〈一般研究課題〉　水熱処理による生活廃水（汚泥）
の減容化に関する研究
助 成 研 究 者　名古屋大学　　小林 信介

水熱処理による生活廃水(汚泥)の減容化に関する研究

小林 信介
(名古屋大学)

Effect of hydrothermal Reaction conditions on volume reduction and filtration performance of sewage sludge

Nobusuke Kobayashi
(Nagoya University)

Abstract：

Hydrothermal treatment was carried out with sewage sludge, and the effect of hydrothermal conditions, such as treatment temperature and treatment period, on dewatering performance by filtration was evaluated. The properties of hydrothermally treated slurry was also analyzed by measuring particle sized distribution, pH and ζ potential to understand physical filtration mechanism. With increasing of treatment temperature, filtration capability of the treated slurry significantly increased. Treatment period also affected on filtration performance, and the filtration performance increased with longer treatment period. Even though particle size decreased with higher treatment temperature by a hydrolysis reaction, the filtration capability increased with increasing hydrothermal treatment temperature or period. The agglomeration effect on the filtration performance might be small, but the characteristic change between particles and filtrate by the decomposition of organic material in sewage sludge, such as polysaccharide and polymeric protein, might influence the filtration efficiency significantly.

INTRODUCTION

Sludge treatment is very important for the comfort and sanitary city life, however, energy consumption in a conventional sludge treatment system is huge, and lack of disposal site of sludge is also one of the biggest problems in sewage treatment process in Japan. In response to these situations, lots of alternative sludge treatment system has been developed of recent years to reduce energy consumption and sludge volume (Ishikawa 1999, Imai et al., 2008, Nakazawa et al., 2009, Yoshida et al., 2001, Hishio and Nakashimada, 2007)

Hydrothermal treatment is applied for one of volume reduction techniques of high moisture content sludge, because organic materials, which are mostly metabolite and dead shape of microscopic organism (Voet and Voet, 1995), are decomposed by a hydrolysis reaction. Therefore, many research works regarding hydrothermal treatment of sewage sludge has been conducted and clarified the relationship between hydrothermal conditions and hydrolysis behavior of various kind of sludge in many countries (Murakami et al., 1999, Okuda et al., 2001, Ohmura et al., 2004, catallo and Comeaux, 2008). However, significant increase of water treatment load, if the hydrothermally treated liquid returns to aerating tank, was pointed out as the disadvantage of high temperature hydrothermal treatment of sludge. This problem can be solved by decreasing treatment temperature, but volume reduction ratio decreases with decreasing operation temperature. Further research is continuing to find out optimum hydrothermal treatment condition to increase volume reduction and reduce water treatment load.

Another advantage of hydrothermal treatment is improvement of dewatering performance of treated slurry. Easy and efficient dewatering technique in sludge treatment system is important not only for the reduction of energy consumption, but also fuel saving in sludge combustion process. Many filtration experiments have been conducted with no-treated sludge and clarified that metabolite of microscopic organism, which was polysaccharide and high molecular protein, was major cause of deterioration of the filtration performance (Judd, 2004). One the other hand, applying hydrothermal treatment on sludge increasing filtration performance was known empirically (Miyakawa et all, 2003, Kobayashi et al., 2009a). Improvement of filtration performance by applying hydrothermal treatment would estimate

However, detail analysis on the relationship between hydrothermal treatment conditions and filtration performance has not been reported so far. Therefore, in this study, hydrothermal treatment was conducted on sewage sludge and effect of hydrothermal treatment conditions on dewatering performance by a filtration was clarified. In this experiment, filtration experiment was carried out with hydrothermally treated sludge and effect of treatment temperature and treatment period on filtration performance was evaluated. To understand filtration mechanism, treated slurry characteristics, such as particle size distribution, pH and ζ potential of the treated slurry, was also analyzed.

EXPERIMENTAL

Hydrothermal experiment of sewage sludge was conducted in microwave irradiation type batch reactor (Milestone General, Ethos One). Schematic diagram of the experiment unit is shown in Fig. 1. Sludge samples in a reactor are heated to arbitrary temperature by microwave irradiation.

Microwave frequency is 2.455 GHz, and maximum power is 1000 W. The reactor is made by Teflon, which volume is 100 ml and maximum pressure capacity of the reactor is 10 MPa. Temperature of the sample in the reactor is able to measure with a Teflon coating thermocouple. Heating rate of the sample is also adjusted by controlling microwave output power. To create homogeneous reaction condition, a stirring bar was put in the reactor with the sample. The stirring bar usually starts moving around 373 K with 100 rpm, when the sludge sample turns soft.

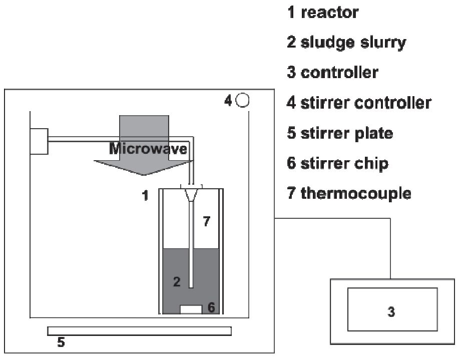

Fig. 1 Schematic diagram of hydrothermal treatment equipment

Dewatering digestive sludge was used as the experimental sample, which moisture content was around 82 %. 40 g-wet of sludge, which filled about half of the reactor, was loaded in the Teflon reactor, and temperature of the sample was raised by irradiating microwave. Treatment temperature was set 453, 473, 493 and 513 K, and heating rate was controlled 100 K/min in all experiments. The pressure in the reactor would be summation of water vapor pressure at the treatment temperature and generated decomposed gas, but in this experiment, pressure of decomposed gas expected vanishingly small from the result of pre-experiment. After the temperature of the sludge sample reached the target temperature, the sample kept arbitrary treatment period. Treatment period set 5, 10, 20 and 30 min. After the hydrothermal treatment, the reactor was immersed into an ice water immediately to prevent the secondary reaction. Then the reaction slurry was taken out from the reactor, when the treated slurry became normal temperature.

Obtained slurry separated the solid residue and liquid by a constant-pressure filtration. Any other treatment was not conducted before the filtration, but note that the slurry concentration was different depends on the hydrothermal condition. Schematic diagram of filtration system is shown in Fig. 2. Cylinder type strainer is made by stainless steel, which diameter is 2. 56 cm and the length is 20 cm. Filtration area is around 5.14 cm^3. Three different size of glass filters paper were used in the filtration, and the opening size of the filter was 1, 7 and 20 μm. Well agitating treated slurry was filled into the strainer and the strainer was sealed. After sealing the strainer, dead-end filtration was conducted with nitrogen gas at normal temperature. The pressure of sealed strainer during the filtration was kept 0.1 MPa. The weight of filtrate against filtration time was measured by microbalance. Filtrate volume was calculated with the filtrate density after the filtration experiment. Cake and filtrate was dried after the filtration experiment to calculate solubilization ratio. Drying temperature was 353 K and drying period was 48 h. Experimental flow and conditions were summarized in Fig. 3. Solubilization ratio was calculated as following equation.

$$\text{Solubilization ratio}[\%] = \left(1 - \frac{Residue\ [g] - \left(CE\ [g] \times \frac{Deposit\ [g]}{Filtrate\ [g]}\right)}{Dried\ sludge\ [g]}\right) \times 100$$

To evaluate the characteristics of hydrothermally treated slurry at different treatment condition, particle size distribution, pH and ζ potential of the slurry was also analyzed. Analysis was applied the treated slurry, which was not separated solid and liquid. The particle size distribution was measured by a laser-diffraction particle diameter analyzer (LA-920, HORIBA). For the measurement of pH, pH meter (HM-20P, Toa DKK) was used. ζ potential was measured with ζ potential analyzer (Model-502, Nihon Rufuto Co. Ltd.). Because obtained slurry concentration was too high to measure with this ζ potential analyzer, treated slurry was diluted with 3 times distilled water of slurry total weight. Biochemical oxygen demand (BOD) and total organic carbon (TOC) of the filtrate also measured to understand water treatment load in hydrothermal treatment. BOD and TOC analysis was conducted with JIS method, which is JIS K 0120- 21 and JIS K 0102-22, respectively.

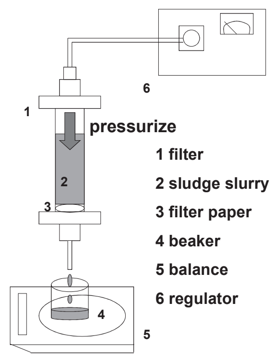

Fig.2 Schematic diagram of constant-pressure filtration

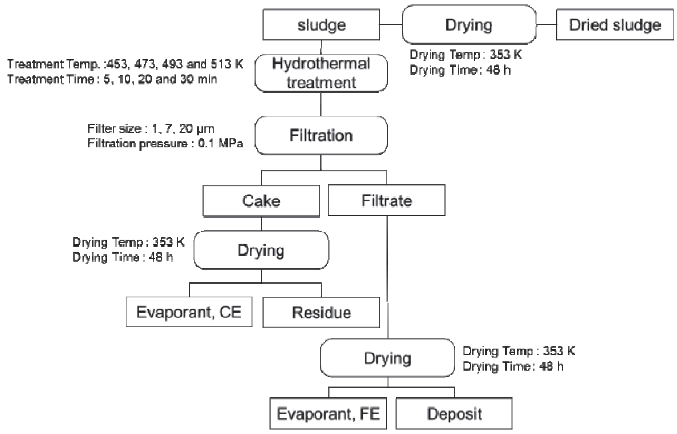

Fig.3 Experimental flow and experimental conditions

RESULTS AND DISCUSSION

Fig. 4 shows the effect of hydrothermal treatment temperature on filtration performance. Treatment period was 5 minutes and filter opening was 1 μm. Depend on the treatment temperature, filtration speed was significantly changed. Under 473 K treatment, filtration was not progress at all in this filtration condition, but the filtration performance drastically improved with high temperature treatment slurry. In previous paper (Kobayashi et al., 2011b), authors conducted a filtration with hydrothermal treatment slurry and clarified that the slurry treated over 473 K, which is around decomposition temperature of organic material, was able to improve filtration performance. However, slurry treated 473 K in this experiment was not filtrated easily. Since the difference those sludge samples are initial slurry concentration and slurry concentration influences hydrolysis reaction of organic material, filtration

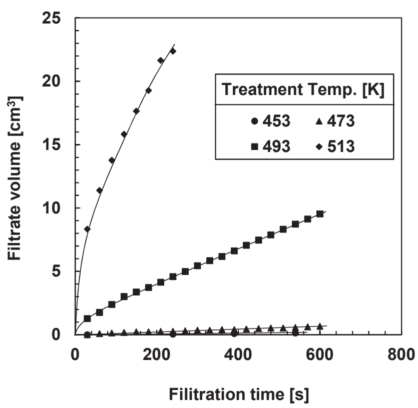

Fig.4 Effect of hydrothermal treatment temperature on filtration speed, hydrothermal treatment periods: 5 min constant.

performance might be effected by the degree of progress of hydrolysis reaction. With increasing treatment temperature from 493 to 513 K, filtration speed of 513 K increased 6 times more than that of the speed of 493 K. This result indicated that the cake resistance of treated slurry at 513 K was drastically improved by hydrothermal treatment. But, even though the slurry of 513 K, filtration speed was getting decrease with growing the cake resistance.

Fig. 5 shows filtration volume against filtration time with hydrothermally treated slurry at different treatment periods. Treatment temperature of the slurries was 473 K, and filter size was 1 μm. Depend on the treatment period, filtration performance significantly changed. With 5 minutes treatment, filtration was not progressed, but with increasing treatment periods, filtration performance was improved drastically. Filtration volume at the same filtration time increased linearly against treatment period, which presumes that cake resistance of the slurries decreased linearly with increasing treatment period at temperature of 473 K. Because 473 K is around the decomposition temperature of saccharine and microscopic organism tissue (Voet and Voet, 1995), reaction period influences on decomposition ratio of organic materials, and the decomposition ratio may effect on the filtration performance. In consequence, filtration performance of 30 minutes treatment closed to the filtration performance of 493 K treatment of 5 minutes. Without increasing treatment temperature, filtration performance was able to improve by prolonging treatment time, but further experiment is necessary to clarify the optimum treatment period at different treatment temperature.

Fig. 6 also shows the filtration volume against filtration time, but different size of filters was used in this case. Treatment period of this slurry was 5 minutes, and filter size was 1, 7 and 20 μm. Depend on the filter size, difference was not observed with the treated slurries of 513 and 453 K. Since filter resistance is deferent between the filters, cake resistance dominates the filtration performance with these slurries. However, the filtration mechanism expected to be different between the slurries of 513 and 453 K, because filtration performance was totally different. It is assumed that 513 K is much higher temperature than decomposition temperature of organic substance, resistance of the cake itself influences the filtration performance. On the contrast, because 453 K is much lower temperature than decomposition temperature, organic substance, such as polysaccharide and high molecular protein, is still remains in filtrate and those materials hinders filtration performance. On the other hand, the slurry treated at 473 and 493 K showed the difference in filtration performance depends on filter opening size. Difference in 473 K was negligibly small, but the slurry treated at 493 K indicated significant difference between the filter sizes. Increasing the opening size of filter, filtration speed increased in case of 493 K, especially filter of 1 and 7 μm. However, the filtration speed was not increased linearly with filter opening size or area, and filtration performance gradually deteriorated with bigger filter opening. This filtration performance may be also explained by the decomposition of organic material. Decomposition material dissolves in the liquid at 493 K, but the organic material in liquid is not decomposed as small as in the case of 513 K condition and some organic substance is not decomposed at 493 K in 5 minutes treatment. Since filtration resistance is also determined by decomposition ratio and size of decomposed organic materials, the difference is showed up in the filtration performance, because the slurry at 493 K may be having broad molecular size distribution of organic substance. Further research is necessary to understand the relationship between molecular size and filtration performance.

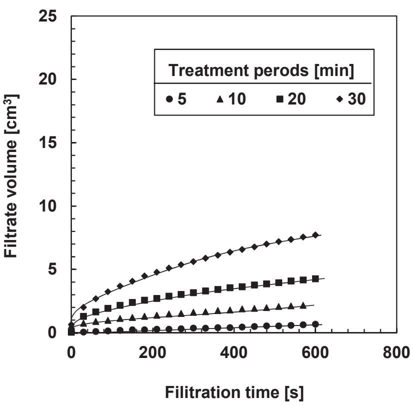

Fig.5 Effect of hydrothermal treatment periods on filtration speed, hydrothermal treatment temperature: 473 K

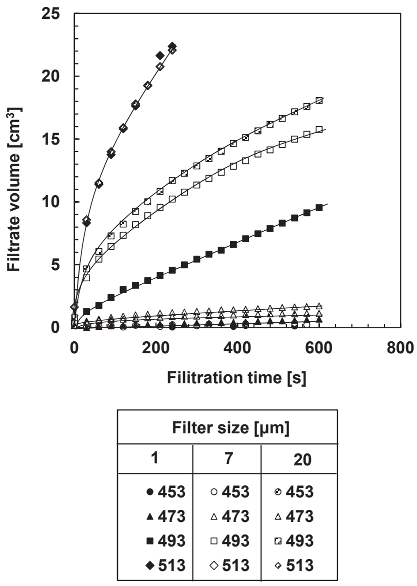

Fig.6 Effect of filter size on filtration speed, hydrothermal treatment periods: 5 min

One of the biggest factors, which influence the filtration performance and cake resistance, is particle size in treated slurry. To understand the hydrolysis effect on the particle size and filtration performance, particle size distribution of the slurry was measured. Fig. 7 shows the particle size distribution of treated slurry. This figure shows the particle size distribution measured with both ultrasonic wave irradiation and non-ultrasonic wave irradiation. 3 minutes ultrasonic wave was applied the sample. Agglomeration of the particles in initial sludge sample was observed as expected, because of the addition of agglomerating agent in dewatering process of digestive sludge. Agglomerated particle easily break into a small particle by the ultrasonic wave irradiation, and a number of lager particle decreased. By applying hydrothermal treatment, particle size decreased with increasing reaction temperature, especially, a number of fine particles were increased. But significant difference was not observed between the slurries, even though the treatment temperature was different. The particle size distribution was not also changed by even the ultrasonic wave irradiation, except 513 K treatment. This means that the agglomeration effect of the particle in the slurries is very small, or coagulation of the particle is very strong not enough to break by ultrasonic wave irradiation. But, considering the 50 % particle size, the particle size is around 120 μm, it is very difficult to consider that the particle is not coagulated at all. Less difference in particle size distribution was observed between the slurries, however, the filtration performance showed significant difference between the slurries. Usually, filtration performance deteriorated with smaller particle, but this result indicated that the particle size of the slurries was less influence on the filtration performance. Therefore, improvement of the filtration performance was not effect of particle agglomeration, but decomposition ratio and size of organic material would be more importance to the filtration performance of the treated slurry.

Particle size distribution of the slurries treated in different time period was shown in Fig. 8. Treatment temperature was 473 K. Increasing the treatment periods, particle sized decreased gradually. Especially, a number of small particles increased. Since particle size decreased with treatment period, hydrolysis reaction would progress with the periods. But, significant difference in particle size was not observed depend on the treatment periods. Effect of ultrasonic wave irradiation was also negligible. Even though the particle size decreased with longer treatment period, the filtration performance increased drastically, as seen as in fig.5. Reaction period also influences decomposition of organic materials, and decomposition ratio may significantly infect on the filtration performance.

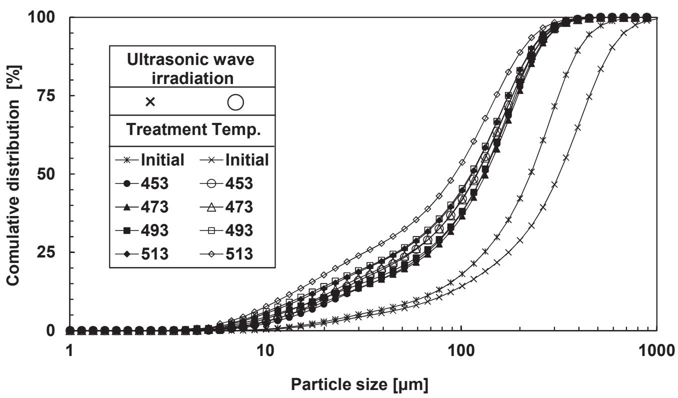

Fig.7 Effect of hydrothermal treatment temperature on particle size distribution, hydrothermal treatment periods: 5 min, Filter size: 1μm

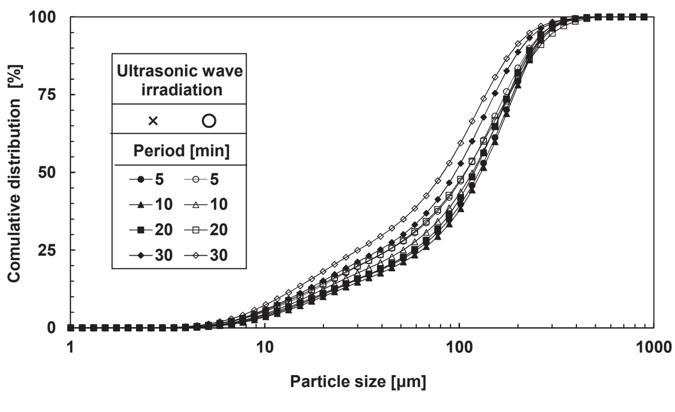

Fig.8 Effect of hydrothermal periods on particle size distribution, hydrothermal treatment temperature: 473 K, Filter size: 1μm.

To evaluate treated slurry characteristics, pH and ζ potential of the slurry was measured. Tables 1 and 2 show the pH value and absolute ζ potential of slurries. Table 1 shows those values in different treatment temperature. The pH value decreased with increasing the treatment temperature, but over 493 K, the slurry pH value increased on the other hand. Decrease of the pH value at lower treatment temperature would be by the hydrolysis reaction of organic material. Since hydrolysis reaction creates an acid substance, such as formic acid and acetic acid, this kind of acid production decreases the pH value. On the other hand, increase of the pH value may be the production of ammonia. Because, nitrogen content in sludge is high, ammonia production influences the pH value during the hydrothermal treatment. Since the decomposition of high molecular weight organic material progressed at the treatment temperature of 493 K, filtration performance was drastically improved by the inhabitance of filtration resistance.

ζ potential of all slurries had negative electrification. The value of absolute ζ potential also changed with the treatment temperature, and it decreased with increasing treatment temperature, but ζ potential also turned increased over 473 K. Usually pH value and ζ potential has a strong relationship, but the pH value decreased from 473 to 493 K against ζ potential slightly increased from 473 to 493 K. This result indicated that the surface characteristics of the sludge changed by the hydrolysis reaction. Looking into the value of absolute ζ potential, the value obtained from non-treated slurry was also very low. One of the reasons of the low ζ potential value is agglomeration agent. Since the treated slurries are diluted before ζ potential analysis, the dilution also influenced the value of ζ potential. However, in general, ζ potential value of this range encourages the particle agglomeration. But, significant agglomeration was not observed by the particle size analysis. This result suggested that the treated particles were coagulated strongly and the particles couldn' t break into small particles by ultrasonic wave irradiation.

Table 1 pH value and absolute ζ potential of hydrothermally treated slurry

Treatment temperature	K	293	453	473	493	513
pH	-	-	7.14	6.94	6.25	6.49
Absolute ζ potential	mV	1.94	1.56	1.18	1.23	1.63

* Treatment period: 5 min.

Table 2 shows the pH value and absolute ζ potential of the slurry treated in different treatment period. The pH value was not changed drastically, but gradually decreased with increasing treatment period. Minimum value of pH was not observed in this treatment period. Gradual decrease of the pH value would be the hydrolysis reaction, and the gradual progress of reaction would improve the filtration performance. ζ potential, keeping low value in this operation range, was not changed depend on the pH value. Since filtration performance was changed with treatment period, the particle-liquid interaction might be changed gradually with reaction period by decomposing soluble organic material, but particle-particle interaction might not be changed drastically by changing treatment periods.

Table 2 pH value and absolute ζ potential of hydrothermally treated slurry

Treatment periods	min	5	10	20	30
pH	-	6.94	7.04	6.54	6.52
Absolute ζ potential	mV	1.44	1.35	1.34	1.38

* Treatment temperature: 473 K.

The solubilizaiont ratio, deposit ratio, BOD and TOC of slurries or filtrates was summarized in Table 3. Treatment period of this experiment was 5 minutes and 1 μm filter was used. Solubilization ratio increased with increasing treatment temperature. Only 7 % of the initial solid substance decomposed to liquid soluble substance at the treatment temperature of 453 K, but around 15 % at 513 K. Comparing previous results (Kobayashi et al, 2011b), which conducted low slurry concentration, around 35 % of solubilization ratio was achieved. In this process, since slurry concentration was higher than previous one, proton concentration during hydrolysis reaction was less, and limitation of solubility of decomposition material would effect on the solubilization ratio. Since the solubiliztion ratio increased with the reaction temperature, deposit ratio in the filtrate also increased with increasing treatment temperature. Only 0.02% of initial substance passed though the 1 μm filter at the temperature of 453 K, but the around 0.22 % of initial substance passed though at 473 K, because decomposition of organic material in sludge starts around 473 K. Significant difference was also observed between 473 and 493 K with the progress of decomposition. At 513 K treatment, deposit ratio increased more. Since decomposition starts around 473 K, BOD and TOC value at 473 K increased significantly. However BOD and TOC value was not changed between 473 and 513 K, even though the deposit ratio increase. It indicates that not only organic material, but also the other inorganic material was passing through the filter as liquid soluble substance, and the soluble inorganic material also increased with increasing treatment temperature. Regarding the carbon ratio in filtrate, it was not changed the total amount with increasing treatment temperature, but the chemical form of the carbon would be different depend on the treatment temperature. At high treatment temperature, decomposition of organic material progress and molecular weight and size would become small. Therefore, filtration performance improved with increasing reaction temperature, even though the particle size decreased. Consequently, chemical form of carbon, molecular weight and size would influence the filtration performance significantly.

Table 3 Deposit, BOD and TOC in filtrate

Treatment Temperature	K	453	473	493	513
Solubilization ratio	%	7.42	8.73	11.75	15.39
Deposit ratio	%	0.02	0.22	2.73	3.07
BOD	g/L	5.8	25	26	27
TOC	g/L	13	29	28	30

* Treatment period: 5 min, filter size: 1μm.

CONCLUSIONS

Filtration experiment with hydrothermally treated slurry was carried out, and filtration performance significantly improved by increasing treatment temperature and treatment period. Over 493 K in 5 minutes hydrothermal treatment, filtration speed was drastically improved. With increasing treatment period, filtration speed of the slurry also improved linearly against treatment period at 473 K.

Particle diameter was decrease with increasing treatment temperature and period, and the particle in treated slurry might be coagulated strongly. The effect of particle size would not be significantly influence on the filtration performance.

Decomposition of organic materials, evaluated from pH, BOD and TOC, started around 473 K, and the decomposition ratio, weight and size of organic materials might strongly influence the filtration performance of the treated slurry.

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