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ABSTRACT: Water sources are currently facing great challenges from rapid population growth and industrial developments. Investigations into how to remove algal organic matter (AOM) are thus of great importance from an environmental point of view because most lakes and reservoirs in South Korea suffer from algae problems, especially in the summer. Many efforts have been made to remove AOM from the aquatic environment in South Korea. In this study, we focus on development of a new AOM removal system, utilizing waste oyster shells and ferrihydrite as the media of the filtration system. Using this system, the removal rate of AOM was investigated regarding the concentrations of chlorophyll a, total phosphorus, and alginate. It was found that about 92% of the total phosphorus was removed through this system when raw oyster shell powders were heated at 900°C to convert them into calcium oxide powders. The use of a continuous system also led to a reduction of 94.2% in total phosphorus, 78.8% in chlorophyll a, and 43.6% in alginate.

KEYWORDS: algal organic matter, oyster shell, ferrihydrite, algae removal

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Introduction

Water scarcity is possibly the most underestimated resource issue faced by the world today.[1] As world water demand has more than tripled over the last half-century, current freshwater resources are unable to meet all requirements of the global demand.[2] As such, the reuse of wastewater has been considered as a feasible alternative technology for ensuring a sustainable water supply, as available water sources become depleted.

When wastewater is treated, however, the treatment plants may not remove certain pollutants that can have a negative impact on people and the ecosystem.[3] For example, these pollutants commonly contain organic compounds that may cause algae growth.[4]

Algae are a diverse group of organisms that with the right amount of nutrients, sunlight, and water have the capacity to rapidly grow.[5] Algae acquire carbon dioxide from the air, energy from the sun, and nutrients from the soil. These nutrients include nitrogen, phosphorus, and potassium.[6]

There is a growing appreciation of the importance of harmful algal blooms (HABs) and HAB-related illnesses to public health. With the dramatic increase in the number of HABs, as well as their frequency and intensity in coastal regions throughout the world, there are more toxic algal species, more algal toxins, and more geographic areas affected than ever before.[7] Organic substances produced by algae may comprise various forms and differing concentrations of polysaccharides, proteins, lipids, nucleic acids, and other dissolved organic substances.[8]

The concentration of algae is commonly measured as chlorophyll a.[9] Algal growth in natural water bodies is primarily influenced by dissolved species of nitrogen and/or phosphorus, with water-quality parameters such as pH, conductivity, levels of organic contamination, sediment, and pesticides influencing algal growth to a lesser extent.[10]

Of interest, however, is that a substantial volume of oyster shells are released from the oyster farming industry, which is considered as an important recycled resource of limestone.[11] Using these recycled oyster shells, few studies have been conducted on their using in water treatment.[12,13] Even fewer works have focused on the development of algal organic matter (AOM) removal systems to increase the efficiency of algae removal; few studies have attempted to apply a new combined media into the contract bed.[14] Oyster shells have been calcined as an adsorbent and ferrihydrite was then applied to remove chlorophyll a and alginate. Accordingly, this current study aims to improve AOM rejection using a newly developed hybrid media filtration system.

Experimental

Adsorbent materials

The AOM removal systems were prepared using oyster shells and ferrihydrite. Figure 1 shows the preparation of oyster shell calcination. First, the oyster shells were locally collected and then cleaned by washing in de-ionized water and boiled for 20 minutes to remove the impurities. The washed shells were placed in oven at 110°C for 12 hours. Using a mill apparatus, the dried shells were powdered and ground to fine powder of 3 to 5 mm by physical sieving separation. Then, it is further calcined at 800°C, 900°C, and 1000°C for 1, 2, and 4 hours in a furnace. When the calcination temperature reached 900°C, the

Figure 1. Preparation of oyster shell calcination.

Table 1. Properties of oyster shell powder.

PROPERTIES	VALUES
Particle size (mm)	0.125-0.841
Shape factor (-)	0.65
BET surface area (m^2/g)	18.0
Average pore radius (Å)	13.0
Total pore volume (cm^3/g)	0.014
Density (g/cm^3)	1.68

Abbreviations: BET, Brunauer-Emmett-Teller.

calcium carbonate present in the oyster shells was completely converted into calcium oxide as[15]:

$$CaCO_3 \rightarrow CaO + CO_2 \uparrow \tag{1}$$

Under neutral or alkaline condition, direct precipitation $Ca_3(Po_4)_2$ and $Ca_5(Po_4)_3OH$ are readily achieved. Moreover, $Ca_5(Po_4)_3OH$ is the most thermodynamically stable and most difficult to solubilize. However, under more acidic conditions, $CaHPo_4$, $Ca_4H(Po_4)_3$, and $Ca_3(Po_4)$ are thermodynamically more stable. The precipitation of $Ca_3(Po_4)_2$ and $Ca_5(Po_4)_3OH$ most likely follow as

$$5Ca^{2+} + 3HPO_4^{2-} + 4OH - = Ca_5\left(PO_4\right)_3 OH \downarrow + 3H_2O \tag{2}$$

$$3Ca^{2+} + 2HPO_4^{2-} + 2OH - = Ca_3\left(PO_4\right)_2 \downarrow + 2H_2O \tag{3}$$

The oyster shells were subsequently washed, dried, ground, and sieved to obtain an oyster shell powder having particle sizes of 0.125 to 0.841 mm. Table 1 highlights the properties of the oyster shell powder. The surface areas of the samples were measured using the Brunauer-Emmett-Teller (ASAP™; Micromeritics Instrument Corp., USA) technique, after pretreating to remove vapor at 1×10^{-3} torr (vacuum) and heating at 180.0°C for 2 hours. The specific surface area increases from 2.8 to 8.5 m^2/g, and the average pore size increases from 3.7 to 6.4 nm.

Ferrihydrite is a naturally occurring material and can be synthesized by the rapid hydrolysis of Fe(III) solution.[16,17] Although the structure of ferrihydrite remains—somewhat—a matter of controversy, most proposed formulae are essentially equivalent and can be reduced to $FeOOH{\cdot}nH_2O$.[18,19] Ferrihydrites are then qualified as either two line or six line depending on the number of X-ray diffraction peaks they exhibit. The following sections include methods for preparing 6-line ferrihydrite and 2-line ferrihydrite. These samples have an average diameter of 30 Å. Their surface region comprises more than 30% of the total volume, and a spherical surface is assumed.[20] Due to its high surface area and intrinsic reactivity, ferrihydrite serves as a dominant sink for numerous metals (eg, As) and nutrients (eg, P).

An appropriate amount of ammonium hydroxide was added to 1 L of 0.1 M $Fe(NO_3)_3{\cdot}9H_2O$ solution to bring the pH to 10. The reddish brown precipitate was next filtered and washed until the pH decreased to 7. The resulting cake was then oven-dried at 50°C before being ground into a fine powder.

Adsorption isotherm

Adsorption isotherms are usually used to describe interaction between the adsorbent and the aqueous solution and furnish information for understanding the nature of the reaction, which is significant when an adsorption system is to be designed. Langmuir and Freundlich isotherm models are widely used for investigating and representing adsorption processes and mechanisms. The Langmuir model is based on a hypothesis that only one layer adsorbates are adsorbed at the adsorbent surface, where the adsorption potential is constant, and the Freundlich model is an empirical application suited to highly heterogeneous surfaces. Equation (4) describes the Langmuir system:

$$\frac{C_e}{Q_e} = \frac{1}{ab} + \frac{C_e}{a} \tag{4}$$

where Q_e is the amount of AOMs adsorbed by oyster shell powder and ferrihydrite, C_e is the equilibrium concentration in

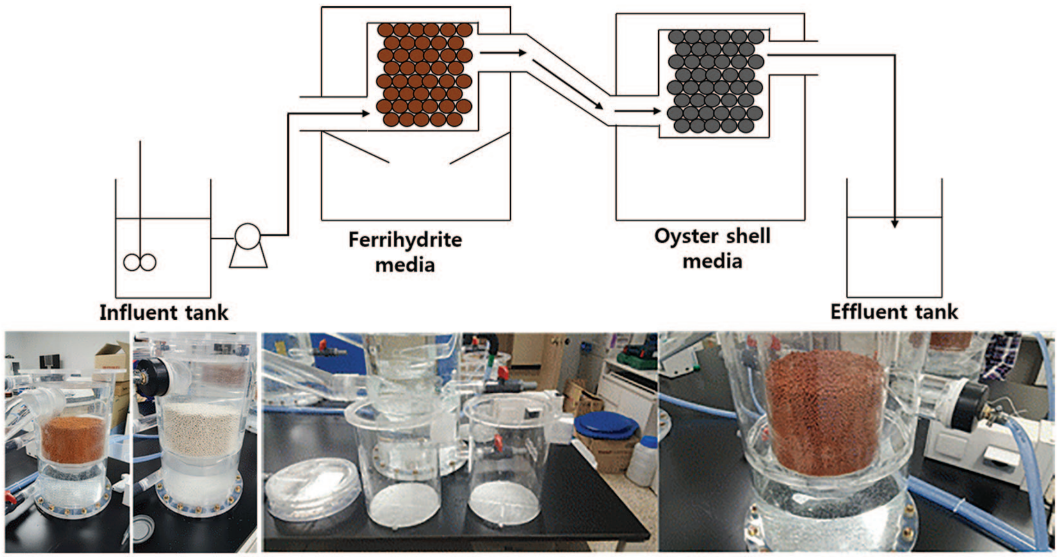

Figure 2. Schematic diagram and real photographs of ferrihydrite/calcined oyster shell hybrid process.

the aqueous solution, a is saturation capacity, and b denotes saturation constant.

Equation (5) describes the Freundlich isotherm:

$$\ln Q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{5}$$

where K_F is the Freundlich isotherm constant and $1/n$ is the Freundlich isotherm's intensity constant.

Experimental setup and procedure

The experiment consists of two parts. In the first part, the rejection effect of the oyster shell powder and the ferrihydrite was investigated. The oyster shell powder and ferrihydrite were applied to investigate the rejection of specific matters. First, the optimal calcination condition for the high removal rate of total phosphorus using oyster shell powder was examined. We used a 5 ppm total phosphorus solution as the influent to investigate the rejection of total phosphorus; 50 g/L of calcined oyster shell powder was used. We also used 20 ppm chlorophyll a and 0.1 ppm alginate solutions as the influent to investigate the rejection effect of ferrihydrite; 50 g/L of ferrihydrite was used for this investigation.

The second part was carried out using the hybrid media process with the two developed media beads. Schematic diagram and real photographs of ferrihydrite/calcined oyster shell hybrid process are shown in Figure 2. The hybrid process consists of ferrihydrite and calcined oyster shell media beads. During these experiments, 5.5, 20, and 0.1 ppm of total phosphorus, chlorophyll a, and alginate were the respective influent solutions used to study the removal efficiency of the system.

To measure the removal efficiencies of the system, the effluent samples were measured using a laboratory spectrophotometer (DR270; HACH, USA) for total phosphorus, chlorophyll a, and liquid chromatography-mass spectrometry (LC/MS; 1200 Series; Agilent, USA) for alginate.

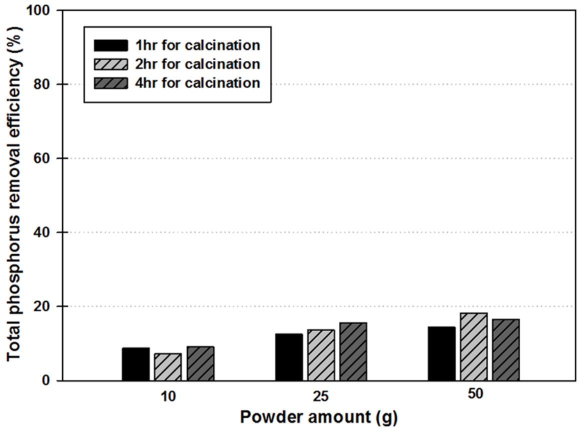

Figure 3. Removal efficiency of total phosphorus as a function of 800°C calcined oyster shell powder dose.

Results and discussion

Removal rate through oyster shell powder

To begin, the optimum conditions for oyster shell calcination to remove total phosphorus were investigated. The results show that by increasing the calcined oyster shell powder dose increased the total phosphorus rejection for all experimental conditions.

Figure 3 shows that the overall rejection for total phosphorus was below 20% at an 800°C calcined temperature. The maximum rejection rate was 18.2% when a 50 g/L dose of calcined oyster shell powder was applied. It is well known that at over 900°C, the calcined oyster shell has a similar structure with calcium oxide.[21,22] In this study, a weight loss of 26% occurred after complete combustion of the natural oyster shell

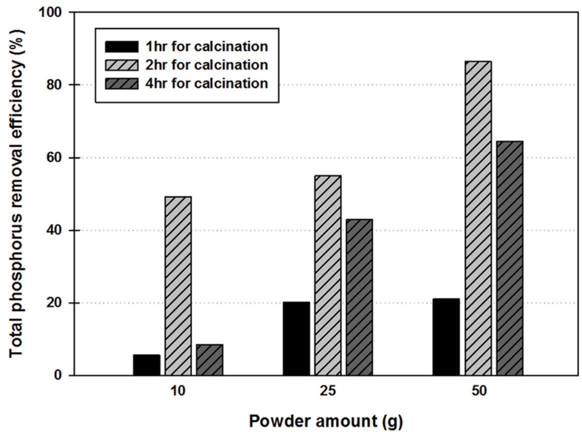

Figure 4. Removal efficiency of total phosphorus as a function of 900°C calcined oyster shell powder dose.

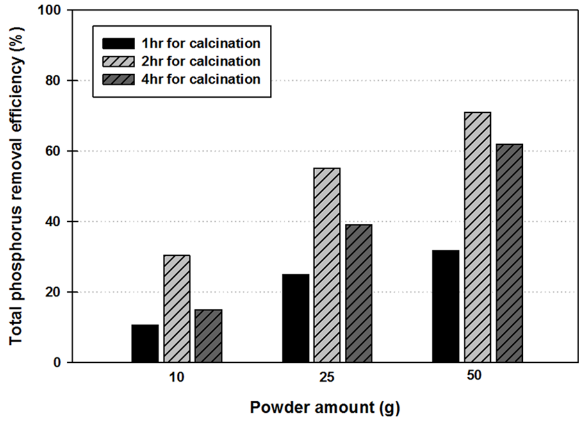

Figure 5. Removal efficiency of total phosphorus as a function of 1000°C calcined oyster shell powder dose.

at 900°C for 1 hour, which was similar to the weight loss measured at 2 hour. Therefore, the economically optimum calcination condition for oyster shells to be used in the total removal of phosphorus was 900°C for 2 hour.

At 900°C, for a 2 hour calcined oyster shell powder dose of 50 g/L, and 86.5% removal of total phosphorus was achieved in Figure 4. At 1000°C, the rejection rate was 71.0% when a 50 g/L dose of a 2 hour calcined oyster shell powder was applied in Figure 5. Note that this does not mean that the high calcined temperature is directly proportional to the total phosphorus removal rate.

Removal rate through ferrihydrite

To study the effect of ferrihydrite powder as an adsorbent, chlorophyll a and alginate removal experiments using ferrihydrite powder were also conducted. For this study, 50 g/L of ferrihydrite was used as the adsorbent. As expected, increasing the ferrihydrite dose increased the alginate rejection for all experimental conditions in Figure 6. However, it is noticed that a further increase in ferrihydrite contact time beyond 5 minutes resulted in only a minimal improvement in the alginate removal. Therefore, the optimum condition of alginate removal was deemed to be 50 g/L at a 5 minutes contact time. Figure 7 illustrates that the high removal rate for mixing time to remove chlorophyll a was 10 minutes, at an over 70% removal of chlorophyll a.

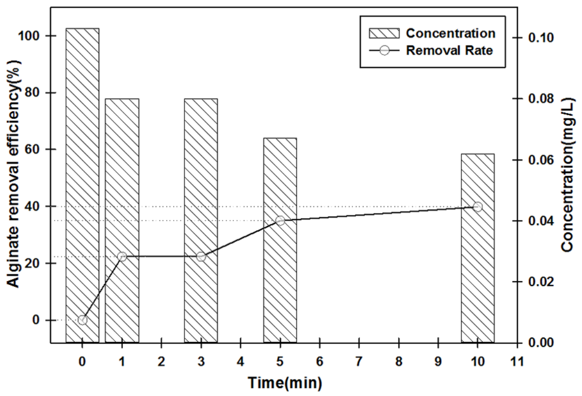

Figure 6. Removal efficiency (line graph) and concentration (bar chart) of alginate as a function of contact time.

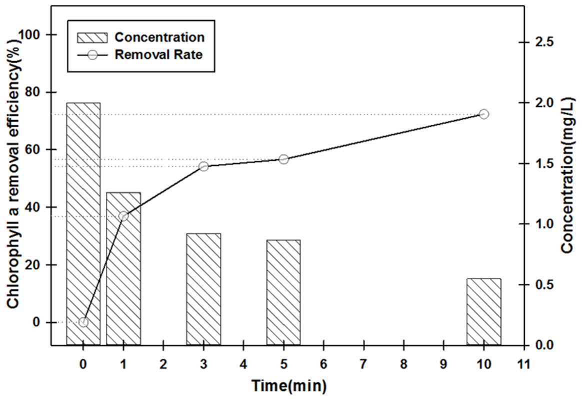

Figure 7. Removal efficiency (line graph) and concentration (bar chart) chlorophyll a as a function of contact time.

Removal rate through continuous adsorption process

Figure 8 shows the total phosphorus removal rate as a function of the contact time. Ferrihydrite only, calcined oyster shell only, and the ferrihydrite/calcined oyster shell hybrid processes were compared. Predictably, the combined process had a higher removal efficiency than the separate systems. An increase in the contact time was found to slightly increase the total phosphorus removal rate in the hybrid system. In Figure 8, the percentage removal at a contact time of 5 minutes was below 50%, which increased to about 90% as the time approached 10 minutes. The percentage removal at the different time intervals was 91.7%, 96.2%, 94.2%, 88.7%, 91.1%, and 92.0% for 10, 20, 30, 40, 50, and 60 minutes, respectively. These results clearly show that increasing the contact time beyond 20 minutes for this specific adsorbent is wastage because the increase in adsorption efficiency after a contact time of 20 minutes was insignificant. Therefore, the equilibrium time selected for the removal of total phosphorus from the initial influent solution using the ferrihydrite/calcined oyster shell hybrid was 20 minutes.

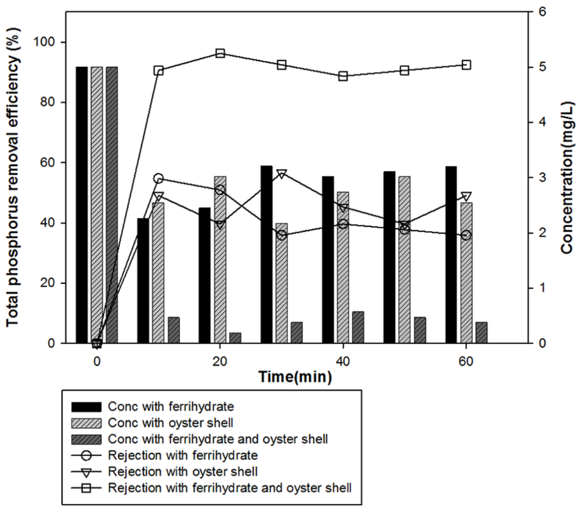

Figure 8. Removal efficiency of total phosphorus as a function of contact time under three operations: ferrihydrite beads only, calcined oyster shell beads only, and a ferrihydrite/calcined oyster shell hybrid processes.

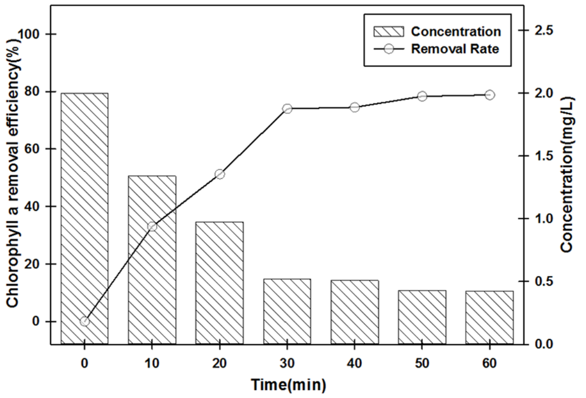

Figure 9. Removal efficiency of chlorophyll a as a function of contact time under the ferrihydrite/calcined oyster shell hybrid process.

Figure 9 shows that the removal rate of chlorophyll a significantly increased with an increase in the contact time. The maximum adsorption of chlorophyll a was achieved after a 30 minutes reaction time. The chlorophyll a adsorption of ferrihydrite/calcined oyster shell hybrid process rapidly increased from 30% to 80% as the contact time increased from 10 to 30 minutes. There was negligible increase in the adsorption efficiency after a contact time of 30 minutes; it is likely that the adsorption equilibrium was reached at this time.

Figure 10 depicts the effect of contact time on the adsorption of alginate for the ferrihydrite/calcined oyster shell hybrid process, from contact with the initial influent. It is clear that increasing the contact time increases the removal efficiency; although again, at a certain time the percentage of removal becomes almost constant. In Figure 10, the percentage removal at a contact time of 10 minutes was approximately 40%. After 10 minutes, the increase in percentage removal became negligible. Thus, the equilibrium time for the ferrihydrite/calcined oyster shell process to remove alginate was 10 minutes from initial contact with the influent solution.

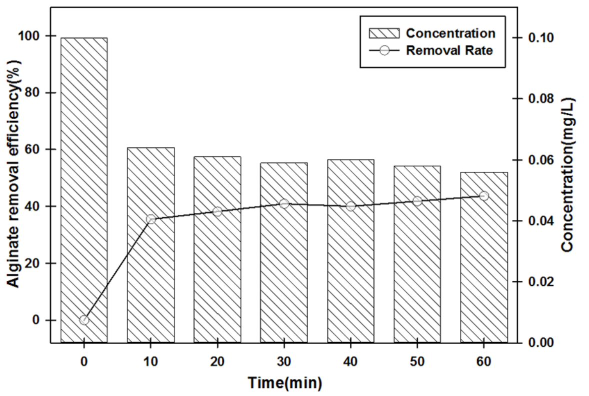

Figure 10. Removal efficiency of alginate as a function of contact time under the ferrihydrite/calcined oyster shell hybrid process.

Conclusions

In this work, a novel AOM removal process that combined ferrihydrite and calcined oyster shell beads was developed as an efficient adsorbent for the removal of total phosphorus, chlorophyll a, and alginate. The optimum condition to prepare oyster shells to remove total phosphorus was a calcining temperature at 900°C for 2 hours. From the continuous experimental phase, the following process-related conditions were then identified as optimum contact times for removing each target matter: 10, 30, and 10 minutes for total phosphorus, chlorophyll a, and alginate, respectively. Based on these results, it is likely that the hybrid removal system may be applied to control AOM in aqueous solutions. Further study is needed to fully optimize the developed process.

Author Contributions

CGP conceived the study and contributed to data interpretation. HK designed the study, contributed to data interpretation. And critically wrote andrevised manuscript. IY author work for experiments, contributed to data interpretation.

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