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ARTIFICIAL SLUDGE BASED ON COMPOSITIONAL INFORMATION OF A NATURAL SEA SLUDGE

*Hirosuke Hirano[1], Takeshi Toyama[2], Nobuyuki Nishimiya[2], Davin H. E. Setiamarga [1,3], Shugo Morita[1], Yuto Uragaki[1], and Kyoichi Okamoto[2]

[1] National Institute of Technology, Wakayama College, Japan
[2] College of Science and Engineering, Nihon University, Japan
[3] Graduate School of Science, The University of Tokyo, Japan

*Corresponding Author, Received: 15 June 2016, Revised: 09 August 2016, Accepted: 24 Nov. 2016

ABSTRACT: The chemical and physical properties of sludge collected from different aquatic areas differ from one another. Such differences have made the universal standardization of early settings difficult. Usage of artificial sludge with stable characteristics has been thus proposed in the present study. First, values of organic matter, sulfide content, and the inorganic content were measured for the sea sludge collected from Funabashi Port in Japan. Using the obtained chemical and physical properties as reference, we then produced artificial sludge by mixing dry yeast made from yeast cultured in liquid sodium sulfide nonahydrate solutions (3.5-4.0%) and zeolite for inorganic material. In the present study, we understood that we couldn't obtain the desired organic content for the artificial sludge, simply by adding the yeast with the amount similar to the organic content percentage we aimed. We thus calibrated the amount of yeast by measuring the actual organic content of several artificial sludge samples by thermo-gravimetry analysis. We found out that we need only to write a calibration curve of three measurements (zeolite-dry yeast w/w% = 0%, mid-point, and 83.3%) in order to obtain the information about the right amount of dry yeast addition to produce an artificial sludge with desired percentage of organic material. Finally, we mixed 31.4% of dry yeast (zeolite and other inorganic materials = 68.6%), in order to obtain an artificial sludge with 23.6% organic content. This percentage is similar to the organic content of the sludge collected from Funabashi Port.

Keywords: Artificial sludge, Zeolite, Dry yeast, Water area

1. INTRODUCTION

Sludge easily accumulates in closed water system, such as lakes, ponds, and bays. This problem occurs because such systems lack the ability of extensive water circulation. The accumulation of sludge might then cause problems because the anaerobic condition of the sludge might then cause decompositions by microorganisms. In order to solve this problem, it has conducted a study of cleaning sludge in closed water area by using aerobic microorganisms and micro bubbles [1]. In such studies, it is important to collect fresh sludge from water area every time, because the organic content of the sludge makes storage difficult. However, collecting fresh samples every time makes universal standardization of early settings difficult, because of differences in weather and environmental conditions such as temperature and humidity.

In order to overcome the difficulties of setting initial values, we propose the usage of artificial sludge with stable characteristics for such studies. An artificial sludge, with its early values set, will not be affected by even the subtle differences of environmental and weather changes, thus making standardization possible. However, producing an artificial sludge with characteristics mimicking those of the natural one is not easy, since many factors must be calculated in during the production process.

Here, we report our result of producing an artificial sludge useful for research requiring sludge with its early values constant. Moreover, we also achieved our aim of constantly reproducing the artificial sludge, with stable standard values and easy to reproduce.

2. ANALYSES OF NATURAL SLUDGE PROPERTIES

In order to produce an artificial sludge useful for studying the environment, we need the artificial sludge to mimic the characteristic and properties of the natural one. However, since natural sludge samples taken from different locations and times would show different starting values, it has needed to choose one sample to use as the point of reference. For this purpose, we decided to use the natural samples taken from Funabashi Port in Chiba, Northeast Japan, as the reference of the present study. This is because Funabashi Port is located close to our campus hence allowing multiple sampling trips easy and practical, and since it has been using the samples from the location in other studies (e.g. [2]).

Thus, in order to understand the natural properties of the sludge, in first studied material of natural sludge it has collected from Funabashi port in Chiba, northeast Japan.

2.1 Organic contents

We conducted thermo-gravimetry (TG) analysis in order to check the value of organic content. At temperatures above 100ºC, moisture content of the sampled material will boil away, while above 600ºC, the organic content of the material will completely evaporate, leaving only the inorganic part. Accordingly, in order to allow us to measure the pure value of the organic content, TG analyses were conducted between the values of 100ºC and 600ºC. The result of TG analyses on the natural sludge sample collected from Funabashi Port showed that the organic content is 23.6% (Fig. 1, solid line). For comparison, we also measured natural sludge samples collected from other the Hidaka-port in Wakayama in southwest Japan, where is located about >350 km in Funabashi port in southwest Japan. The Hidaka-port sludge has a 7.3% organic content (Fig. 1, dashed line).

2.2 Inorganic contents

In order to check the property of inorganic matter, we conducted energy dispersive X-ray spectrometry (EDX) on the samples. From EDX analyses, we found out that this sample has the mineral content of: silicon (Si), aluminum (Al), iron (Fe) and sulfur (S) (Table 1). X - ray diffraction (XRD) analysis also showed that the Si content were silicon dioxide (SiO_2) and kyanite (Al_2SiO_5) (Fig. 2).

2.3 Sulfide

We then used gas detector tube to check the value of hydrogen sulfide (H_2S). And about the value of H_2S by gas detector tube, it was tried like these conditions about sample water; by mixing 1 g of sludge and 100 cm3 of water. As a result, value was 0.016 g/1g, so concentration of S in sludge was 1.5% by molecular weight.

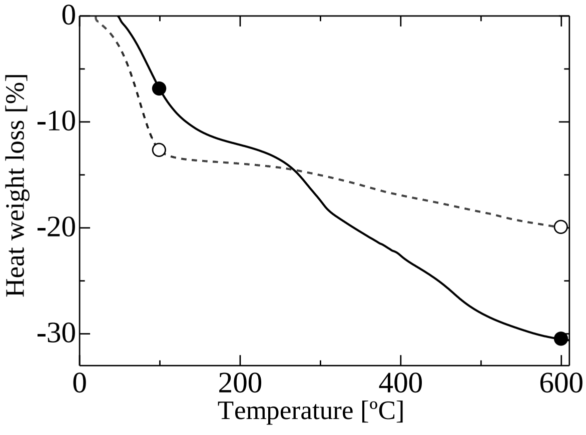

Fig. 1: Values of organic contents by TG
○: in Hidaka port, ●: in Funabashi port

3. ARTIFICIAL SLUDGE PRODUCTION

3.1 Preliminary artificial sludge production

In order to obtain the data about the amount of materials needed to produce the final artificial sludge, we conducted a preliminary experiment of mixing materials to synthesize an artificial sludge. In this experiment, it has mixed dry yeast and aqueous solution of sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$), which was 3.5 to 4.0 mass%, that ratio was 1 g of dry yeast to10 cm^3 of $Na_2S{\cdot}9H_2O$. After discarding the supernatant, we collected the "dry yeast mud", and mixed it with SiO_2 three times the amount of the yeast mud. It was measured this trial artificial sludge by TG and compared the value with Funabashi's sludge, but we were unable to mimic the organic content of the natural sludge, and thought that this was caused because the inorganic content (sulfur compounds, etc.) in the yeast mud was added to the total inorganic content of the preliminary artificial sludge, causing a decrease in the

Table 1 Conditions of inorganic matter in sludge

Funabashi	Si [%]		Al [%]		Fe [%]		S [%]	
1st	46.41	47.9	20.02	20.6	19.20	21.3	14.37	10.3
2nd	46.47		19.70		22.19		11.64	
3rd	50.98		21.09		18.19		9.74	
4th	46.17		21.19		24.69		7.95	
5th	49.26		20.88		22.12		7.74	
Hidaka	**Si [%]**		**Al [%]**		**Fe [%]**		**S [%]**	
1st	65.84	65.7	23.69	23.5	7.01	7.4	3.47	3.4
2nd	68.54		23.04		6.40		2.02	
3rd	67.95		22.60		6.30		3.16	
4th	62.65		24.27		8.69		4.39	
5th	63.42		23.92		8.68		3.97	

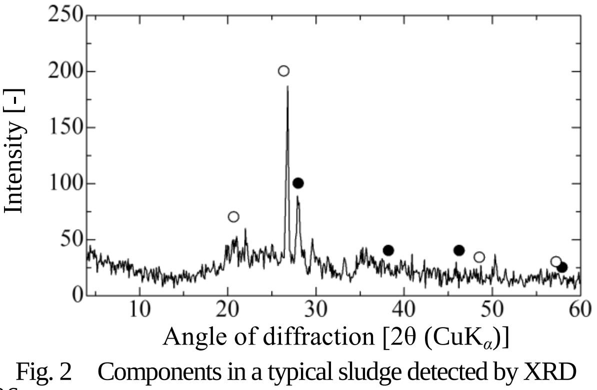

Fig. 2 Components in a typical sludge detected by XRD
○: SiO_2, ●: Al_2SiO_5

percentage of the organic content.

We tried varying compositions of organic contents (= yeast mud; 0%, 25%, 50%, 75%, and 100% of yeast mud, of the total SiO_2 yeast mud mix). The results are plotted on the calibration curves shown as Fig. 3 and Fig. 4. However, we still could not mimic the value of the organic content of Funabashi Port sludge when it has followed the values shown in the figures.

We then switched to use average of the values in the first order and quadratic, and were successful in obtaining an artificial sludge with the organic content of 23.8%, which was within 1.0% error. In second trial, it was successful to make 23.6% of organic matter in artificial sludge. Although reasons why we were able to reproduce the value of organic matter in artificial sludge by averaging the first order and quadratic values was still unknown, it was able to set the value of organic content in artificial sludge by any numerical values, if we use the average values of the callibration curve mentioned above.

We also found an interesting characteristic of the calibration curves in Fig. 5: calibration curves by approximation formula of first order and quadratic must intersect at 83.3%. It is unknown about this reason too. However, this information helps in drawing an easier calibration curve: rather than writing the intersection points at several standard points, it is able to use the calibration curves 0% and 83.3%, and the middle point.

3.2 Zeolite addition

After success on finding the right amount of organic matter addition as explained in the previous section, it was tried to use artificial sludge to reproduce previous studies about sea sludge, and see if the results of such studies were reproduced, when using artificial sludge. We chose trying to reproduce previous experiments about cesium ion (Cs^+) decontamination [3], and set the experimental conditions to be similar with that. For the study, it was added cesium nitrate ($CsNO_3$; 1000 ppm) to preliminary artificial sludge (dry yeast and SiO_2; totaling to 10 g). We prepare 5 samples of the mix, and then further added 20cm^3 of hydrogen peroxide solution (H_2O_2) with 5 types of concentrations, between from 0% to 34.5%.

In the present study, no decontamination effect was observable in artificial sludge like what we expected (Fig. 6: white dots = expected result,

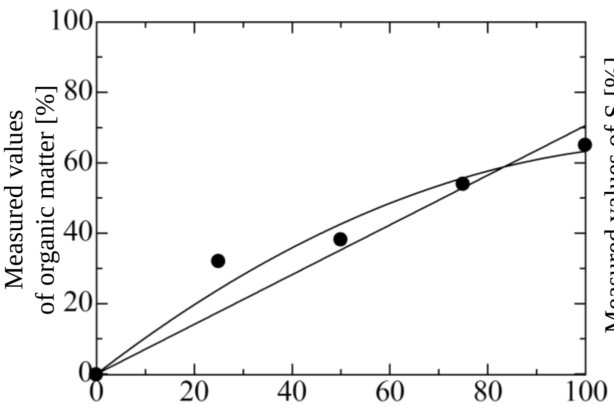

Fig. 3 Calibration curve in trial (1)

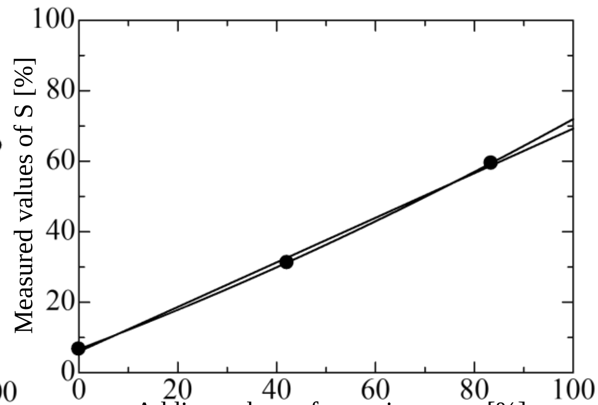

Fig. 5 Calibration curve in artificial sludge

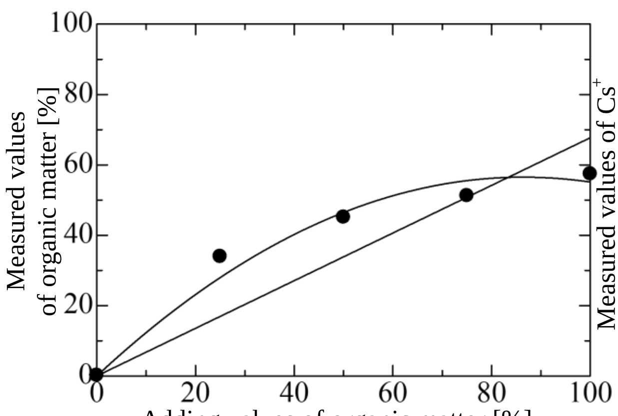

Fig. 4 Calibration curve in trial (2)

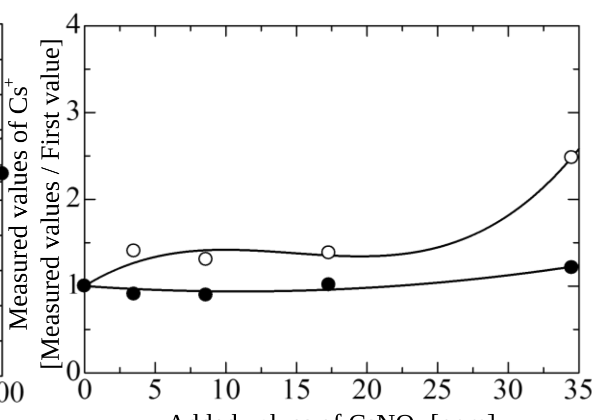

Fig. 6 Results of Cs^+ decontamination
○: Funabashi's sludge, ●: Artificial sludge by SiO_2

black dots = obtained result). This suggested that the artificial sludge could not adsorb Cs^+, and it was difficult to show the effect of decontamination reproducively as in the previous study [3], by the lack of as the sludge, or in other words, the absence of adsorbed Cs^+ in the first place.

Previous studies have shown that in sludge, the organic content has Cs^+ adsorption ability (e.g. [4] and [5]). However, our study here also suggests that besides the organic content, the inorganic content has a Cs^+ adsorption ability (Table 2) by [6], which was lacking in preliminary sludge.
Based on the result of XRD analysis, we added zeolite (vermiculite, kind of silicate mineral) to preliminary artificial sludge for the inorganic material, in order to add the Cs^+ adsorption ability of artificial sludge. Another reason of choosing zeolite as one of the inorganic content ingredients was because previous studies have shown that zeolite has the ability of Cs^+ adsorption (e.g. [6]), similar to the inorganic matter in natural sludge, which is also a Si compound (e.g. kyanite).

3.3 Final result

After succeeded in deciding the best composition of materials for artificial sludge through various trials and analyses, we synthesized final artificial sludge, and then analyzed its characteristics and values. We plot the results in another calibration curves as shown in Fig. 5. According to the new calibration curves, it was found that in order to reproduce Funabashi sludge, we found to need the addition of 28.8% organic materials to the total mixture. To test the accuracy of recipe based on new calibration curves, and made additional artificial sludge with various amount of organic material additions (27.1% and 27.7%). The resulting organic contents based on TG analyses were 23.2% and 22.6%, respectively. These values theoretically are less than 1% of error, when compared to the expected values (22.6% and 23.0%, respectively).

Table 2 Adsorption ability of zeolite

	First value of Cs^+ [ppm]	Captured [ppm/g]
Nothing to add	640.7	-
Zeolite (Large)	632.4	8.2
Sea sand	637.3	3.4
SiO_2	641.2	-0.5
Inorganic matter by sludge	621.4	19.3

		Values of Cs^+ (Before) [ppm]	Values of Cs^+ (After) [ppm]	Captured values by inorganic matter [ppm/g]
Inorganic matter in sludge（1 g）		640.5	588.9	51.6
Zeolite （1 g）	Large	647.5	617.7	29.8
	Small		607.8	39.6
	Powder		536.4	111.1
	Avarage	-	-	60.2

4. CONCLUDING REMARKS

4.1 An artificial sludge as a model system for environmental studies

In previous studies, we have analyzed the characteristics of sludge such as cesium adsorption [4] and [6], and cesium decontamination by [3]. We used the obtained data from such analyses as references when making artificial sludge.

In the present study, in order to obtain preliminary data to produce an artificial sludge with the characteristics mimicking those of the natural one, we initially studied material of natural sludge collected from Funabashi port. We also produced different preliminary artificial sludge, by trying various amount of compositions and materials. These preliminary data have allowed us to find the best composition and materials to utilize in order to produce artificial sludge.

We used dry yeast in order to recreate the organic content of artificial sludge, because it has similar ability of Cs^+ adsorption as the organic matter collected from the supernatant of a sludge suspension liquid (Fig. 3). Moreover, that will be like mud when added water. Also, a natural sludge obtains its organic content from biological sources such as carcasses of living organisms. Using dry yeast as the organic content source will mimic this condition. Dry yeast is also easy to obtain, making artificial sludge production easy.

We used SiO_2 and zeolite in artificial sludge for the inorganic material, basing on the result of

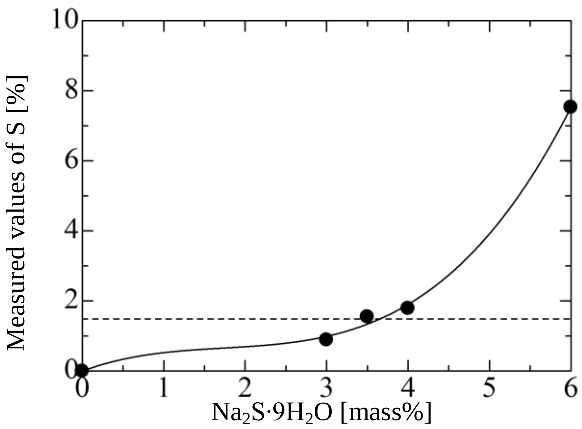

Fig. 7 The best value of adding $Na_2S{\cdot}9H_2O$

XRD analysis. Moreover, previous studies have shown that zeolite has the ability of Cs^+ adsorption (e.g. [5]), similar to the inorganic matter in natural sludge, which is also a Si compound (e.g. kyanite). EDX analyses showed that the organic content of a natural sludge also contain sulfur. In order to mimic such condition, it was added $Na_2S{\cdot}9H_2O$ to dry yeast. The amount of the added $Na_2S{\cdot}9H_2O$ was found to be 3.5 to 4.0 mass% in aqueous solution of $Na_2S{\cdot}9H_2O$ for the dry yeast culture (Fig. 7).

4.2 Future prospects

In the present study, we had tried to use artificial sludge for experiment of Cs^+ decontamination. Thus, we can safely say that artificial sludge can be beneficial for future experiments about Cs^+ decontamination.

About results with H_2O_2 addition to artificial sludge containing $CsNO_3$, Cs^+ was leached out by the H_2O_2 into the liquid phase. This has caused the measured values to differ from result by Fig. 6. But when we compared this result and a previous study using the natural sludge, our artificial sludge did not reproduce the study. By the way, natural sludge samples collected from Funabashi Port and Hidaka Port, showed similar values, suggesting that the decontamination ability of these natural sludge samples taken from two different areas could be similar [5].

Future studies would also include trying to reproduce the characteristics of the natural sludge taken from various locations with a variability of differing characteristics, conditions, and setting values. Such studies will allow for further testing of the robustness of our result reported here.

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