International Journal of GEOMATE, May 2019, Vol.16, Issue 57, pp.49 - 55
Geotec., Const. Mat. & Env., DOI: https://doi.org/10.21660/2019.57.4619
ISSN: 2186-2982 (Print), 2186-2990 (Online), Japan

THE REPRODUCTION OF NATURAL SEA SLUDGE (HEDORO) USING PRESERVED NATURAL INORGANIC MATTERS

Hirosuke Hirano[1,2,*], Davin H. E. Setiamarga[2,3]

[1] Department of Civil Engineering, National Institute of Technology, Wakayama College, Japan
[2] Department of Ecosystem Engineering, Faculty of Advanced Engineering, National Institute of Technology, Wakayama College, Japan
[3] Department of Applied Chemistry and Biochemistry, National Institute of Technology, Wakayama College, Japan

*Corresponding Author, email: Received: 15 Nov. 2018, Revised: 18 Dec. 2018, Accepted: 29 Dec. 2018

ABSTRACT: Comprehensive studies on sea sludge utilization have been hampered by the impossibility of re-obtaining samples with similar characteristics from nature. Previously, we reported the creation of an artificial sludge mimicking the general properties of the natural seafloor sludge of the Funabashi in Chiba. Although this method is useful for recreating sludge with high organic content (Funabashi = 23.61%), it could not be used for recreating sludge with low organic content (e.g. Hidaka in Wakayama = 5.58%), with the high organic content of one of the ingredient, zeolite (7.79%), as a limiting factor. In this study, we focused on the creation of a semi-artificial sludge using inorganic matters obtained from natural sea sludge. Sludge samples from Hidaka Port were collected and burnt at 600ºC to remove their organic content. Artificial organic materials were then added to the obtained inorganic matters, following the method described in our previous study. The resulting semi-artificial sludge mimics the properties of the original sludge. Thus, we revised our previously proposed method of artificial sludge production, by recreating a sludge with low organic content, by utilizing inorganic matters collected from natural samples.

Keywords: Artificial Sludge, Sea Sludge, Inorganic Content, Hidaka Port

1. INTRODUCTION

Hedoro, or sludge, is composed of inorganic matter such as mud or sand, organic matter from nutrient salt or protein, and sulfide as the cause of the “rotten egg” smell [1]. Hedoro is also known to bring malicious environmental effects such as eutrophication (which, in turn, might cause microbial blooms), bad smell caused by hydrogen sulfide, and capture radioactive cesium. Accordingly, in order to purify the water environment, methods have been devised to clean the hedoro from aquatic environments, such as decontamination. Some decontamination methods have been reported by previous studies, e.g. decomposing hydrogen sulfide by oxygen [2], and decontamination by organic matter decompositions [3].

In such studies, it is crucial to collect hedoro each time from nature. However, the condition of the natural environment (e.g. weather and seasonal changes) during sampling affects the characteristics of the hedoro. Thus, it is impossible to set all environmental conditions to be the same for all samples. For example, we have shown that the organic contents in Hidaka Port in Wakayama in Japan changes each month [4]. Meanwhile, it's been known that long-term preservation of hedoro might cause its compositional changes of hedoro samples composition (e.g. [5–6]).

1.1 Report of Our Previous Studies

Previously, we proposed the production of an artificial sludge with its early values, constant. In the study, we created an artificial sludge by using dry yeast as the source of organic matter, zeolite for the inorganic matter, and sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$) to recreate sulfide content. The resulting artificial sludge mimicked the hedoro collected from the Funabashi port in Chiba, Japan [7]. We also showed that dry yeast, as the source of organic matter in artificial sludge, has the ability to capture cesium, and thus similar to natural hedoro [8–9]. Therefore, artificial hedoro could be useful for research requiring constant early values.

1.2 Artificial Sludge Weaknesses

During our previous experiment to produce the artificial sludge described above, we first made the “artificial sludge base” by mixing dry yeast and $Na_2S \cdot 9H_2O$. Next, zeolite was added to the sludge base, with base composition equals to 0:100, 41.7:58.3, and 83.3:16.7. We calculated the calibration curve of the heat-weight loss analysis (TG; Thermo-Gravity analysis) (Fig. 1) by the primary equation and quadratic equation, and use the average value as the best addition rate of sludge base to produce artificial sludge. However, we found out that the 0:100 sample shown the organic content of 7.79%, despite no addition of organic content. The main ingredient zeolite, being made of only inorganic matter (silicon and aluminum), is supposed to content no organic material. We considered that the ingredient zeolite probably captured microorganisms and/or other organic materials in the air, and thus obtained its organic content.

To test the possibility of zeolite capturing organic matter from the air, a sample of zeolite was burnt at 600 ºC to get rid all of the possibly contained organic matter, and left in the open air, in the lab. Organic content was measured by TG once a day for four days. We found the organic content 6.91% as the maximum value (Fig. 2). From this result, we can conclude that zeolite has the possibility to obtain organic matter during preservation. Therefore, it is impossible to produce an artificial sludge with the organic content lower than that of the zeolite used as an ingredient.

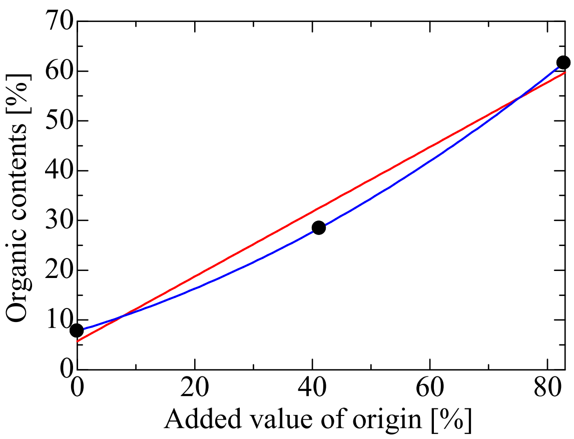

Fig. 1: Calibration curve in artificial sludge

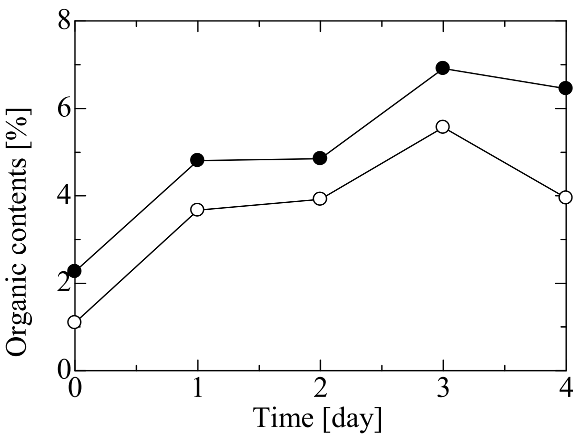

Fig. 2: Change of zeolite by time series

2. CHANGES OF HEDORO PROPERTIES DURING STORAGE

As mentioned previously, it is difficult to reproduce low organic content sludge by using our previously reported method. Meanwhile, long-term storage of natural hedoro might change its composition. Some have anecdotally suggested storing samples at low temperature (freezing at –20 ºC to –18 ºC, cold storage at 0 ºC, and refrigeration at 2 ºC to 6 ºC).

To see if cold storage really work, we conducted an experiment by putting hedoro samples (collected in in February and March 2018 from the Hidaka Port) in a freezer for the –20 ºC treatment, ice pack for the 0 ºC treatment (Fig. 3), and in a fridge for the 2 ºC–6ºC treatment. The initial organic content of the samples was 2.00% for the February sample and 1.16% for March. The organic and moisture contents of each sample were measured twice, after one week of cold storage. Both measurement results showed only slight differences, as shown in Table 1 (-0.36% to 0.19% after 7 days).

We also checked changes of the compositions of hedoro samples collected from a channel in Gobo city at Wakayama. At 16.40% and 4.69%, the initial organic contents of the channel's hedoro samples were relatively high, compared to the samples from Hidaka Port. Interestingly, our organic content measurement showed that both samples had an organic content increase of +10.75% to +24.17% after seven days in cold storage (Table 2). The standard deviation of the results is shown in Table 3.

In our present study, we are unable to pinpoint with confidence the reason for the daily increase, because the samples were put in airtight ziplock bags to prevent outside contamination. Some possibilities could be related to temperature chan-


Fig. 3: Ice petri dish

ges [10–15] and possible microbial contaminations and proliferations [6, 16–17].

Our result indicates that refrigeration (2 °C to 6 °C) and/or another cold storage method might work if the organic content of the sample is very low, such as the Hidaka Port hedoro samples, as indicated by the relatively slight change (Table 2), with refrigeration as the better method of storage. However, it still could not prevent the changes in organic content. The organic content of a hedoro sample changes, even only days after sample collection. For example, hedoro in Hidaka port collected in April 2018 and kept at room temperature was measured on the next day to have an organic content of 12.54%, but after 11 days, the value changed to 1.38%, and after 13 days, to 1.61%.

Table 1: Change of organic contents in storage (1)

Cold Storage Method	Organic contents [%]	Initial organic contents [%]	Change after one week [%]
Freezing	1.75	2.00	-0.25
	1.38	1.16	0.22
On ice	1.70	2.00	-0.30
	1.35	1.16	0.19
In Fridge	1.64	2.00	-0.36
	1.41	1.16	0.25

Table 2: Change of organic contents in storage (2)

Cold Storage Method	Organic contents [%]	Initial organic contents [%]	Change after one week [%]
Freezing	31.09	16.40	14.69
	24.69	4.69	20.00
On ice	27.14	16.40	10.75
	28.83	4.69	24.14
In Fridge	30.71	16.40	14.31
	20.82	4.69	16.62

Table 3: Results of standard deviation to change organic contents in storage

	n	Standard deviation in organic contents		
		Free zing [%]	Save in ice [%]	Refrige ration [%]
Natural hedoro in Hidaka port	3	0.22	0.47	0.32
	3	0.21	0.18	0.20
Channel's hedoro in Gobo city	3	1.13	3.73	1.47
	3	1.16	1.89	3.46

The changes of the moisture content during cold preservation of the hedoro sample was also measured through TG analysis. Hedoro samples analyzed were samples collected from the Hidaka port (organic contents: 2.00% and 1.16%) and from a channel in Gobo City (organic contents: 16.40% and 4.69%), and artificial sludge samples (organic contents: 20.64% and 28.01%). The artificial sludge production method follows our previous report [5]. First, samples were heated at 100ºC for five minutes to sterilize possible contaminations. After that, measurements were done for every five minutes, while the samples were continuously heated at 100°C. The results are shown in Fig. 4 to Fig. 9 (●: Refrigeration, ▲: Freezing, □: cold storage in ice).

The values of released moisture content of the hedoro collected from Hidaka Port were 2.81% for the first sample (organic content: 2.00%; preserva-

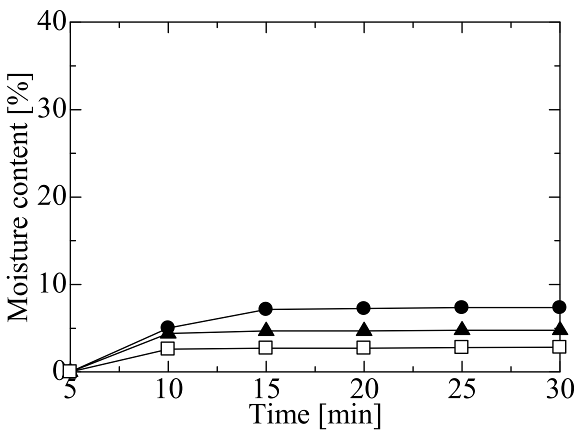

Fig. 4: Change of moisture content in hedoro (1)

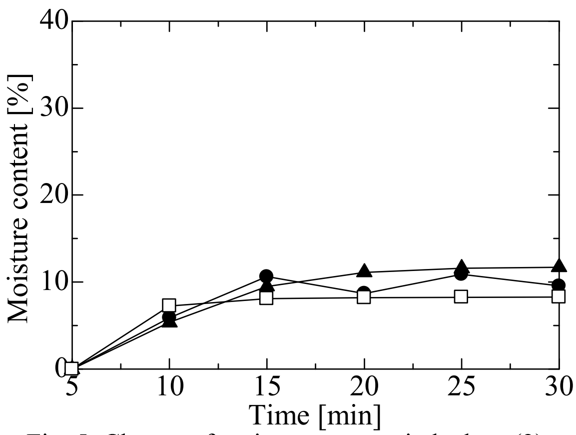

Fig. 5: Change of moisture content in hedoro (2)

tion method: cold storage in ice; Fig. 4), and 8.28% for the second sample (organic content: 1.16%; preservation method: cold storage in ice; Fig. 5). For hedoro samples from the Gobo City channel, the values were 17.51% (first sample; organic content: 16.40%; preservation method: cold storage in ice; Fig. 6) and 13.24% (second sample; organic content: 4.69%; preservation method: refrigeration; second sample). This result, however, emphasizes the difficulties of maintaining both the moisture and Fig. 7). Our result for the artificial sludge was inconclusive (Fig. 8 and 9; organic contents were set to 20.64% for the first sample, and 28.01% for the organic content of samples during preservations, regardless of the method utilized (Table 4, p was calculated with the value of t from T.TEST function). Without a doubt, such changes will affect the physical and chemical properties of the hedoro samples.

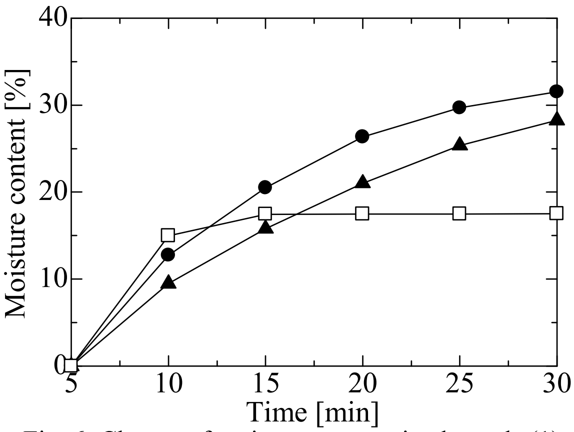

Fig. 6: Change of moisture content in channels (1)

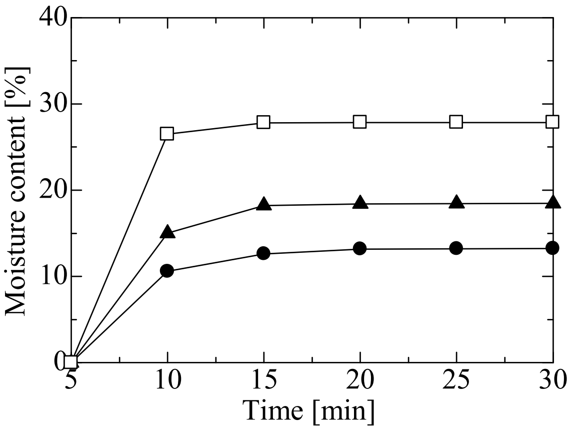

Fig. 7: Change of moisture content in channels (2)

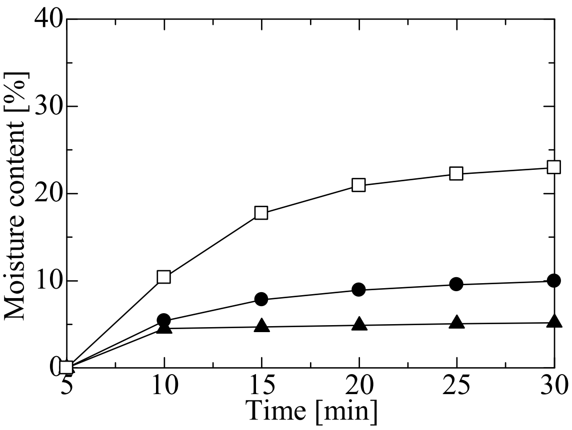

Fig. 8: Change of moisture content in artificial (1)

3. SEMI–ARTIFICIAL SLUDGE CREATION

3.1 The Production of Semi-Artificial Sludge Using Inorganic Matter Extracted from Natural Hedoro

In our present study, inorganic matters from two hedoro samples collected from the Hidaka port (February 2018 and May 2018) were extracted by combustion at 600 ºC to completely burn organic materials off. Three types of artificial sludge with differing organic contents were then made, by using the leftover inorganic matters from the burnt samples. The organic content was calibrated using the previously mentioned "artificial sludge base"

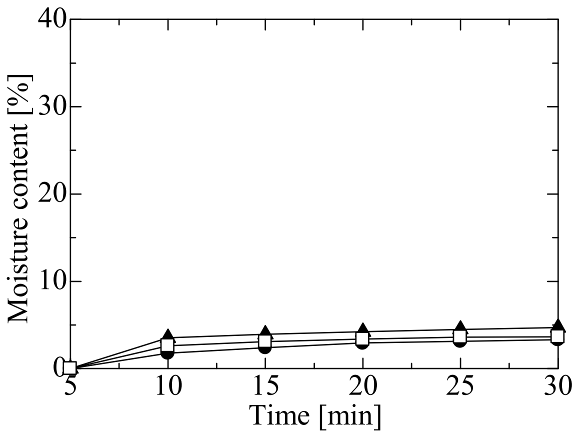

Fig. 9: Change of moisture content in artificial (2)

Table 4: Significant difference in moisture content

	n	Significant difference		
		● and ▲	▲ and □	● and □
Natural hedoro (1)	3	p = 0.495	p = 0.498	p = 0.497
Natural hedoro (2)	3	p = 0.367	p = 0.446	p = 0.421
Channel’s hedoro (1)	3	p = 0.498	p = 0.363	p = 0.469
Channel’s hedoro (2)	3	p = 0.498	p = 0.498	p = 0.498
Artificial sludge (1)	3	p = 0.498	p = 0.498	p = 0.496
Artificial sludge (2)	3	p = 0.494	p = 0.496	p = 0.496

(= sludge base). The three types of samples are as follow: sludge base/natural sludge inorganic matter = 0/100, 41.7/58.3, and 83.3/16.7. The organic/inorganic ratio was then plotted on a calibration curve (Fig. 10–11). These compositional ratios enabled us to recreate samples mimicking the natural hedoro collected in February (organic content = 1.30%; Fig. 10), and in May (organic content = 1.50%; Fig. 11). Based on these analyses, the resulting calibration curve indicates that the best ratio of sludge base powder addition vs. the total mix (sludge base + inorganic material from the natural sludge) is 3.10% to recreate the February sample, and 0.73% for May sample. Thus, we succeeded in following the recipe, with the margin error during addition between 0.13% – 0.14%.

3.2 Results and Discussions

The resulting semi-artificial hedoro, interestingly, showed different organic content ratio than what was predicted by the calibration curve. For the February sample recreation, the expected

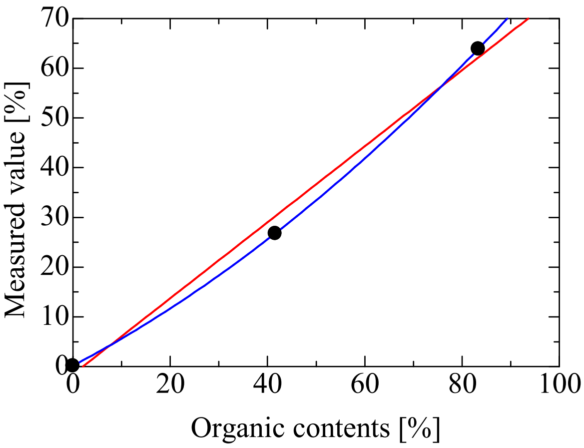

Fig. 10: Calibration curve of organic contents of the semi-artificial sludge (1)

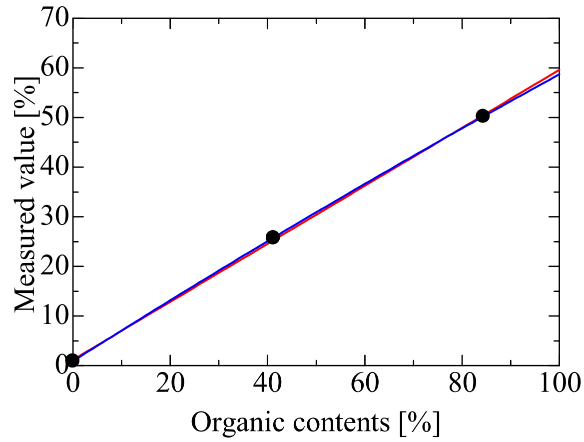

Fig. 11: Calibration curve of organic contents of the semi-artificial sludge (2)

organic content was 1.22%, and for May was 1.58%. However, the actual observation value we obtained was 1.31% (Table 4) and 2.86% (Table 5), respectively. Therefore, the February sample-mimicking semi-artificial hedoro had +0.09% than the expected value, while the May one showed +1.28% than the expected value.

The result indicated that we were unable to recreate the May sample, because the margin of error was bigger than 1.0%. This is probably because it is difficult to add the sludge base powder less 1.0% of the total organic/inorganic mix, since in this experiment we only made ca. 1 gram of semi-artificial sludge.

The calibration curve indicated that some inorganic content values were too high (more than 98.94% = organic content values were under 1.06%), causing the ideal values of sludge base needed in the mix, in effort to reproduce such samples, to be less than 0.0%. This also indicates that there are rooms for improvements of the method presented here.

Table 4: Result of reproduction (1)

22th Feb., 2018	Organic contents [%]	
Natural	Average as 1.30	0.92
		1.43
		1.53
Semi-artificial (Added 2.96% of A. S. powder)	Average as 1.31	1.09
		1.37
		1.47

Table 5: Result of reproduction (2)

25th May, 2018	Organic contents [%]	
Natural	Average as 1.50	1.40
		1.77
		1.33
Semi-artificial (Added 0.86% of A. S. powder)	Average as 2.86	2.80
		3.17
		2.61

Table 6: Standard deviation and significant difference of organic contents in semi-artificial vs. natural hedoro

	Standard deviation	significant difference
Natural (1)	0.268	p = 0.197
Semi-artificial (1)	0.161	
Natural (2)	0.196	p = 0.499
Semi-artificial (2)	0.232	

Despite some weaknesses, however, we were successful in improving our previous artificial sludge production method [7]. In that study, we mentioned that it was impossible to recreate natural hedoro with low organic contents (less than 6.91%). With our method presented here, we succeeded in recreating low organic contents hedoro, such as those of the Hidaka port (Table 6).

4. CONCLUSION

Inorganic matter storage is easier and more reliable, as indicated by our cold storage experiment with low-organic content samples. Our experiments indicated that inorganic contents are robust and thus could endure relatively long-term storage. Previous studies have also indicated that such stability of inorganic contents (e.g. [18–19]). Meanwhile, organic content changes drastically during storage, causing changes to the properties of the hedoro samples. Therefore, the recreation of a semi-artificial sludge using preserved inorganic materials extracted from the original natural samples would allow successful recreations of original natural hedoro samples, including those with low organic contents.

The stability of inorganic contents, and the success of our success in recreating natural hedoro with low organic content (high inorganic content) by utilizing inorganic matter extracted from the original natural hedoro, also allow us to propose methods of storage: (1) hedoro samples could be first burnt to get rid of the organic content, and the inorganic matters cold-stored, or (2) hedoro samples are refrigerated or frozen during storage, and when needed, burnt to get rid of their organic contents. However, future studies to pinpoint which method is more effective and accurate are still needed.

Future studies will include, for example, improving the method of recreating natural hedoro with low organic content and/or high inorganic content presented here, and testing other possible sources of organic matter besides yeast extract, and inorganic matter besides zeolite.

5. REFERENCES

[1] Yoshida T., About generation and the removal of the sludge - In bottom sampler examination of the Gulf of Minamata, HEDORO, No. 1, 1974, pp.11–27.

[2] Okamoto K., Toyama T., and Komoriya T., Ocean Decontamination: High Ability Removal Method to Radioactive Cesium from Ocean Sludge by Using Micro Bubbles and Activating Microorganisms. International Journal of GEOMATE, Vol. 12, Issue 32, 2017, pp.57–62.

[3] Hirano H., Toyama T., Nishimiya N., and Okamoto K.., Removal of Cesium from Sea Sludge through Decomposition of Organic Matter with Aqueous Hydrogen Peroxide. International Journal of GEOMATE, Vol. 8, Issue 1, 2015, pp.1203–1206.

[4] Hirano H., Semura D., Sakamoto K., Toyama T., and D. H. E. Setiamarga, A Dynamic changes of organic content over time in the sea sludge collected from the Gobo/Hidaka coastal area in Wakayama, southwest Japan. IOP Conference Series: Earth and Environmental Science, Vol. 176, 2018, Paper No. 012007,

[5] Hirano H. Toyama T., Nishimiya N. Preparation of prototype artificial sludge based on compositional information of sea sludge. 48th Annual Conference of Japan Society on Water Environment, 2013, pp. 298.

[6] Hua K., Jiang J. Q., Zhao Q. L., Lee D. J., Wanga K., and Qiu W., Conditioning of wastewater sludge using freezing and thawing: Role of curing. Water Research, Vol. 45, issue 18, 2011, pp. 5969–5976.

[7] Hirano H., Toyama T., Nishimiya N., D. H. E. Setiamarga., Morita S., Uragaki Y., and Okamoto K., Artificial Sludge Based on Compositional Information of a Natural Sea Sludge. International Journal of GEOMATE, Vol. 12, Issue 31, 2017, pp.95–99.

[8] Uragaki Y, Morita S, Hirano H, Ability of adsorbed cesium by organic matter from sea sludge. 50th Annual Conference of Japan Society on Water Environment, 2016, pp. 622.

[9] Hirano H., Sakamoto K., and Semura D., Comparison of adsorbed ability for cesium, by inorganic matter and sea sludge Part2: changing decontaminate ability by values of Cs in a sample. 51th Annual Conference of Japan Society on Water Environment, 2017, pp. 404.

[10] Tamamura S, Sakai T, Shimizu S, Ishijima Y, Igarashi T, Variation in inorganic nitrogen and organic carbon concentrations in groundwater samples stored under cold and frozen conditions. Journal of Groundwater Hydrology, Vol. 54, Issue 2, 2012, pp.107–116.

[11] Ide T., Kawasaki K., Yamashiro H., and Matsuda A., Conditioning of excess activated sludge by freezing and thawing process - the

change of physical-chemical properties of sludge with half-freezing and extended freezing -. Suishitsuodakukenkyu, Vol. 10, No. 10, 1987, pp. 618–623. (in Japanese)

[12] Kawasaki K., Matsuda A., and Ide T., Conditioning of excess activated sludge by freezing and thawing process - the change of settling characteristics of sludge floc -. Kagakukogakuronbunshu, Vol. 16, No. 1, 1990, pp. 16–22. (Japanese)

[13] Fujita M., Sludge dewatering by freezing. Japanese Journal of Freezing and Drying, Vol. 36, 1990, pp. 10–13. (in Japanese)

[14] Sanin F. D., Vesilind P. A., and Martel C. J., Pathogen reduction capabilities of the freeze.thaw sludge conditioning. Water Research, Vol. 28, No. 11, 1994, pp. 2392–2398.

[15] Örmeci B., Freeze-thaw conditioning of activated sludge: effect of monovalent, divalent, and trivalent cations. Journal of Residuals Science & Technology, Vol. 1, No. 3, 2004, pp. 143–150.

[16] Noda S., Koyama K., Takakuwa T., and Akutsu T., Experimental studies on dewatering of digested sludge by freezing-thawing and filtration method. Eiseseikougaku, Vol. 9, 1964, pp. 41–53. (in Japanese)

[17] Sato A., Nakamura D., Suzuki T., and Nishimoto S., Change of the moisture content of unsuitable soil through freezing and thawing process appeared in a natural cold climate. Japanese Geotechnical Journal, Vol. 4, No. 2, 2009, pp. 205–214. (in Japanese)

[18] Abe O., Kanzaki S., and Tanabe H., Thermal Decomposition of Silicon Nitride along with Powder Characteristics, The Chemical Society of Japan, No. 2, 1989, pp. 275-281 (in Japanese)

[19] Yoshida S., Some Aspects of the Role of Silicon on Plants, Japanese Society of Soil Science and Plant Nutrition, Vol. 31, Issue 1, 1960, pp. 42-48 (in Japanese)