

Effects of Hydrothermal Process on the Nutrient Release of Sewage Sludge

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Abstract

Hydrothermal treatment has demonstrated the ability of improving the dehydration and drying performances of sewage sludge, as well as shown its suitability for producing fuel. On the other hand, because of the abundant nutrient matters in sewage sludge, the produced liquid may be used as the liquid organic fertilizer. In this work, the effect of the hydrothermal treatment on the nutrient behavior in sewage sludge was investigated. The effects of the reaction temperature (180-240°C), and the reaction time (30-90 min) were investigated, and both of solid and liquid products were analyzed individually. The results showed that 40%-70% of nitrogen, 50%-70% of potassium and 10%-15% of phosphorus in sewage sludge could be dissolved into the liquid product, and that the solubilization was highly influenced by the temperature and the reaction time during the hydrothermal process. The hydrothermal treatment can effectively transport nutrient components in sewage sludge into the liquid product.

Keywords: Sewage sludge; Hydrothermal treatment; Nutrient

Introduction

In recent years, huge amount of sewage sludge production has become a serious problem in many countries. Especially in developing countries, for instance, China, the sewage sludge production is increasing together with the increase of wastewater discharge, causing very serious environmental pollutions. Thus, the sludge pollution problem should be solved as soon as possible.

Sewage sludge is a kind of biomass, which comes from waste water treatment, its moisture content could reach above 80% and also the organic matter content is high. Thus, it is very easy to rot, and the odor problem is also very prominent. With the increasing production of sewage sludge, the disposal method is also gathering interests. At present, the methods for sludge disposal include landfill, incineration, and agricultural use and so on. These traditional sewage sludge disposal methods, however, cannot meet the treatment need, because even with these methods the sludge is still a serious risk to human health and the environment. For the method of landfill, the heavily polluted leachate will pollute the groundwater; and the landfill gas, which is mainly methane, has a hidden peril of causing explosion and fire. In addition, the choice of suitable sludge landfill sites is also another awkward problem. On the other hand, if the sewage sludge is used for incineration, the operating cost is very expensive due to its high moisture content and the emissions of toxic air pollutants such as NO_x, SO₂ and dioxins are also problems. Originally, sewage sludge is a good agricultural fertilizer. Its nitrogen, phosphorus and potassium content are much higher than manure. However, unfortunately, sewage sludge also contains parasites, bacteria and so on, coupled with unpleasant odor, therefore, it is more unwelcomed as fertilizer. The accumulation of heavy metals in soils and subsequent accumulation along the food chain are the potential threat to animal and human health. Therefore, all of these issues motivate the development of more economic and environmentally friendly approaches to the disposal of sewage sludge and simultaneously utilize its valuable components as soon as possible. Converting the sewage sludge into valuable products can not only alleviate the disposal problem, but also can bring economic benefits, so it is of great interest and should be intensely investigated.

The hydrothermal treatment employing high pressure (around 2 MPa) saturated steam to convert wastes into usable products is a new

applicable technology to sewage sludge. It has been already applied to sewage sludge to improve their dewaterability [1]. It is proved that at certain temperature and pressure, hydrothermal treatment will rupture the cell wall and membranes of organics in sewage sludge, and will improve the dewaterability of the sludge at the same time [2]. Added with the fact that the hydrothermal process uses water as reaction medium, high moisture content waste can be directly processed without the need for the predrying process, and the hot water can serve as a solvent, reactant and even a catalyst for the raw material [3]. After the treatment, the solid product is always used as a kind of RDF (Refuse Derived Fuel) or reused for agricultural fertilization after anaerobic digestion. However, the liquid phase, which is rich in dissolved organic compounds, is always treated as wastewater or discarded. In addition, on one hand, the expenditure for treating this so-called wastewater is not inexpensive; on the other hand, there are actually plenty of nutrients, such as nitrogen, phosphorus and potassium and so on in the sewage sludge. During the hydrothermal processes, accompanied with the destruction of bacterial cells, a certain amount of these nutrients will also dissolve into the liquid phase. Thus treating the liquid byproduct as wastewater seems regretful. If this so-called wastewater can be recycled and utilized, it could not only solve the wastewater treatment problem of sewage treatment, but also could achieve a huge economical benefit.

Basing on all the merits of the hydrothermal treatment, many researches are not only limited on the manufacture of fuel, but also focused on using this technology to produce other products. In recent years, using the hydrothermal treatment for converting organic wastes into more valuable substances has been investigated. According to the investigation about microalgae, an additional benefit

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Received October 03, 2013; **Accepted** October 28, 2013; **Published** November 01, 2013

Citation: Sun XH, Sumida H, Yoshikawa K, Sumida H, Yoshikawa K (2013) Effects of Hydrothermal Process on the Nutrient Release of Sewage Sludge. Int J Waste Resources 3: 124. doi: [10.4172/2252-5211.1000124](https://doi.org/10.4172/2252-5211.1000124)

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of the hydrothermal processing routes had been found, which has the potential to recycle liquid byproduct rich in nutrients, as well as other mineral matter and polar organics [4]. The hydrothermal treatment was also demonstrated to be able to produce high yield of amino acid from biomass waste by controlling reaction temperature and reaction time range [5]. Fish meat and silk fibroin can reportedly be converted into organic acids and amino acids by the hydrothermal treatment [6,7]. As more detailed investigation, hydrothermal conversions of cellulose and disaccharides [8-11] were also studied and had been found readily convertible into glucose and low-molecular-weight carboxylic acids [12].

In the application of the hydrothermal treatment to sewage sludge, most of the previous researches have been focused on the improvement of the dewatering performance for solid fuel production [13], or enhancement of the anaerobic digestion [14]. Nevertheless, due to the complicate components of the sludge, few researches are focused on the nutrient release during the hydrothermal process. Considering the abundant nutrient concentration in the hydrothermally treated liquid residue, it is also possible to make use of it as fertilizer. Therefore, the hydrothermal effect on the nutrient release of sewage sludge is gaining interest. The investigation on the nutrient solubilization is of great significance.

The objective of this study is to investigate the impact of hydrothermal treatment on the solubilization of the nutrient component in sewage sludge and the characteristics of the liquid products. The influences of process variables such as reaction temperature and reaction time have been studied. The influence of process variables on the yield and quality of the nutrient is discussed including the carbon balance and the nitrogen partitioning between the product phases. Since the level of macronutrients as well as micronutrients and heavy metals released from sewage sludge also depend on the process variables, their concentrations in the liquid product and the release quantity at various treatment parameters is tested to investigate their variation trend during the hydrothermal process. The results are expected to be favorable for optimizing the hydrothermal treatment process for

treating sewage sludge and creating a new component for constructing the systematic hydrothermal theory to use sewage sludge as a resource in a maximum range, and suggest a new theoretical basis for reusing the byproduct from hydrothermal process.

Experimental Materials and Methods

Material

In this research, the sewage sludge was obtained from a wastewater treatment facility located in Shimane city of Japan. The nutritional value along with other properties of the sludge is provided in Tables 1 and 2.

Methods

Hydrothermal treatment: In this research, a bench-scale hydrothermal reactor with 0.5 L capacity was utilized. The schematic view of the facility is shown in Figure 1. The reactor is a batch type (MMJ-500, Japan) which is equipped with an automated stirrer, a pressure sensor and a temperature controller. 60 g of sludge (as received based) mixed with 60 ml of distilled water, was introduced into the reactor without any pretreatment. After sealing the reactor, the air inside the reactor was purged by inert gas (argon) to prevent combustion during the treatment. Initial pressure inside was set to near atmospheric. Then, the reactor was heated to target temperature (180, 200, 220 and 240°C) with the average heating rate of 7°C/min and the constant stirring speed of 100 rpm. After reaching the target temperature, the mixture was further kept in the reactor for a certain period of time (30, 60 and 90 min) called as the holding time. Once the holding time is completed, the reactor was cooled down (< 90°C) and depressurized. Then the treated mixture was taken out and was subjected to centrifugation 3000 rpm, 30 min for solid and liquid separation. The solid phase was oven-dried (105°C for 24 hours), cooled in desiccators and subjected to chemical analyses. The liquid phase was filtered through sterile analytical filter units (with a membrane of 0.2 μm pore size) before it was used for analytical measurements.

pH	Moisture (%)	N(%)db	C(%)db
6.28	85.94	7.2	39.95

Table 1: Characteristics of sewage sludge.

Raw	unit	P	K	S	Na	Mg	Ca	Fe	Al	Mn	Pb	Zn	Cu	Cr
db	mg/g	13.88	1.43	7.60	0.35	1.4	7.44	20.69	8.71	0.16	0.02	0.33	-	-

Table 2: Nutrient and heavy metal of sewage sludge.

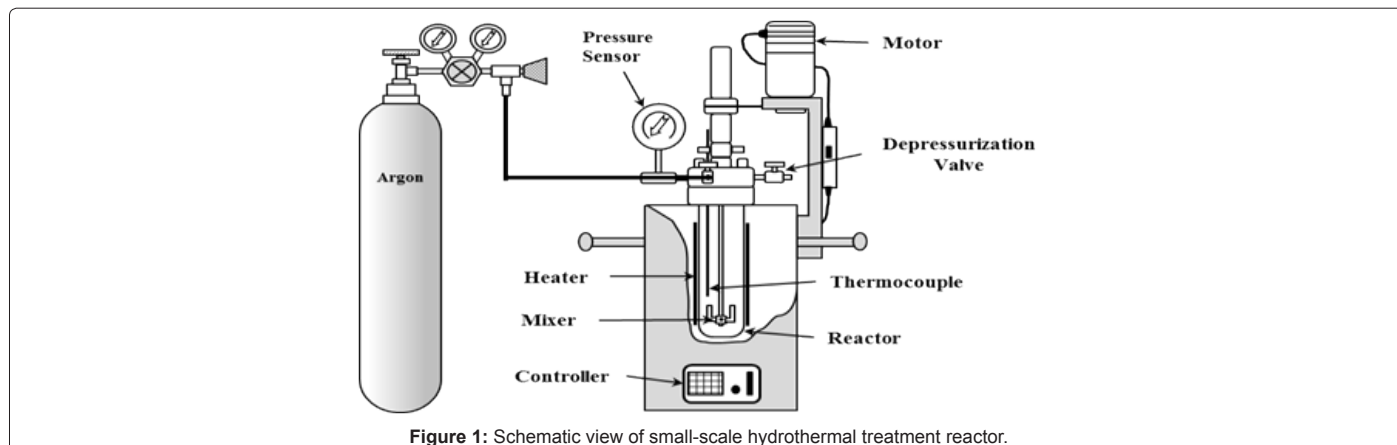


Figure 1: Schematic view of small-scale hydrothermal treatment reactor.

Analyses: The total carbon (Total-C) and the total nitrogen (Total-N) contents in solid were measured using an automatic high sensitive analyzer (Sumigraph NC-220F, SCAS, Japan). The macro and micro nutrients were analyzed after pretreatment of subsample of solid in HClO₄ and HNO₃ solution by a DigiPREP block digestion system (SCP SCIENCE, Canada). The phosphorus (P), sulfur (S) and other heavy metal were determined using the ICP emission spectroscopy (ICPE-9000, SHIMADZU), while potassium (K), calcium (Ca), sodium (Na) and magnesium (Mg) were analyzed by the atomic absorption spectrophotometer (180-50, HITACHI).

The total-C (TC) and inorganic carbon (IC) in liquid phase was determined by the total organic carbon analyzer (TOC-5000, SHIMADZU), the total organic carbon (TOC) is represented by the difference between TC and IC. The Total-N was measured using the Kjeldahl method; it involved acid digestion of the sludge followed by distillation and measurement of the released ammonia. The ammoniacal nitrogen (NH₄⁺-N) was analyzed by employing distillation procedure. The nitrate and nitrite were detected in negligible amount, and therefore omitted in this research. The difference between the Total-N and NH₄⁺-N was then taken as the organic nitrogen (Org.-N). The potential of the hydrogen ion (pH) and Electrical Conductivity (EC) values were measured using glass pH and EC electrodes (HORIBA, JAPAN).

In order to show the result of the hydrothermal treatment to the solid fraction, the solubilization ratio of the solid phase and the chemical elements had been defined as the ratio of the initial sample content minus the treated sample content divided by the initial sample content. It can also be defined as follows:

$$\text{Solubilization ratio} = \frac{\text{content in initial sample} - \text{content in treated sample}}{\text{content in initial sample}} \times 100 \quad (1)$$

Results and Discussion

Effects of hydrothermal treatment on the solid solubilization

The effects of the reaction temperature and the holding time on the reaction are demonstrated in Figure 2, which showed the solid solubilization ratio at various reaction temperatures ranging from 180°C to 240°C and the holding time from 30 min to 90 min.

The reaction temperature positively affected the solid solubilization ratio for all the examined conditions, while the holding time only showed the positive effect on the solubilization ratio at the reaction temperature below 200°C. The solubilization ratio gradually increased with the increase of the reaction temperature. It also can be inferred that with the dissolution of the solid component, the organic matter in the solid phase also dissolved correspondently. When the reaction temperature was 180°C, in the case of 30 min holding time, only about 32% of the solid is dissolved; however, by increasing the holding time to 40%, the solid solubilization ratio reached to about 40%. On the other hand, when the reaction temperature was higher than 200°C, the holding time had a minor influence.

It is well studied that the main composition of sewage sludge is complex organic compounds, and Barlundhaug and Odegaard [15] reported that carbohydrates were easier to be degraded but more difficult to be solubilized than proteins, which indicates that not all organic compounds react in the same way. In order to understand better the behavior of each kind of compounds, the forms and concentrations

of carbon, nitrogen and other elements in the liquid phase should be investigated in the future.

Effects of hydrothermal treatment on the nutrient components of solid phase

Effects of hydrothermal treatment on the solubilization of macronutrient: In this section, the solubilization of nitrogen (N), phosphorus (P), and potassium (K) and carbon were investigated. N, P, and K are the three major macro nutrients for fertilizer production. Therefore, the investigation of the effectiveness of the hydrothermal treatment for the dissolutions of the three components in the solid phase is essential. On the other hand, carbon component also plays an important role during the hydrothermal treatment since the main content of sewage sludge is organic component.

Figure 3 shows the effect of the reaction temperature and the holding time on the nitrogen solubilization ratio in the solid phase. In general, a certain amount of nitrogen in the solid phase (from 40% to 70%) was dissolved during the hydrothermal treatment and similar trends with those of the solid solubilization were observed for all examined conditions. The nitrogen solubilization ratio significantly increased with the temperature increase while it was only affected by the holding time at the temperature below 200°C. At 180°C, by increasing the holding time from 30 min to 60 min, the nitrogen solubilization ratio increased from 42% to 51%; but when the holding time was increased to 90 min, there was no obvious effect. When the reaction temperature was elevated to higher than 200°C, it is shown that the reaction temperature played the dominate role.

The nitrogen content in sewage sludge mainly comes from the protein contained in the microorganisms and debris inside sewage sludge. Before the treatment, the nitrogen is present in the form of

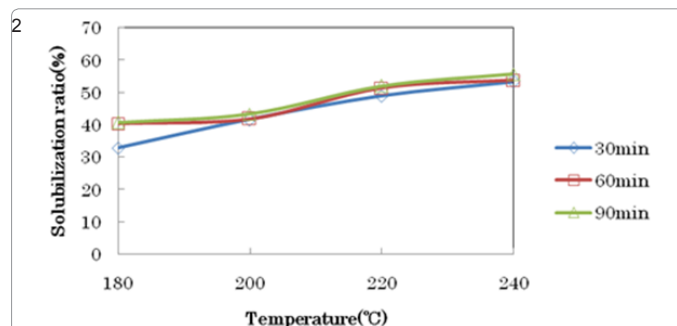


Figure 2: Solid solubilization ratio as functions of the reaction temperature and the holding time.

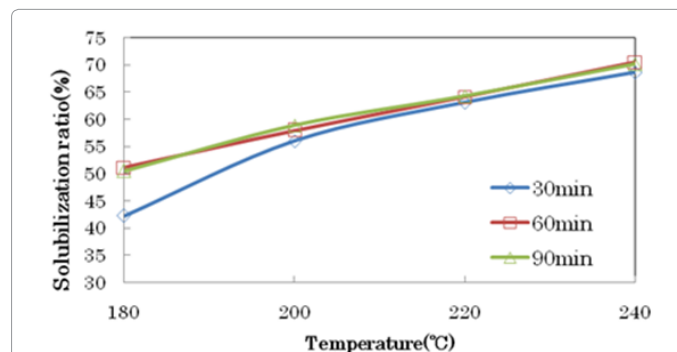


Figure 3: Nitrogen solubilization ratio as functions of the reaction temperature and the holding time.

macro molecular organic nitrogen in the solid phase of the sludge. As the reaction temperature and the pressure in the reactor increased, the organizational structure of sewage sludge starts to break up simultaneously with the nitrogen solubilization into the liquid phase. At the temperature of 180°C, the macromolecular protein in the sludge dissolved into the liquid phase gradually. In addition at this temperature, the extension of the holding time from 30 to 60 min made more protein dissolve, but further extension to 90 min created insignificant effect on the solubilization. As the holding time increases, a large amount of organic compounds get into the liquid phase and formed a high organic concentration until the equilibrium state is reached (at the holding time around 60 min). Higher reaction temperature and the pressure seem to able to transfer more nitrogen content from the solid phase to the liquid phase, but considering the material recovery and the operating cost, a relatively lower reaction temperature (lower than 200°C) and a shorter holding time (30 min) seems more suitable for large-scale production.

Figure 4 shows the effect of the hydrothermal treatment on the carbon content in the solid phase. Similar to nitrogen, the solubilization of carbon also increased with increasing the reaction temperature. However, for all the conditions tested, the holding time of 60 min and 90 min showed no difference. It is observable that at 180°C, the solubilization ratio increased with the increase of the holding time from 30 min to 60 min and above. At the temperature higher than 200°C, the reaction temperature becomes the dominant factor over the holding time. This phenomenon might be explained by the presence of extracellular polymers (ECP), whose main components are polysaccharide, protein and DNA that are significant in sewage sludge [16]. Under the relatively lower reaction temperature (180°C), the sludge structure break up was followed by the gradual ECP solution into the liquid phase and the longer holding time enhanced the solubilization. Mok and Antal [17] reported that when biomass was heated in hot-compressed water, solvolysis of hemicellulose and lignin began to occur at 190°C and all of the hemicellulose and much of the lignin dissolved in water at 220°C. Therefore, it can be inferred that during this process, accompanied with the polysaccharide dissolve, a certain amount of celluloses, hemicelluloses or lignin in the solid phase also dissolved gradually. Some previous studies had been demonstrated that for the biomass conversion process in hot-compressed water, the temperature was the most critical parameter and the holding time has little influence on the solubilization [1,18]; however, in this study, it seems that the holding time, in a relatively low reaction temperature, also plays an important role. At the temperature above 200°C, the holding time showed little effect. It indicates that all the micro-molecule soluble organic matters (mainly saccharide) has been fully

dissolved into the liquid, and the further observed solubilization might be related to the macromolecules (cellulose, lignin and so on), which is much more difficult to dissolve.

Figure 5 shows the solubilization of phosphorus (P) and potassium (K). The solubilization of phosphorus does not show a significant increase by increasing the reaction temperature as well as extending the holding time. Similar to those of nitrogen and carbon, potassium solubilization was significantly affected by the reaction temperature but not by the holding time. In addition, it is obvious that the amount of dissolved potassium far exceeds the amount of dissolved phosphorus. From 180°C to 240°C, the potassium solubilization ratio increased by about 20%, from about 50% to about 70%. The solubilization of phosphorus is only around 10% to 15% at all conditions, and from its high initial content together with the presence of high Fe initial content (Table 2), it can be inferred that phosphorus was added as flocculants to the sludge, is mainly in the form of insoluble $FePO_4$ precipitate. In addition, the small amount of phosphorus solubilization mainly comes from the DNA content in the ECP component. As for potassium, because its concentration in the sludge is not high, and it is very easy to dissolve in water, so when high temperature and pressure were applied, it is released simultaneously with the broke up of the complex sludge flocculation network and the breakdown of organic matter.

Effects of hydrothermal treatment on the micronutrient: The contents of micronutrients and heavy metal in the solid phase are also determined before and after the hydrothermal treatment. The results are shown in Table 3.

In Table 3, the release ratio of the micronutrient and heavy metal from the solid phase is provided. With exception of Na and Pb, most of the elements follow the trend that the higher the reaction temperature is, the greater the release is. The holding time only showed a minor influence on the solubilization.

On the other hand, for the elements of Na and Pb, the holding time showed very significant effects. For Na, when the reaction temperature increased from 180°C to 240°C, the solubilization ratio increased at most by only about 8% (the holding time of 90 min); however, for each reaction temperature, obvious decreasing trend can be seen when the holding time increased. By increasing the holding time from 30 min to 90 min, the solubilization of Na can decrease around 15%. It is implied that increasing the holding time is not beneficial for the releasing of Na. On the other hand, the solubilization of Pb showed significant decreasing trend with the increase of both the reaction temperature and the holding time. From 180°C to 240°C, the solubilization ratio decreased around 45% (with 60 min holding time), and the highest solubilization ratio decrease reached about 53% when the holding time was extended from 30 min to 90 min at the temperature of 180°C. It is

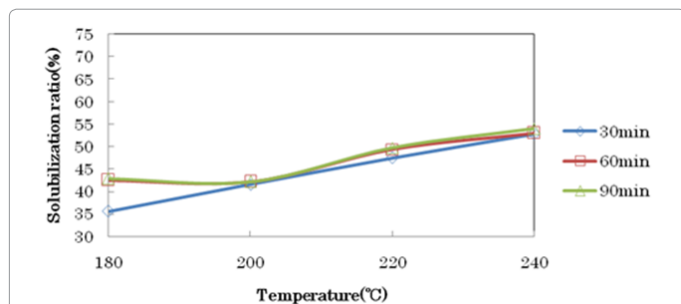


Figure 4: Carbon solubilization ratio as functions of the reaction temperature and the holding time.

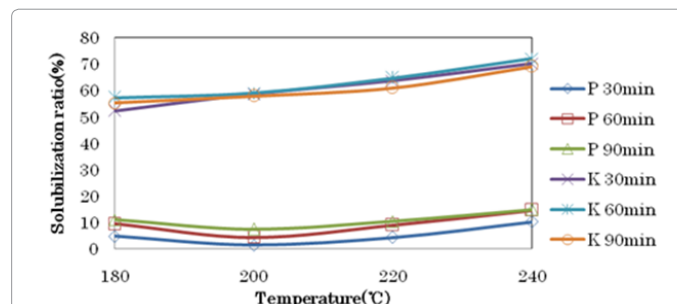


Figure 5: Phosphorus (P) and potassium (K) solubilization ratios as functions of the reaction temperature and the holding time.

Element	Unit	180°C			200°C			220°C			240°C		
		30min	60min	90min	30min	60min	90min	30min	60min	90min	30min	60min	90min
Na	%	62.21	58.51	45.74	62.16	57.67	48.44	65.76	56.43	50.75	69.98	57.99	52.19
Mg		8.08	9.11	10.82	10.54	12.32	9.16	4.62	5.03	5.87	5.13	4.32	4.39
Ca		5.14	7.92	6.78	3.52	3.65	6.19	10.11	11.12	10.98	7.80	7.68	12.88
Fe		4.16	4.53	5.27	5.76	6.59	5.35	3.53	3.63	5.78	7.71	8.73	9.04
Al		11.53	16.74	12.21	14.09	17.75	14.08	19.09	18.79	16.34	24.28	20.05	22.89
Mn		8.67	9.52	9.23	5.06	6.46	9.81	8.41	11.64	7.73	8.75	13.40	15.15
Pb		82.89	74.11	29.66	71.06	53.93	29.97	68.80	30.22	26.17	68.83	29.58	17.82
Zn		0	7.72	3.28	0.92	5.18	5.11	5.25	7.75	3.39	5.78	9.23	11.55
S		44.08	51.49	54.22	52.87	54.91	56.51	59.77	60.86	61.83	62.81	66.33	68.96

Table 3: Solubilization of the inorganic material and heavy metal.

shown that at a lower reaction temperature and a shorter holding time, most of Pb will be released from the solid phase. When the reaction temperature and the holding time increased, it can be seen that some complex reactions were happened and that the release of Pb amount was decreased. There are many different forms of metals in sludge, including those forms of exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to organic matter and residual. The exchangeable fraction is likely to be affected by changes in water ionic composition, sorption and desorption processes. The carbonate fraction is sensitive to changes in pH, while the reducible fraction, which consists of iron and manganese oxides, is thermodynamically unstable under anoxic conditions [19]. At the lower temperature and shorter holding time, the release of Na and Pb are huge, indicating that these two elements most likely appear in the form of exchangeable, and thus are easy to dissolve. On the other hand, at a higher temperature and at a longer holding time, accompanying the hydrolysis of protein and carbohydrate, some organic monomers are produced. The monomers reacted with these dissolved metal ions, generating more complex water-insoluble precipitate, thus the solubilization ratio of Na and Pb was significantly reduced.

However, the solubilization ratios of other elements showed very low levels entirely. Generally, in addition to Al and S, the solubilization ratios of other measured elements are less than 20%, most of which are less than 10%. As for Al, although the effect of the holding time is not obvious, the reaction temperature showed a linear relationship. In addition, for S, the solubilization was improved from 44% to around 70% during the treatment process; therefore, by adjusting the treatment parameters, most of the S content can be transported from the solid phase to the liquid phase.

It is reported that heavy metals, incorporated in the sludge flocs, can only be transported from the flocs to the aqueous phase by diffusion [19]. For a relatively lower temperature, the rate of extraction as the function of ions diffusivity is promoted [20]. Conformational changes of the sludge flocs enhance further the mobility of the metal ions. Moreover, a large part of heavy metals is adsorbed to the EPS, which shows a lot of potential binding sites including carboxylates, amines and thiols. The degradation of these structures leads also to the release of the adsorbed metals [19]. However, in this study, the heavy metal contents are too low, and thus, the release ratio can only be seen as a reference.

Effects of hydrothermal treatment on the liquid phase

pH and EC value: After the hydrothermal treatment, the liquid phase became not transparent anymore and turned brown to a large extend after the treatment which confirms visually that chemical reaction happened. At the same time, not only the unpleasant odor

disappeared completely, the liquid product even gives off a coffee like smell, which suggested the caramelizing reaction or maillard reaction as was discussed in our previous work [21]. During the hydrothermal process, because of the hydrolysis of the organic components, a lot of reducing sugar and amino acids were produced. Under high temperature and high pressure, the C- in the open-chain carbonyl radicals in reducing sugar are attacked by the lone pair electrons in N in the amino group nucleophilically to lose H₂O and closed chain to form new kind of substances [22], which caused the change of both the color and odor of the liquid product.

The pH and EC values were measured as soon as possible after each experiment. The results are shown in Tables 4 and 5. For the case of pH values, when the reaction temperature was 180°C, with extending the holding time, the solution's pH value showed a decreasing trend. However, an obvious difference was observed at the temperature of 200°C with a longer holding time. In the first 60 min, the same as the trend of 180°C, the pH value decreased to lower than 6, and then when the holding time was extended to 90 min, the pH value showed an increasing trend. The pH decrease indicates the destruction or transformation of organic matters to organic acids in the liquid product. Under a comparative low temperature ($\leq 200^\circ\text{C}$), it is obvious that chemical reactions happened in the dissolved organic matters. With extending the holding time, more organic acid is produced, and this reaction is exhibited by the decrease of the pH value. Then pH increase could be due to the organic acid decomposition or acidic compounds volatilization. The EC value also increased with the reaction temperature increase, which can be attributed to some dissolved macromolecular organic compounds decomposed into small and inorganic molecules, and as we had discussed before, metals, released into the liquid phase caused the EC increase.

Yields of TOC, Org-N and ammonium: We have found that both the reaction temperature and the holding time are very important parameters for the nitrogen solubilization. A large number of previous studies have shown that during the hydrothermal treatment process, part of the protein will degrade to inorganic matters due to decomposition. Some lectures also pointed that while the protein dissolves, it is also hydrolyzed to form multi-peptide, dipeptide and amino acid [13]. By the hydrothermal treatment, more than 40% of nitrogen components are dissolved into the liquid phase; to take advantage of this liquid, it is necessary to know the characteristics of the dissolved nitrogen in the liquid. In order to know the effect of the operating parameters of the hydrothermal treatment on the protein degradation, Org-N and NH₄⁺-N concentrations were also measured. The degradation of protein was characterized by the percentage of Org-N and NH₄⁺-N in the total nitrogen.

The result is presented in Table 6. The NH₄⁺-N ratio increased

pH	30 min	60 min	90 min
180	7.05	6.68	6.41
200	6.08	5.89	6.28
220	6.78	7.12	7.49
240	8.17	8.31	8.41

Table 4: The pH value of liquid products after each hydrothermal process.

EC(ms/cm)	30 min	60 min	90 min
180	7.49	8.13	8.94
200	9.17	9.89	10.19
220	10.29	11.16	11.42
240	11.43	11.99	12.57

Table 5: The EC value of liquid products after each hydrothermal process.

Parameter	unit	180°C			200°C			220°C			240°C		
		30 min	60 min	90 min	30 min	60 min	90 min	30 min	60 min	90 min	30 min	60 min	90 min
Or-N	%	73.08	72.20	64.09	64.52	62.39	61.25	59.87	56.80	55.75	53.90	50.26	49.22
NH4+-N	%	26.92	27.80	35.91	35.48	37.61	38.75	40.13	43.20	44.25	46.10	49.74	50.78

Table 6: The ratio of different kind of nitrogen in liquid phase.

and Org-N decreased with increasing the reaction temperature, demonstrating that a certain amount of Org-N in the liquid phase was decomposed to NH₄⁺-N with increasing the reaction temperature. At the temperature of 180°C, in the first 60 min holding time, the NH₄⁺-N ratio did not show obvious change, demonstrating that during this process, the main reaction is dissolution; when the holding time was extended to 90 min, the NH₄⁺-N ratio increased by about 8%, and the Org-N ratio decreased. However, when the reaction temperature was increased to 200°C, it seems that even though the holding time was extended, the NH₄⁺-N ratio maintained constant levels in this temperature. At the temperatures of 220°C and 240°C, by changing the holding time from 30 min to 90 min, the NH₄⁺-N ratio increased by 4.12% and 4.68%, respectively, which can also be considered to be maintained at the constant level. The NH₄⁺-N ratio change showed almost a linear relationship with the reaction temperatures, demonstrating that the degradation of organic nitrogen is influenced by the reaction temperature. For the case of protein decomposition, at a low reaction temperature, protein was decomposed into amino acid first, and then, when more energy was applied, the destruction of amino acids was broken up, and the decarboxylation and the deamination happened [23]. Then the amino acid further hydrolyzed to form organic acid, NH₄⁺ and CO₂ [22]. At a high reaction temperature, since no obvious effect can be seen from extending the holding time, the dissolution and the decomposition can be completed in less than 30 min.

Referring to Table 5, it can be inferred that the pH change, not only depends on the production of NH₄⁺-N, but also depends on the carbon form extremely since even though a certain amount of ammonia was produced, the total content is not high enough to affect the pH value. Particularly, in the low reaction temperature region, with the decomposition of protein, ammonia content increased, but the liquid phase showed a certain degree of acidity, and, the reaction temperature of 200°C can be seen as an inflection point. The pH value showed a trend of decreasing first, and then increasing later by increasing the reaction temperature. When the reaction temperature is higher than 220°C, the liquid phase showed alkalinity and the pH value reaches higher than 8. Therefore, the huge amount of carbon content in the liquid phase played the dominant role for both the physical and chemical characteristics of the liquid phase.

To identify the carbon morphology change in the liquid phase,

the TC and IC concentrations of the liquid phase was measured with a TOC analyzer. TOC was calculated by subtracting Inorganic Carbon (IC) from the Total Carbon (TC). The IC values were less than 3% of the TC values for all samples examined. The TOC yield of liquid phase is defined by the following equation:

$$\text{TOC yield} = \frac{\text{TOC concentration} \times \text{liquid phase volume}}{\text{dissolved carbon}} \quad (2)$$

Where the unit of the TOC concentration is [mg/l], the liquid phase volume is [l], the dissolved carbon is [mg], respectively.

The TOC yield is shown in Figure 6. It can be seen that even though the carbon solubilization ratio increased with increasing the reaction temperature, visually reverse trends were observed for the yields of total carbon and TOC with regard to the holding time at the temperature of 180°C and 200°C: an increased holding time results in a larger carbon solubilization ratio but a lower yield of TOC. The highest decreasing ratio of 17% happened at 200°C from 30 min to 90 min. Moreover, at the temperatures of 220°C and 240°C, there are no obvious differences between different holding times. This result suggested that during the hydrothermal treatment, in different treatment conditions, the carbon decomposition rates are also different. Generally speaking, the TOC yield decreased with increasing the reaction temperature, and for all the situations tested, the results for 30 min and 60 min holding times are almost identical; but at 180°C and 200°C, when the holding time was extended to 90 min, the TOC ratio showed obvious decrease, which means the formation of gaseous product.

The trend of 180°C and 200°C showed that the dissolved organic carbon in the solution, decomposed to gaseous products gradually, and most of the gaseous products were produced between 60 min and 90 min. As can be seen from Table 5, the conclusion showed that during the first 60 min holding time, the dissolution and the organic acid formation are main processes. That is because at temperatures lower than 200°C, only exopolymers were affected by the hydrothermal treatment, carbohydrates and also a few proteins were dissolved. As carbohydrates are located in exopolymers whereas proteins are mainly located inside the cells, carbohydrates decomposition was superior to proteins decomposition [24]. Therefore, the organic content from exopolymers, dissolved into the liquid phase first, then, with the holding time increase, polysaccharide decomposed into organic acid,

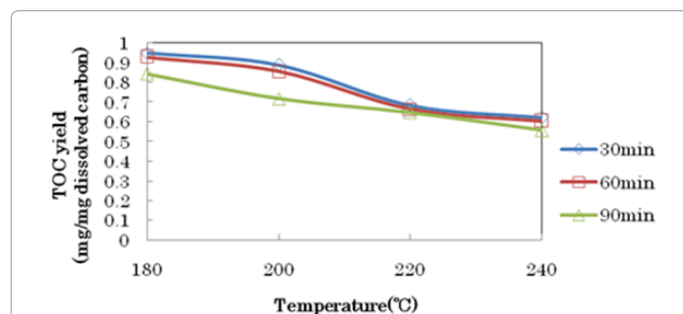


Figure 6: TOC yield as functions of the reaction temperature and the holding time.

and with a further extension of the holding time, the organic acid was decomposed into gases and the organic nitrogen also decomposed into inorganic nitrogen.

The formation of gaseous products from biomass in hot-compressed water mainly results from the decarboxylation and the fragmentation reactions of the intermediates or liquid products [25]. At a comparatively higher temperature, it seems that the decomposition of organic substance happened in a very short time, because at 220°C, no obvious difference in the TOC content was shown by extending the holding time. That is because under a higher reaction temperature, with more energy was applied, the pressure in the reactor also became higher, which caused the reaction acceleration. In addition, at this temperature, the pH value of the solution showed obvious increase trend, expressing the decomposition of the organic acid. By referring to Figure 6 and Table 5, this assumption could be demonstrated very well.

It is found that the hydrothermal treatment of sewage sludge at 190°C and 2 MPa can considerably enhance the dehydration performance of the slurry like product, and then the water content can be reduced to lower than 60% by the mechanical dehydration [25]. The fragmentation of ECP caused the sludge dewaterability improvement, so it can be seen that at 180°C to 200°C, nearly all of the carbohydrates dissolved into the liquid phase accompanied with the fragmentation of ECP and decomposed gradually, which caused the dewaterability improvement; when the temperature is higher than 200°C, the TOC product kept consistent, expressing that all of the carbohydrates were decomposed into gaseous product, leaving only complicate organic matters which is difficult to decompose.

Cost Effectiveness of Hydrothermal Process for Sewage Sludge Treatment

The cost effectiveness of the hydrothermal process has been analyzed based on the Japanese tipping fee for sewage sludge treatment (100US\$/ton) and the expected selling price of the liquid fertilizer produced (100US\$/ton) for the 30tons/day capacity plant. The detail assumptions and calculations are shown below. From this analysis, we can expect that the total expenditure of the plant will be 0.7 MUS\$/year, while the total income of the plant will be 2.0 MUS\$/year. This analysis clearly shows the cost effectiveness of liquid fertilizer production from sewage sludge employing the hydrothermal process.

- Treatment capacity of sewage: 30 tons/day
- Investment for full treatment plant: 2 MUS\$
- Moisture content of sewage sludge: 80%
- Annual operation period: 330 days

- Daily operation: 24 hours/day
- Daily solid fuel production (dry base): 6 tons/day (30 tons/day x 0.2)
- Daily liquid fertilizer production: 30 tons/day
- Boiler fuel consumption: 100% of produced solid fuel will be utilized as a boiler fuel
- Maintenance cost per annum (5% of the capital cost): 0.1 M US\$/year
- Labor and utility costs per annum: 0.2 MUS\$/year
- Capital cost (5 years depreciation) per annum: 0.4 MUS\$/year
- Total expenditure per annum: 0.7 MUS\$/year
- Tipping fee income per annum: 1.0 MUS\$/year (100US\$/ton x 30tons/day x 330days/year)
- Fertilizer sales income per annum: 1.0 MUS\$/year (100US\$/ton x 30tons/day x 330days/year)
- Total income: 2.0 MUS\$/year

Conclusions

The present paper studied the application of moderate temperature hydrothermal treatment (180, 200, 220, 240°C) as a new treatment method of nutrient recycling from sewage sludge. It is observable that the hydrothermal treatments are effective to solubilize sludge. For the temperature lower than 200°C, the holding time was found to be more important factor for the solid solubilization, but when the temperature was higher than 200°C, the solid solubilization was found to increase linearly with the reaction temperature and the effect of the holding time was insignificant. Nitrogen, potassium and sulfur solubilization linearly increased as the reaction temperature was increased and they reached the maximum values of about 70%, while only less than 20% of phosphorus was dissolved. In addition, with different treatment parameters, different kinds of organic and inorganic nutrients are also produced; protein and saccharine components will be decomposed into amino acid and other organic acid first and finally into ammonia and CO₂, with different reaction rates. Considering the large quantity of nutrient in the liquid product, the hydrothermal treatment also suggested a possibility of producing more valuable products from sewage sludge with a lower cost.

References

1. Neyens E, Baeyens J (2003) A review of thermal sludge pre-treatment processes to improve dewaterability. *Journal of Hazardous Materials* 1: 51–67.
2. Rui Xun, Wei Wang, Wei Qiao, Keqing Yin (2008) Status of Urban sludge treatment and hydrothermal reduction technology of enhanced dewatering. *Environmental Sanitation Engineering* 16: 28-32.
3. Mark Crocker (2010) Thermo chemical Conversion of Biomass to Liquid Fuels and Chemicals, RSC Publishing Cambridge.
4. Ross AB, Biller P, Kubacki ML, Li H, Lea-Langton A, et al. (2010) Hydrothermal processing of microalgae using alkali and organic acids. *Fuel* 89: 2234–2243.
5. Cheng H, Zhu X, Zhu C, Qian J, Zhu N, et al. (2008) Hydrolysis technology of biomass waste to produce amino acids in sub-critical water. *Bioresource Technology* 99: 3337–3341.
6. Yoshida H, Terashima M, Takahashi Y (1999) Production of organic acids and amino acids from fish meat by sub-critical water hydrolysis. *Biotechnology Progress* 15: 1090–1094.
7. Kang K, Chun B (2004) Behavior of hydrothermal decomposition of silk fibroin to amino acids in near-critical water. *Korean J. Chem. Eng.* 21: 654–659.
8. Park JH, Park SD (2002) Kinetics of cellobiose decomposition under subcritical

- and supercritical water in continuous flow system. *Korean J Chem Eng* 19: 960-966.
9. Sasaki M, Kabyemela B, Malaluan R, Hirose S, Takeda N, et al. (1998) Cellulose hydrolysis in subcritical and supercritical water. *Journal of Supercritical Fluids* 13: 261-268.
 10. Sasaki M, Fang Z, Fukushima Y, Adschiri T, Arai K (2000) Dissolution and hydrolysis of cellulose in subcritical and supercritical water. *Ind Eng Chem Res* 39: 2883-2890.
 11. Oomori T, Khajavi SH, Kimura Y, Adachi S, Matsuno R (2004) Hydrolysis of disaccharides containing glucose residue in subcritical water. *Biochemical Engineering Journal* 18: 143-147.
 12. Quitain AT, Faisal M, Kang K, Daimon H, Fujie K (2002) Low-molecular weight carboxylic acids produced from hydrothermal treatment of organic wastes. *J Hazard Mater* 93: 209-220.
 13. Jiang Z, Meng D, Mu H, Kunio Y (2010) Study on the hydrothermal drying technology of sewage sludge. *Science China Technological Sciences* 53: 160-163.
 14. Wilson CA, Novak JT (2009) Hydrolysis of macromolecular components of primary and secondary wastewater sludge by thermal hydrolytic pretreatment. *Water research* 43: 4489-4498.
 15. Barlundhaug J, Odegaard H (1996) Thermal hydrolysis for the production of carbon source for denitrification. *Water Sci Technol* 34 : 371-378.
 16. Urbain V, Block JC, Manem J (1993) Bioflocculation in activated sludge an analytical approach. *Water Res* 27: 829-838.
 17. Mok WSL, Antal MJ (1992) Uncatalyzed solvolysis of whole biomass hemicellulose by hot-compressed water. *Ind Eng Chem Res* 31: 1157-1161.
 18. Brooks RB (1970) Heat treatment of sewage sludge. *Water Pollut Control* 69: 221-231.
 19. Dewil R, Baeyens J, Appels L (2007) Enhancing the use of waste activated sludge as bio-fuel through selectively reducing its heavy metal content. *J Hazard Mater*. 144: 703-707.
 20. Veeken AH, Hamelers HV (1999) Removal of heavy metals from sewage sludge by extraction with organic acids. *Water Sci Technol* 40: 129-136.
 21. Namioka T, Morohashi Y, Yoshikawa K (2011) Mechanisms of malodor reduction in dewatered sewage sludge by means of the hydrothermal torrefaction. *Journal of Environment and Engineering* 6: 119-130.
 22. REN L (2006) Impact of hydrothermal process on the nutrient ingredients of restaurant garbage. *Journal of Environmental Sciences* 18: 1012-1019.
 23. Toor SS, Rosendahl L, Rudolf A (2011) Hydrothermal liquefaction of biomass A review of subcritical water technologies. *Energy* 36: 2328-2342.
 24. Bougrier C, Delgen JP, Carrere H (2008) Effects of thermal treatments on five different waste activated sludge samples solubilisation, physical properties and anaerobic digestion. *Chemical Engineering Journal* 139: 236-244.
 25. Xu C, Lancaster J (2008) Conversion of secondary pulp/paper sludge powder to liquid oil products for energy recovery by direct liquefaction in hot-compressed water. *Water Research* 42: 1571-1582.