

SEDIMENT IMPROVEMENT MATERIALS COMPARISON APPLIED TO EUTROPHICATED SEASIDE PARK POND

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ABSTRACT: This study was aimed to analysis the influence on bottom sediment environment by sprinkling shell as regional unused resources. In addition, adsorption isotherm was calculated by culture experiments of bottom sediment material improvement to assess its effect. T-N in pore water showed the low concentration with sprinkling shells as regional unused resources, because $\text{NH}_4\text{-N}$ eluted from sediment into water by the influence of sprinkled CaO . T-P in pore water also showed the low concentration with sprinkling shells, and moreover it was remarkable that in burning-treated system more than in non-treated system. By sprinkling, $\text{Ca}_3(\text{PO}_4)_2$ was formed with Ca^{2+} and PO_4^{3-} bonding on the shell surface, and $\text{PO}_4\text{-P}$ in the pore water decreased. $\text{NH}_4\text{-N}$ and T-N showed the negative adsorption isotherm, because $\text{NH}_4\text{-N}$ eluted in water by sprinkled bottom sediment improvement materials, and nitrogen in the pore water decreased. For T-P and $\text{PO}_4\text{-P}$, all bottom sediment improvement materials showed positive adsorption effects. CRM treatment using CaO showed the highest effect.

Keywords: Sediment Improvement, Langmuir's Adsorption Isotherm, Pore Water, Nutrient, Eutrophicated Brackish Pond

1. INTRODUCTION

With the population growth, eutrophication in enclosed water bodies is progressing by inflows of domestic wastewater into rivers. Therefore, lakes are the environment susceptible to nutrient load and organic matter. Some eutrophication measures have been implemented. However, problems such as the collapse of the ecosystem issues and maintenance and the cost has occurred. Shells were used as the sprinkled material in this study is a principal component of calcium carbonate, it is considered that the influence on the ecosystem is less. Then, the Ca of the components of the shell, also has the ability of adsorbing the nutrients.

Hasunuma Seaside Park pond in Sanmu city of Chiba prefecture locates at 350m inland from Kujyukurihama coast line. This pond is strong enclosed, and its surface area is about $10,000\text{m}^2$, water volume is about $7,400\text{m}^3$, the water depth is 0.74m in average (Fig.1) [1]. In past, a rental boat shop opened in this pond, but the problem of stink and deterioration of landscape occurred because of Aoko in summer. Improvement trials of drying in the sun and drainage work conducted, but Aoko occurred again in summer of next year (Fig.2) [2]. Therefore, the eutrophic cause in these ponds is the elution of the nutrients from bottom sediment.

Dominant species of Aoko in this pond is *Anabeana spiroides*, and it has "air nitrogen fixation ability", therefore, they can multiply explosively if there is even phosphorus in water.

The other side, many shells are scattering in Kujyukurihama coast on nearly of Hasunuma Seaside Park pond.

This study was aimed to analysis the influence on bottom sediment environment of sprinkling shell as regional unused resources. In addition,



Fig.1 Hasunuma seaside park pond



Fig.2 Aoko occurred in Hasunuma

the adsorption isotherm was calculated by microcosm culture experiments of bottom sediment material improvement. And adsorption effect of the nutrient in each processing was assessed

2. MATERIALS AND METHODS

2.1 Regional Unused Resources

In this study, *Anadara broughtonii*, bivalves, was supplied as regional unused resources. This shell was broken into 1-3mm size fragment (Fig.3). More than 90% of shell body component is made from CaCO₃. It sprinkled on the bottom mud of the pond as nutrient resource. Shells are scattered much in Kujyukurihama coast of neighboring of Hasunuma Seaside Park pond. And when the fragment sprayed on bottom mud, the surface of sediment looks bright by a reflection of the sun light.

2.2 Culture Method

Water volume in the microcosm test is generally 300-1,000 ml [3]. From this reason, clear glass container (volume: 470ml, height: 14cm, diameter: 7cm,) was supplied to this study. 100g of bottom sediment collected from the pond was put in the bottom of the container to be flat, and 380mL of pond water was poured without disturbing the sediment. Crashed shells were sprinkled on the surface of bottom sediment.

The microcosm systems were cultured in incubator. Culture period was set to 20 days, and culture system were no-treated system as control and sprinkled systems of 50, 100g/m² of shell fragment. Culture condition was 25 degrees (Celsius) in temperature and 2,400lux in illuminance (L/D = 12/12hr.). Measuring parameters were T-P, PO₄-P, T-N, NH₄-N, NO₂-N, NO₃-N, COD, pH and T-S.

2.3 Extraction of Pore Water

50-100g of bottom sediment was sampled into precipitation tube, and centrifuged under 2,000-3,000rpm for 10min.

2.4 Evaluation by Adsorption Isotherm

This study evaluated CRM (Chemical Remediation Materials) treatment (MgO and/or

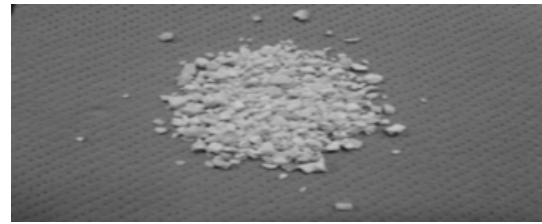


Fig.3 Shell fragment as regional unused resources

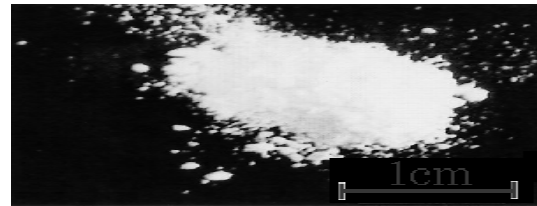


Fig.4 Magnesium oxide (MgO)



Fig.5 Calcium oxide (CaO)

CaO) (Fig.4, 5), hybrid treatment (DAF treatment plus CRM treatment) and the shell sprinkled as regional unused resources treatment (non-burning treated and burning-treated) (Fig.3). MgO can be suppressed occurrence of Chl.a and elution of phosphorus. Therefore, it is expected to be viable in the bottom mud treatment of enclosed lakes [4]. CaO is possible to suppress the elution of phosphoric acid from the bottom mud. However, NH₄-N washout from the bottom sediment and rapid rise in pH occurs. That impact on the ecosystem is considered large in a concern. DAF process is a method for making the aerobic condition sediments.

Adsorption isotherm was calculated using Langmuir's adsorption isotherm as formula (1) as below [5].

$$W = a \cdot W_s \cdot C \quad (1)$$

3. RESULTS AND DISCUSSION

3.1 Water Quality of Pore Water

3.1.1 Concentration ratio of nitrogen

NH₄-N (Fig.6a): In 10g/m² and 20g/m² sprinkled system, no change was observed in the concentration ratio either of the burning system and a non-burning system. In 50g/m² and 100g/m² sprinkled system, reduction of 40-50% concentration was observed in the non-burning system, and 60-70% concentration ratio increased in burning-treated system. Thus, due to the sprinkling of calcium, by increasing the pH of the sediment, NH₄-N elution occurred by washout effect. In a system that has been subjected to a burning treatment in particular, shows a high value of pH11, pore water of the bottom mud is inclined to alkaline. It is thought that the elution amount of NH₄-N was greater than in the non-burning system.

NO₂-N (Fig.6b): As with NH₄-N, there was no change in 10g/m² sprinkled systems and the non-burning system of 20g/m² sprinkled system. In burning-treated system of 20g/m² sprinkled system, 50g/m² and 100g/m² sprinkled system reducing the concentration of 20-30% has occurred in a non-burning system. And concentration was decreased by 20-40% of the burning-treated system.

NO₃-N (Fig.6c): In 100g/m² sprinkled system, it has become a high concentration of 2.5 times of the NO₃-N concentration in the overlying water in comparison with a non-dusting system. Nitrification reaction of just above water has been promoted in the elution of NH₄-N from the sediment. Therefore, it is eluted from the bottom mud NH₄-N of a large amount compared to the non-dusting system, nitrification reaction amount of sediment has been suppressed. Therefore, it thought that change was not observed in the NO₃-N concentration in the pore water.

In this way, the promotion of a series of processes of nitrification denitrification has been suggested by sprinkling shells and burning process. For a porous material is widely used for denitrification and nitrification promote, further study is necessary in the future.

T-N (Fig.6d): Pore water showed the low concentration of T-N by sprinkled shells as regional unused resources. As reason for this, NH₄-N eluted from sediment into water with the influence of sprinkled CaO.

3.1.2 Concentration ratio of phosphorus

PO₄-P (Fig.6e): In PO₄-P, adsorption effect has

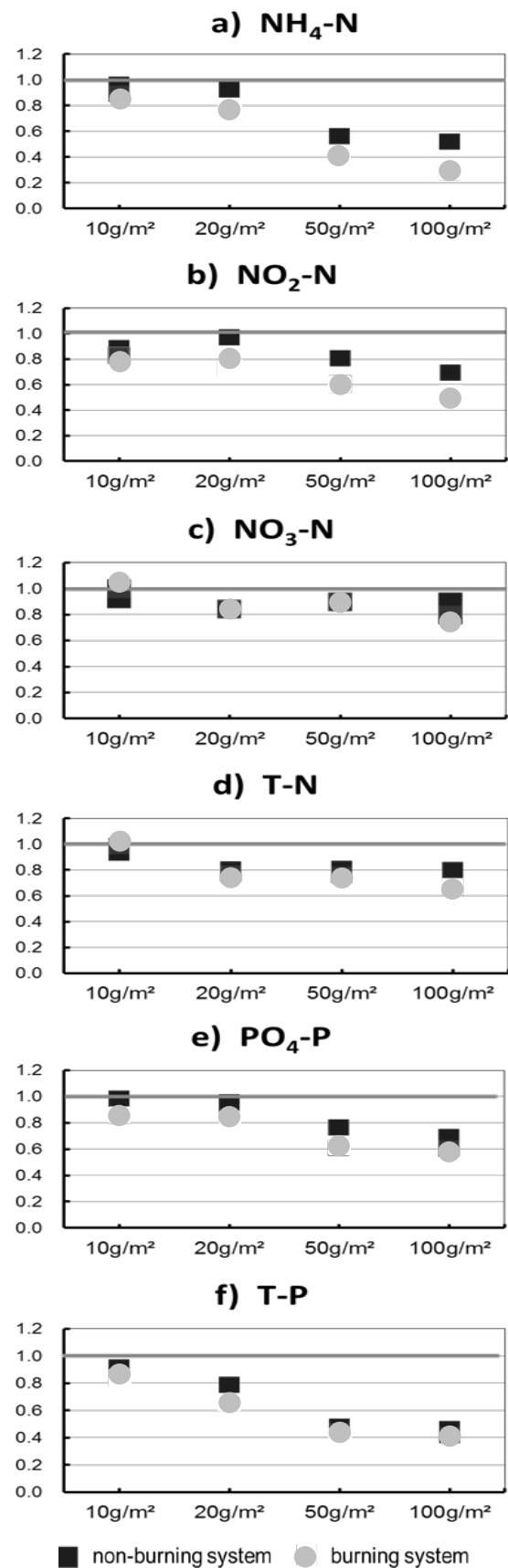


Fig.6 Nutrient concentration ratio in the pore water with shell sprinkling

not been seen in 10g/m² sprinkling system and 20g/m² sprinkling system. However, gradually concentration decreased from 50g/m² sprinkling system and high adsorption effect has been shown in the burning system than non-burning system. By sprinkled shells, Ca₃(PO₄)₂ was formed with Ca²⁺ and PO₄³⁻ bonding on the shell surface, and PO₄-P in the pore water decreased..

T-P (Fig.6f): As with T-P, as the application rate is large, the concentration of the pore water is reduced in a system subjected to a burning treatment was shown.

3.1.3 Concentration ratio of total sulfide

T-S (Fig.7): The decrease of sulfide amount was observed by sprinkled the shells, and moreover it was remarkable in burning-treated system more than in non-treated system, as same as T-P. In 100 g/m² sprinkled system, sulfide concentrations were decreased by about 1.3 times more in burning system than non-burning system. As reason for this, CaSO₄ was formed with Ca²⁺ and SO₄²⁻ bonding. As reason adsorption force was higher in the system that has been subjected to a burning treatment, porosity of the shell is increased by burning [6][7]. Thus, the surface area of the suction surface increases than non-burning system.

3.2 Assessment by Adsorption Isotherm

3.2.1 Comparison of CRM treatment and hybrid treatment

Fig.8-11 shows the adsorption of various nutrients of CRM treatment and hybrid treatment.

NO₃-N (Fig.8): The adsorption equation of NO₃-N was shown below.

$$\begin{aligned} \text{MgO:} & \quad W=1.6 \times 10^{-2}C \\ \text{CaO:} & \quad W=3.2 \times 10^{-3}C \\ \text{DAF+Mg:} & \quad W=1.4 \times 10^{-2}C \\ \text{DAF+CaO:} & \quad W=1.3 \times 10^{-3}C \end{aligned}$$

From these equations, adsorption effect was shown to be higher in the following order.

$$\text{MgO} > \text{DAF+MgO} > \text{CaO} > \text{DAF+CaO}$$

The highest adsorption effect was showed in MgO. MgO showed higher adsorption effect than 12.1 times of that of DAF+CaO.

NH₄-N (Fig.9): The adsorption equation of

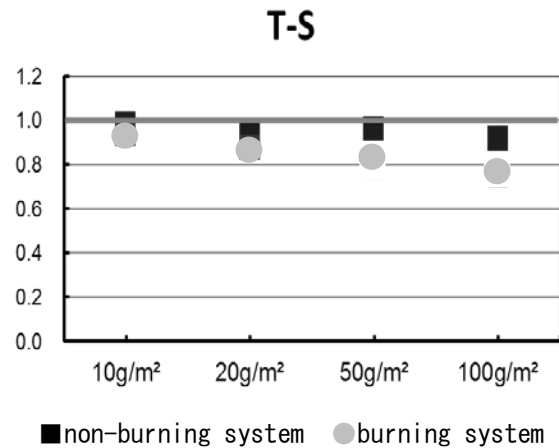


Fig.7 Total Sulfide concentration ratio in the pore water in the shell sprinkled

NH₄-N showed below.

$$\begin{aligned} \text{MgO:} & \quad W= 1.1 \times 10^{-4}C \\ \text{CaO:} & \quad W= -2.2 \times 10^{-4}C \\ \text{DAF+MgO:} & \quad W= 2.4 \times 10^{-5}C \\ \text{DAF+CaO:} & \quad W= -1.5 \times 10^{-4}C \end{aligned}$$

From these equations, adsorption effect was shown to be higher in the following order.

$$\text{MgO} > \text{DAF+MgO} > \text{DAF+CaO} > \text{CaO}$$

Adsorption isotherm of CaO and DAF+CaO showed negative adsorption. As reason for this, wash out effect occurred that weakly basic of NH₄-N is eluted into water by sprinkled Ca.

T-N (Fig.10): The adsorption equation of T-N showed below.

$$\begin{aligned} \text{MgO:} & \quad W= 1.5 \times 10^{-5}C \\ \text{CaO:} & \quad W= -2.6 \times 10^{-4}C \\ \text{DAF+MgO:} & \quad W= 7.3 \times 10^{-5}C \\ \text{DAF+CaO:} & \quad W= -1.7 \times 10^{-3}C \end{aligned}$$

From these equations, adsorption effect was shown to be higher in the following order.

$$\text{DAF+MgO} > \text{MgO} > \text{DAF+CaO} > \text{CaO}$$

PO₄-P: Similarly, it became negative adsorption equation in a system that was sprinkled with CaO.

T-P (Fig.11): The adsorption equation of T-P showed below.

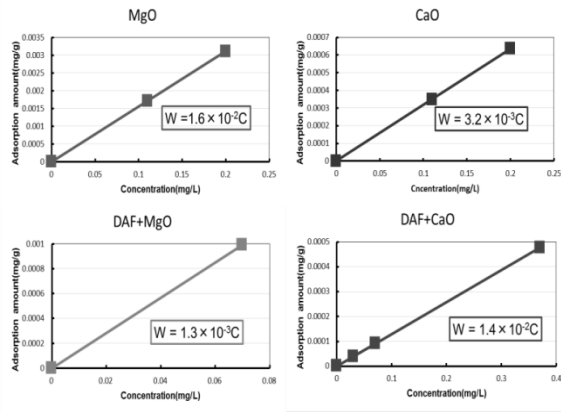


Fig.8 Adsorption characteristics of $\text{NO}_3\text{-N}$ in various sediment material improvement

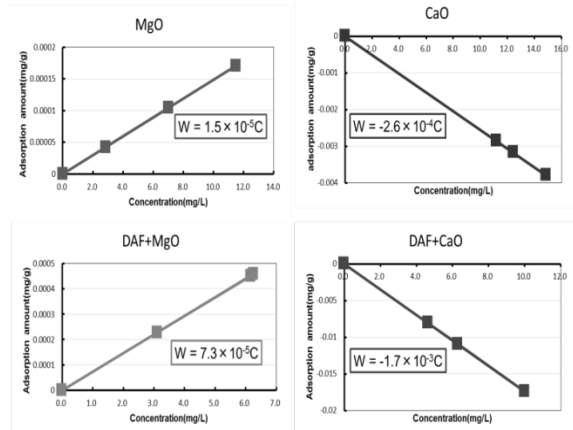


Fig.10 Adsorption characteristics of T-N in various sediment material improvement

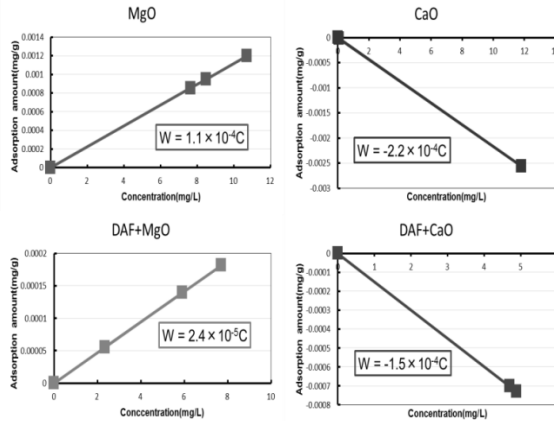


Fig.9 Adsorption characteristics of $\text{NH}_4\text{-N}$ in various sediment material improvement

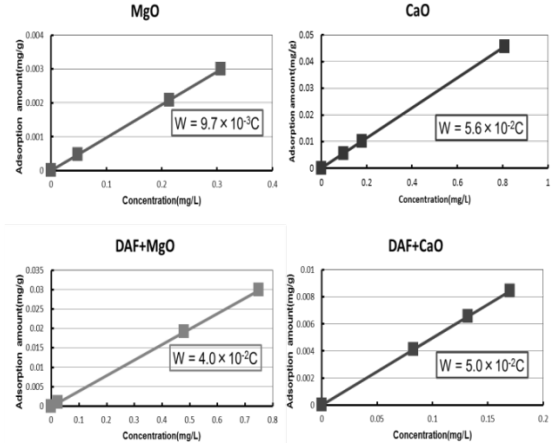


Fig.11 Adsorption characteristics of T-P in various sediment material improvement

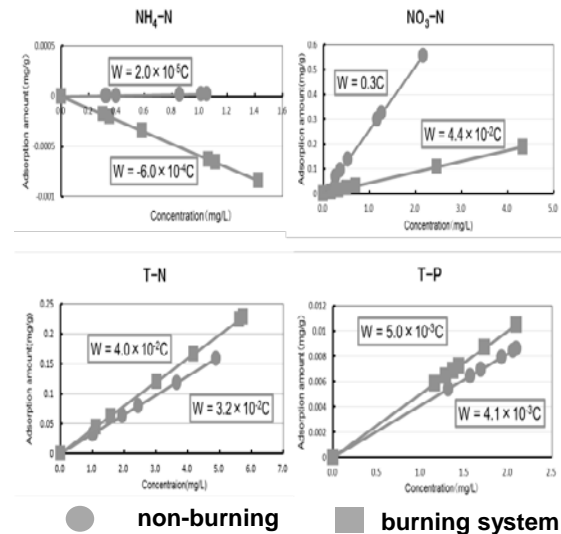
MgO: $W = 9.7 \times 10^{-3} C$
 CaO: $W = 5.6 \times 10^{-2} C$
 DAF+MgO: $W = 4.0 \times 10^{-2} C$
 DAF+CaO: $W = 5.0 \times 10^{-2} C$

From these equations, adsorption effect was shown to be higher in the following order.

$\text{CaO} > \text{DAF+CaO} > \text{DAF+MgO} > \text{MgO}$

CaO showed higher adsorption effect 5.81 times higher than MgO. As reason for this, binding force of CaO is higher than that of the MgO [3][8]. CaO showed higher adsorption effect 1.14 times higher than DAF+CaO. As reason for this, organic matter is reduced by applying the DAF process.

From the results above, high adsorption effect in nitrogen was obtained in MgO sprinkled system that was sprinkled. And that adsorption is highly effective in a system that was sprinkled with CaO



● non-burning ■ burning system

Fig.12 Adsorption characteristics of various nutrients in the shell

has been shown in phosphorus.

3.2.2 Comparison with regional unused resources

Fig.12 shows the adsorption of various nutrients by regional unused resources.

It compared the adsorption isotherm in the case of using the shells and adsorption isotherm of bottom sediment improvement process adsorption effect was highest.

In $\text{NO}_3\text{-N}$, non-burning system showed adsorption effect of 16.5 times compared to MgO but showed adsorption effect of 2.8 times compared with MgO at the burning treated system.

In $\text{NH}_4\text{-N}$, non-burning system showed adsorption effect of 0.18 times compared higher with MgO but showed adsorption effect of 40 times lower compared with MgO at the burning treated system.

In T-N, non-burning system showed adsorption effect of 43.8 times higher compared with DAF+MgO it showed adsorption effect of 54.8 times compared to DAF+MgO at the burning treated system.

In T-P, non-burning system showed adsorption effect of 13.8 times lower compared with CaO but showed adsorption effect of 11.3 times compared to CaO at the burning treated system. Adsorption effect of regional unused resources sprinkled in T-P is about 1/10 of CaO treatment has been shown.

By CaO sprinkling, elution of $\text{NH}_4\text{-N}$ was observed from the bottom mud due to the rise in pH. It has resulted that affect possibility is suggested to ecosystem

In this study, culture period of microcosm system was set to 20 days, and this was too short for saturated adsorption. The values of adsorption capacity are important, but it was not detected in this study. Furthermore, studies followings are required to practice in action the shells spraying as regional unused resources. Some growth suppression effect on the benthos which play an important role of consumer of sediment ecosystem directly affected by sediment material improvement [9], need to continue considering about what would affect the ecosystem structure consisting of complex food chain. To investigate these problems, on-site scale mesocosm system experiment should be conducted, and from the comparison between laboratory scale microcosm system and on-site scale mesocosm system, the results obtained from this study can be implemented in the field.

4. CONCLUSIONS

Pore water quality analysis of bottom sediment where the shell sprinkled treatment as regional unused resources and the comparison of the adsorption characteristics using Langmuir's adsorption isotherm with a variety of sediment improvement materials were conducted. Results can be concluded as follows.

1) In sediment pore water, $\text{NH}_4\text{-N}$ is eluted into upper water by wash-out effect especially in the burning treatment system, and the concentration of nitrogen in the pore water was reduced. T-P and $\text{PO}_4\text{-P}$ also reduced the concentration in pore water, with combine of phosphate and Ca as the main component of the shell. T-S also reduced in pore water as same as phosphate.

2) In adsorption characteristics calculated using Langmuir's adsorption isotherm as various sediment improvement materials, nitrogen was reduced in MgO sprinkled treatment (MgO and DAF+MgO), and phosphate was reduced in CaO sprinkled treatment (CaO and DAF+CaO). In shell fragment sprinkled treatment, higher adsorption effect was demonstrated in nitrogen, but only 1/10 adsorption effect in phosphorus.

From these outcomes, shell fragment as regional unused resources can be considered as one of the effective tools for sediment eutrophication remediation.

5. ACKNOWLEDGEMENT

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