competitive with other wastewater treatment chemicals.

Keywords: Oyster shells; Pyrolysis; Phosphorus; Mariculture; Wastewater; Eutrophication; Economics

1. Introduction

Oysters grow naturally in reefs that provide habitat for many species of fish and shellfish. They are natural water purifiers that filter algae and other particulates from coastal waters, increasing water clarity and improving light penetration. Seagrass beds, which require light,

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benefit from the oysters' filtering effects and, in turn, provide habitat and feeding grounds for many important species of fish and birds.

The southeastern coastal sea in Korea was designated part of National Marine Park in 1968 because of its perfect harmony between a beautiful scenery and inhabited life. This coastal sea is also one of the most productive oyster-farming waters in the world, with shellfish-farming constituting a large part of the regional economy. Calm seas, an indented coastline, and numerous bays present a favorable geographic framework for mariculture and the custom of eating shellfish as a major element of the diet creates a ready market for marine products. The area has 4100 ha of shellfish farms that produce 280,000 tons of oyster shells every year. Until recently, the development of Korean mariculture was based solely on immediate economic benefits. The industry now recognizes that it must take account of environmental factors, including wise stewardship of ecosystem resources and environmentally benign recycling of natural waste products, if it is to remain viable in the future.

Recycling of waste oyster shell has arisen as an imminent issue in the mariculture area. Approximately one-half of shells from oysters harvested from the bays of southern Korea are utilized for spat. The remainder (140,000 tons per year) constitutes a serious solid waste problem. Some of the waste oyster shells are substituted for limestone in fertilizers and chicken feed. This use is limited, however, wherever limestone is readily available. Thus, alternative approaches for recycling waste oyster shells must be found. The ideal solution would be to convert the waste oyster shells to a product that is both beneficial and economically viable.

Eutrophication of coastal waters is another problem threatening the mariculture industry. Enrichment by nutrients, especially phosphorus, which has been identified as the growth-limiting nutrient in near-shore, static water bodies (Anderson et al., 1993; Kalchev and Botev, 1999; Okada, 1996), leads to blooms of microalgae and red tide microorganisms that interfere with oyster farming or make the product unsafe for consumption. Removal of phosphates from wastewater discharges to coastal water is an important component of eutrophication control strategies.

The purpose of the present research was to develop a means of converting waste oyster shells into a material that can be used for removal of phosphate from wastewater. Heating was employed to convert the shells, which are composed primarily of calcium carbonate, into calcium oxide that reacts with phosphates in water and converts them to insoluble forms that can be readily separated. The effects of major processing variables (temperature, furnace atmosphere) on effectiveness of heated oyster shell for phosphorus removal from water were studied. Preliminary economic feasibility estimation for an oyster shell recycling plant was then carried out.

2. Materials and methods

Waste oyster shells were obtained from temporary storage near the workplace at which oysters were separated from shells. Salt and other debris were washed out of the shells with tap water and then the shells were sun-dried for 3 days. The dried shells were crushed with a mortar and pestle before heating in a horizontal tube furnace. After heating, the oyster shells were cooled to room temperature and stored in a closed container.

Standard phosphate solution was prepared by dissolving anhydrous potassium phosphate (K_2HPO_4) (ACS reagent, Sigma) in deionized water to give a concentration of 30 mg l^{-1}. Phosphorus concentration was measured by the ascorbic acid method (APHA, 1995). The phosphate solution was transferred to 1 l acrylic plastic jars (11.5 cm × 11.5 cm × 20 cm). The jars were stirred at 120 rev/min using a jar test apparatus (Phipps & Bird Model 7790-400) and then raw, heated, or pyrolized oyster shells were added at a dose of 5 g l^{-1}. Stirring was continued for specific periods, after which the oyster shell suspensions were allowed to settle for 10 min and then samples were taken of the supernatants.

Chemical composition of raw oyster shell was analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES, Optima 3000DV, Perkin Elmer, USA).

Powders of raw, heated, and pyrolized oyster shell were analyzed by X-ray diffractometer (PW1830 APD system, Philips, The Netherlands). This instrument operates at 40 KV/30 mA and uses Cu Kα radiation (1.5418 Å). XRD diagrams were recorded in the interval $10^\circ \leq 2\theta \leq 80^\circ$ at scan speed of 8 min and step size of 0.04°. Raw, heated, and pyrolized oyster shells were inspected with a scanning electron microscope (FE SEM, S-4200, Hitachi, Japan) of 15 KV.

3. Experimental results and discussion

The raw oyster shell was analyzed for cations typically found in biological material (Table 1). Calcium was the major cation, comprising 37.4% of total dry mass. Sodium and magnesium were present at 0.6 and 0.3% of total dry mass, respectively. All other cations were present at concentrations of 0.09% or less.

The key goal of waste oyster shell processing in the present research was to convert the relatively non-reactive calcium (in the form of calcium carbonate) that makes up the raw shells into a form that readily reacts with aqueous phosphates. Temperatures in the range of 650–800 °C were chosen for treatment of oyster shells in order to achieve decomposition of carbonates. Heating was carried out in presence of nitrogen (pyrolysis) or under an air atmosphere. The heat-treated materials are referred to as heated oyster shell (HOS) or

Table 1
Analysis of cations in raw oyster shell

Cation	Percentage of dry weight
Ca	37.4
Na	0.594
Mg	0.269
K	0.012
Fe	0.034
Al	0.036
Mn	0.011
Cu	0.001
Zn	0.011
Sr	0.091
Si	0.023

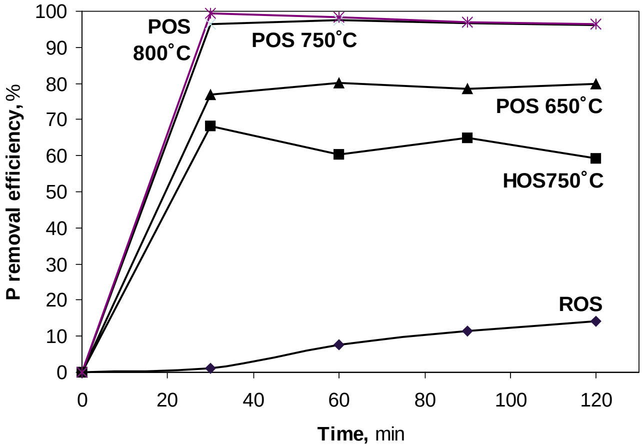

Fig. 1. Time-dependent phosphorus removal efficiencies achieved with oyster shells: ROS; Raw oyster shell, HOS; oyster shell heated under air atmosphere, POS; oyster shell pyrolyzed under nitrogen.

pyrolized oyster shell (POS) depending on whether the oven atmosphere was air or nitrogen, respectively. Their efficacy was evaluated in terms of ability to remove phosphates from water.

Samples of raw, heated, and pyrolized oyster shell were dosed to phosphate solutions at 5 g oyster shell per litre of solution. As Fig. 1 shows, the raw oyster shells removed almost no phosphorus. HOS removed a significant (up to 68%) fraction of the phosphorus initially present. The best removal efficiencies (up to 98%) were achieved with POS. Pyrolized oyster shell produced at oven temperatures of 750 or 800 °C performed equivalently, whereas POS produced at an oven temperature of 650 °C was somewhat less effective. The aqueous reaction time necessary for either HOS or POS to achieve significant phosphate removals was less than 30 min. Beyond this time, the removal percentages remained approximately constant.

X-ray diffraction (XRD) patterns of raw oyster shells, HOS, and POS are shown in Fig. 2. The patterns for oyster shell pyrolyzed at oven temperatures of 750 and 800 °C (Fig. 2d and e) were nearly identical and exhibited peaks characterisic of CaO. The pattern for oyster shell heated under air atmosphere at 750 °C (Fig. 2b) was similar to that of raw oyster shell (Fig. 2a); both exhibited peaks characteristic of $CaCO_3$. Oyster shell pyrolized at 650 °C (Fig. 2c) exhibited a pattern intermediate between heated oyster shell and oyster shell pyrolized at the higher temperatures.

The effect of temperature and heating atmosphere was further examined by thermogravimetric analysis (TGA), as shown in Fig. 3. Pyrolysis under nitrogen atmosphere produced the greatest loss of mass (51%) (Fig. 3b), whereas heating under air atmosphere led to a mass loss of 45% (Fig. 3a). The greater weight loss under N_2 atmosphere indicates that more extensive thermal decomposition is achieved under this condition.

Scanning electron micrographs (SEM) of the surface structures of oyster shells subjected to different treatments are compared in Fig. 4. The surfaces of oyster shells heated under air atmosphere (middle Fig. 4) were relatively smooth, similar to that of raw oyster shells (top

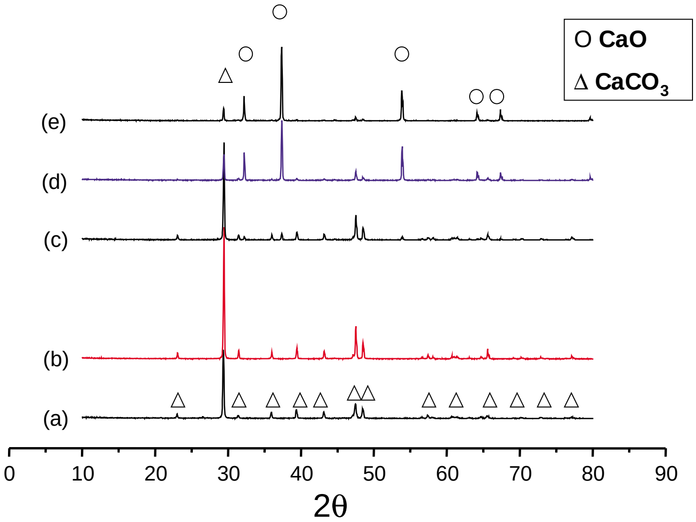

Fig. 2. XRD patterns for oyster shells: (a) raw oyster shell; (b) oyster shell heated under air atmosphere at 750 °C; (c), (d), and (e) oyster shell pyrolyzed under nitrogen atmosphere at temperatures of 650, 750, and 800 °C, respectively. Triangles identify peaks that are characteristic of $CaCO_3$; circles identify peaks that are characteristic of CaO.

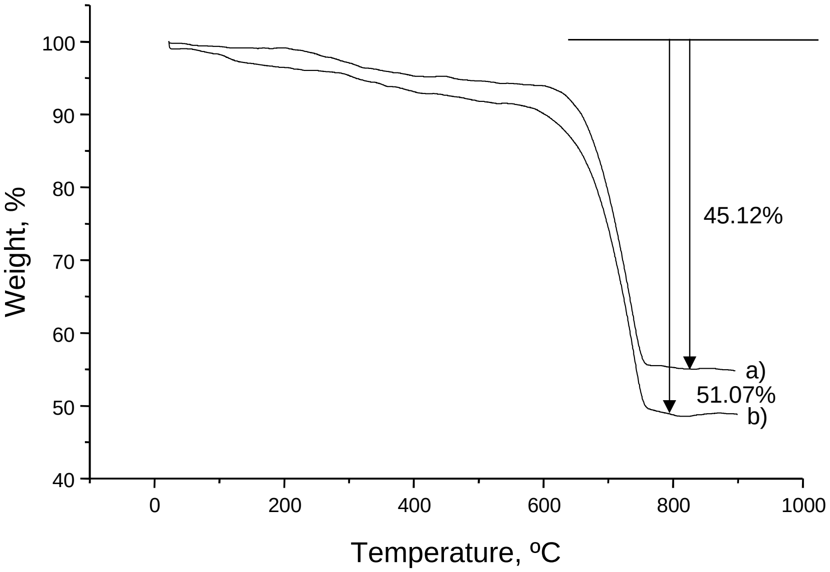

Fig. 3. TGA analysis of oyster shells: (a) air atmosphere; (b) N_2 atmosphere. The heating rate was 10 °C/min.

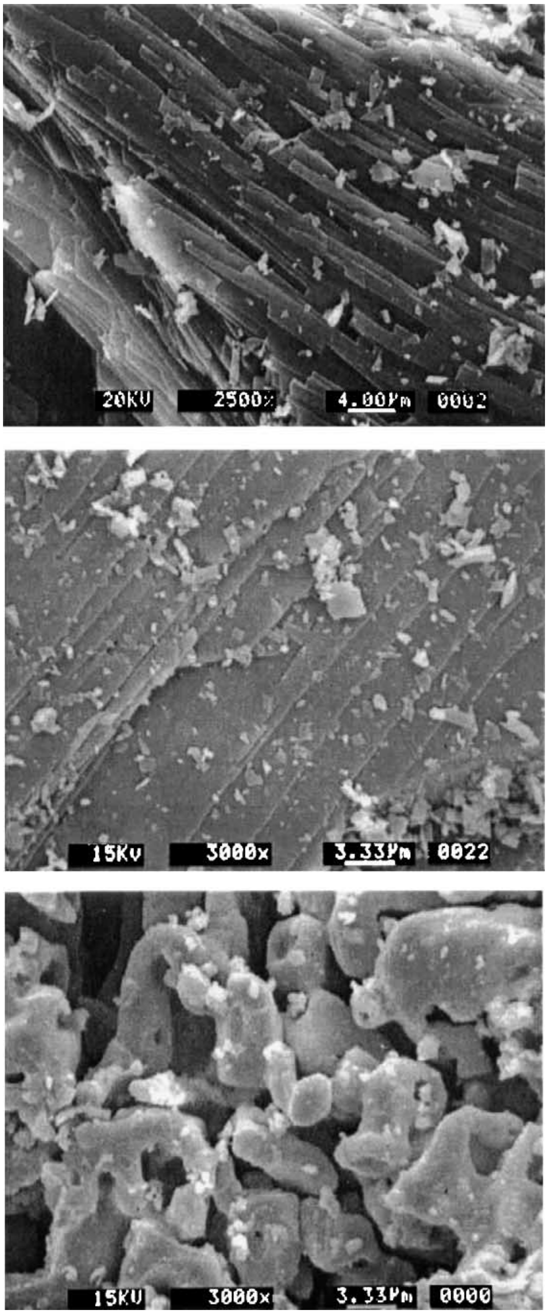

Fig. 4. Surfaces of oyster shells as visualized by scanning electron micrography: Top; raw oyster shell; middle; heated under air atmosphere at 750 °C; bottom; heated under nitrogen atmosphere at 750 °C.

Table 2
Estimated costs of waste oyster shell recycling plant with capacity of 7500 tons per month (all amounts in US $)

Transportation, loading and unloading	$ 83,333
Operating expenses	
Energy	US$ 65,787
Labor	US$ 63,333
Packing	US$ 69,444
Capital costs per month (depreciation over 40 years)	US$ 30,346
Overall costs	US$ 312,243
Cost per ton	US$ 42

Fig. 4). In contrast, the surfaces of pyrolyzed oyster shell were highly convoluted (bottom Fig. 4).

4. Preliminary economic feasibility estimation

Preliminary economic feasibility estimation was carried out for a recycling plant, as summarized in Table 2. The calculations were based on 7500 ton per day of production capacity and a depreciation of 40 years of the investment costs (rotary kiln, grinder and other miscellaneous equipments). The electricity required per day was estimated to be 14,400 kWh. The total cost for manufacturing activated oyster shell was estimated to be US$ 42/ton. The retail prices in the local market for activated carbon, alum powder, and quicklime are US$ 1167/ton, US$ 193/ton, and US$ 120/ton, respectively, whereas for heated oyster shell (as used in fertilizer and chicken feed) the price is US$ 126/ton.

5. Conclusions

The present study has demonstrated that a waste product—oyster shells—can be transformed into an effective reagent for phosphorus removal from wastewaters. The conversion process is simple, consisting merely of heating to a temperature of 750 °C for 1 h under nitrogen atmosphere. Production of activated oyster shell for use in wastewater treatment is a novel means of recycling waste material to provide a beneficial product and promises to greatly reduce problems caused by mariculture in coastal regions. Preliminary economic evaluation indicates that the product is competitive with other wastewater treatment chemicals. Further research is needed to optimize the conditions under which activated oyster shells are produced and to understand the conversion process from calcium carbonate to calcium oxide in the oyster shell matrix.

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References

Anderson JM, Andersen F, Larsen F. Effect of phosphorus removal from wastewater on eutrophication of coastal waters. Eur water pollut Control 1993;3:40–4.

APHA, 1995. Standard Methods for the Examination of Water and Wastewater, 19th ed., American Public Health Association, American Water Works Association and Water Pollution Control Federation, Washington, DC.

Kalchev RK, Botev IS. Long-term eutrophication development in five coastal lake of the Bulgarian Black Sea region. Water Sci Tech 1999;39:1–7.

Okada M. Japanese experiences and current problems in organic pollution and eutrophication control in coastal area. J Korean Soc Environ Eng 1996;18:379–89.