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1 INTRODUCTION

1.1 Research Background

1.1.1 World food crisis

After World War II, the world's food production developed very quickly. From the year of 1950 to 2010, the world's total grain production increased from 630 million tons to 2.28 billion tons, which showed an increase of more than 260%. However, during this period, the world population, which has been exponential growth, has now reached approximately 7.0 billion, increased approximately 90%[1], and is expected to approach 9.5 billion by 2050. Global food requirements have also risen and the expected per capita food requirement is likely to double by 2050[2]. Due to the rapid economic development and population growth, a significant increase in the demand for the food of world had occurred[3][4]. On the other hand, with the improvement of people's living standards, people's requirements on food quality and safety are also improving gradually. With the exponential growth of the global population, the agricultural sector is bound to use ever larger quantities of fertilizers to augment the food supply, which consequently increases food production costs[5].

1.1.2 Fertilizer

In order to develop the agriculture production and meet the increasing food demands, in recent years, the farmers are bound to employ enormous quantities of fertilizers. However, excessive usage of fertilizer far demonstrated undesirable environmental impacts[6]. First of all, it will lead to the deterioration of soil properties. If we applying huge amount of chemical fertilizer with a single element to the cultivated land, the nutrients can not be taken up and used effectively, nitrogen, phosphorus, potassium and some other chemical substances are susceptible to cause soil consolidation, and will constitute variety kinds of chemical salt, which will accumulate in the soil, resulting in soil nutrient structural imbalance, poor physical traits, some plots of harmful metals and harmful bacteria, resulting in deterioration of soil properties. Secondly, it will result in the product quality reduction. Chemical fertilizer bias will result in crop nutrient dislocation, some substance transformation will be restrained, resulting in lower product quality and perishable. Thirdly, it will cause environmental pollution. Due to the excessive fertilizer application, the water soluble nutrients were leaching into the groundwater by the rain washing and the farmland irrigation into the groundwater and the rivers, causing the basin groundwater and river pollution and the eutrophication of the groundwater, rivers and lakes, resulting in the phenomenon of fish and plant death. Finally, lead to the unblance of production and harvest. On one hand, as being limited on the level of farming and cultivation, crop can not get high yields; on the other hand, due to the excessive application of the unity of several fertilizers, causing nutritional imbalance and nutrient dislocation, only increasing the cost but not increasing the production, and cause low-quality agricultural products which is difficult to sell, or the price is low, causing the losses to farmers.

Organic fertilizers are fertilizers derived from biomass. The raw materials for making organic fertilizer can be divided into the following categories:

1. Agricultural waste: such as straw, soybean meal, cottonseed meal and so on.
2. Manure: chicken, cattle manure and rabbit manure;
3. Industrial waste: such as lees, vinegar residue, cassava residue, sugar bagasse, furfural residue, etc;
4. Garbage: for example, food waste, etc;
5. Municipal sludge: river mud, sewage sludge, etc.

Organic fertilizers have many advantages. As the nutrient components inside the organic fertilizer are mainly in the organic form, thus the majority of nutrient-supplying was acted as a slow-release fertilizer. After applying organic fertilizer into the soil, by the decomposition of the microorganisms, nutrients can be taken up by the plant. Therefore, organic fertilizers can increase physical and biological nutrient storage mechanisms in the soil, mitigate risks of over-fertilization. Organic fertilizer nutrient content is solubility, and nutrient release rates are typically much lower than inorganic fertilizer. Organic fertilizers also re-emphasize the role of humus and other organic components of soil, which are believed to play several important roles. First of all, organic fertilizers can mobilize existing soil nutrients, so that good growth is achieved with lower nutrient densities while wasting less. Also, organic fertilizer can release nutrients at a slower and more consistent rate, which helps avoiding a boom-and-bust pattern. As the complicate structure of the organic component, organic fertilizer can help to retain soil moisture, reducing the stress due to temporary moisture stress, improving the soil structure and helping to prevent topsoil erosion.

Biomass waste is an important fertilizer in agricultural production. It is applied to fertilize soil and increase crop yield in the world traditional agricultural production for a long time. Most of the organic fertilizers come from crop residues like rice bran, various oilseed cakes and animal byproducts like meat bone meal, blood meal, fish meal, and sometimes distinguished from animal manure or compost based on animal waste[7]. They contain specifically high levels of nutrients in oil seed cakes and blood meal and P in rice bran and meat bone meal, and are also high in organic matter content and a variety of micronutrients in general[8][9], so that they have been widely used as alternative fertilizers for organically grown fields.

In recent half a century, the use of chemical fertilizers in the world, especially in China, has been rising dramatically[10], while that of organic fertilizers has decreased, which caused an increased risk of secondary soil salinization. So the proper use of fertilizer is important for maintaining sustainable development of agriculture[11]. Currently, the amount of organic fertilizers accounted for 50% of the total in the United States and other western countries. In China, the commercial production of organic fertilizer industry beginning to take shape, but large-scale application of farmland is not yet universal, accounting for only less than 10%. But it also indicates precisely that the organic fertilizer in China has huge development potential and market space. By national policy guidance and fertilizer developing trends for the future potential of organic fertilizer, organic fertilizer application rate is expected to account for about 30% of total fertilizer consumption in the next 10 years. Chinese organic fertilizer production will show a rising trend in recent years.

1.1.3 Sewage sludge

1.1.3.1 Characteristics of the sewage sludge

Municipal and industrial wastewater treatment plants produce large amounts of sewage sludge, containing organic and mineral components. Sewage sludge is a complex heterogeneous mixture of micro- organisms, undigested organics, inorganic materials and moisture[12]. It is accumulated during three phases: primary (solid removal), secondary (bacterial decomposition),and tertiary wastewater treatment (extra filtration)[13]. It contains many kinds of molecules coming from proteins and peptides, lipids, plant macromolecules with phenolic structures or aliphatic structures, along with organic micro-pollutants[14] and mainly microbial cells that are complex polymeric organic materials[15]. As its organic components are very complex and high, and also its moisture content is very high, the sewage sludge is very easy to get rot and always sending out smelly odor. And according to the recent research, heavy metals, such as Cr, Ni, Cu, Zn, Pb, Cd and Hg are also found in the sewage sludge. Bu at the same time, sewage sludge also contains a lot of micronutrients, such as K, Mg, Ca, Fe and so on[16]. Originally, sewage sludge is avaluable resource of organic matter, nitrogen, phosphorus, potassium and the other micronutrients[17-22]. It is reported that a certain amount of nitrogen in the sewage sludge is in mineral form, which is available for rapid uptake by the crops[23], and about half of the phosphorus contained in the sewage sludge is plant-available[24]. Therefore，the utilization of sewage sludge as fertilizer is also gaining attention. Sludge can also be mixed with other feedstock materials, such as manure, plant biomass, and food waste, and used for digestion to methane[25]. Nevertheless, depending on the feedstock materials, sludge often contains heavy metals and bacterium that can be taken up by plants, so its use for food or fodder crops is questionable[26-28]. The accumulation of heavy metals in soils and subsequent accumulation along the food chain are the potential threat to animal and human health. And when be used as fertilizer, high nitrogen content of these biomass wastes causes excessive nitrogen supply to the soil, which significantly pollutes our environment.

Even though its nitrogen, phosphorus and potassium contents are much higher than manure, unfortunately, sewage sludge also contains parasites, bacteria and so on, coupled with unpleasant odor, therefore, it is more unwelcomed as fertilizer. 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.

1.1.3.2 Treatment methods of the sewage sludge

Sludge treatment and disposal is one of the focus points in current environmental science research. At present, the disposal methods are: landfills, ocean disposal, incineration, agricultural use and so on. In developed countries, the sewage sludge has been treated very well or even been used as another resource. Different countries and regions according to the practical situation there choose the most appropriate treatment methods accordingly. For example, in Western Europe, indirect drying is mainly used; in Japan incineration is mostly used; and in U.S. and U.K. landfills, agricultural use are mostly applied. Indirect drying has become a leading treatment method in developed countries; in Europe there are large-scale sludge pre-drying plants. With the further expansion of urbanization， the total production of sewage sludge in China will become more than 60 million tons every year, however, of which only about approximately 15% is used in agriculture.

The characteristics of sewage sludge show that there are two possibility to recycle it as resource, which are nutrients and energy recycles[29]. In recent years, several technologies have been developed for energy recovery from sewage sludge. Incineration and co-incineration of sludge are also used in big scale plants, because they can achieve the energy recovery from the sewage sludge in the form of heat or electricity, which can effectively enhance the sludge dewatering and drying processes[30-31]. The amount of energy that can be obtained strongly depends on the characteristics of the sludge and the change of the treatment process parameters. By anaerobic digestion, the organic component of the sludge will be transformed into a mixture of CH_4, CO_2, which can be utilized as a source of energy in the production of electricity or heat[32-33]. Gasification, which uses the temperature of about 1000-1700◦C, in an atmosphere with a reduced amount of oxygen, usually involves the break down of dried sludge into combustible gases. After removing the small quantity of impure gases, high quality syngas can be produced. The remaining slag can also be used as an ingredient in concrete mixes[35-36]. By the pyrolysis technology, sludge is treated under the temperature of 350-500◦C, and in an oxygen efficient environment. As a result, the sludge is transformed into char, ash, pyrolysis oils, water vapor, and combustible gas[37]. Supercritical water oxidation is seen as a good solution for sludge treatment, because under the 600◦C temperature and 25MPa pressure, approximately all of these reactions have shown transformation of 99.99% with a reaction time of 30s or less. But the cost of this technology is very high, and large-scale practical experience is not available yet[38][39]. Many other technologies are also used for the sewage sludge treatment, and peoples are also trying to recover the byproduct to offset the cost of the operation. In the case of nutrient, some people use sewage sludge for producing magnesium ammonium phosphate (struvite), which can be used as fertilizer directly for soil application[40-42]. Some peoples even recover heavy metals from the sewage sludge. But the easiest method is to use it as fertilizer. However, sewage sludge use in organic agricultural operations in U.S. has been extremely limited due to the toxic metal accumulation.

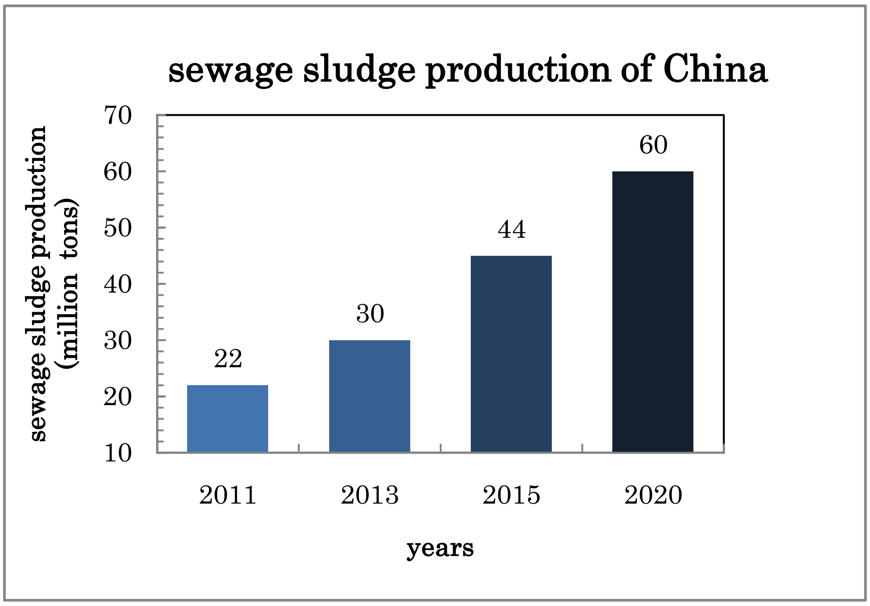

Figure 1.1: sludge production in China

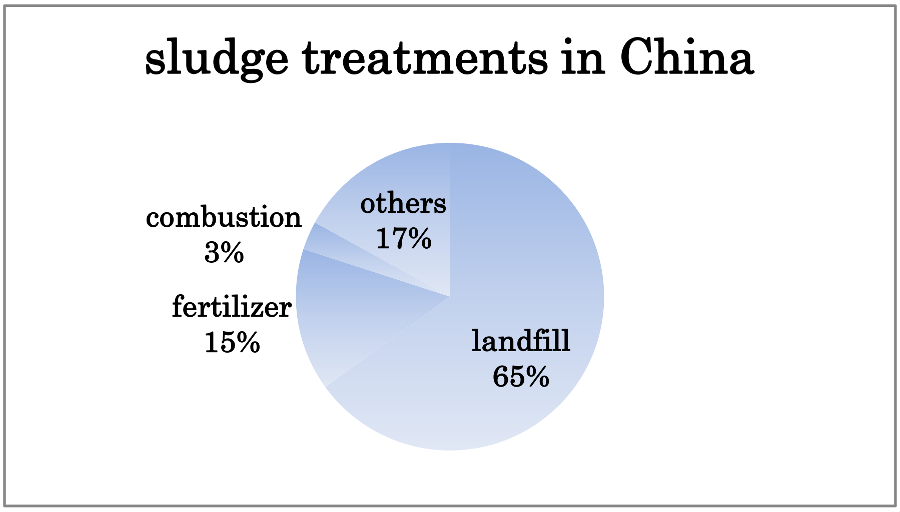

Figure 1.2: sludge treatments in China

1.2 Hydrothermal treatment

1.2.1 Mechanism of the hydrothermal treatment

In recent years, the hydrothermal treatment, as a new technology applicable to biomass waste is gaining attentions in the world due to its cheap, non-toxic, non-flammable and non-explosive operation offering essential advantages.

Generally speaking, the hydrothermal treatment is also a kind of sub-critical water treatment. Sub-critical water refers to water above its normal boiling temperature (373 K), but below its critical temperature, which is kept in the liquid state by applying pressure. Sub-critical water has been gaining increasing attention as environmentally friendly solvent and attractive reaction medium for a variety of applications[43]. Compared with the common water, sub-critical water showed distinctly different behavior, which is due to the dramatic changes in physical properties, namely dielectric strength and ionic product, which in turn can easily be altered by changing the temperature and the pressure[44]. The ionic product of sub-critical water is as much as three orders of magnitude higher than under ambient conditions. Under this condition, the ion concentrations are very high. So, some organic reactions can be carried out without acid-catalyze addition. Hence, acid hydrolyzed cleavages of peptide bonds can pass off without the addition of catalysts. However, the ionic product decreases greatly above the critical point. This fact makes sub-critical water an ideal reaction medium for the hydrolysis of organic compounds[45] and for the recycling of different organic wastes, such as municipal solid wastes, refractory pollutants, sludge and different polymers[46-49].

During the hydrothermal treatment，the biomass waste and saturated steam with high temperature and pressure react, and during the hydrothermal process, depending on the different treatment parameters, the cell wall and membranes of organics in the biomass waste are ruptured. At the same time, it will improve the dewatering ability of the biomass waste. In a hydrothermal treatment system, the biomass waste is kept mixing by a stirrer in the reactor while the high temperature saturated steam is introduced so that the cell of wastes can be broken and then the bound water in the cell can be released to become free water. After the hydrothermal treatment, higher efficiency mechanical dehydration is possible to obtain the solid residue with significantly reduced moisture content and separated liquid. This solid reside shows very good drying performance and 1-2 days natural drying is enough to produce dried solid fuel (RDF) with the moisture content less than 20%. A part of nitrogen content in the raw waste material will be dissolved into the separated liquid so that this hydrothermal treatment also has a function of denitrification. If the raw waste material contains organic chlorine or HCl, this chlorine can be converted into inorganic chlorine by adding alkaline substance such as limestone in the raw waste material before the hydrothermal treatment. Once chlorine becomes inorganic, it can be easily washed out by water washing combined with mechanical dehydration of the hydrothermal products.

Most of the previous researches on the application of this hydrothermal treatment to sewage sludge have been focused on the improvement of the anaerobic digestion ability of the sludge or the improvement of the dewatering performance for solid fuel production[50-51]. The hydrothermal drying process has been developed quickly by Prof. Yoshikawa group of Tokyo Institute of Technology and now is in the pre-commercialization stage. In this investigation, it is demonstrated that the product obtained from the hydrothermal treatment of sewage sludge is slurry-like material whose dehydration and drying performances are much improved compared with raw sludge. And the dry product obtained from the hydrothermal treatment of sewage sludge has almost the same heating value as the raw sludge with much less bad odor and shows good co-firing performance with coal. Fig.3 shows the scheme of the hydrothermal process.

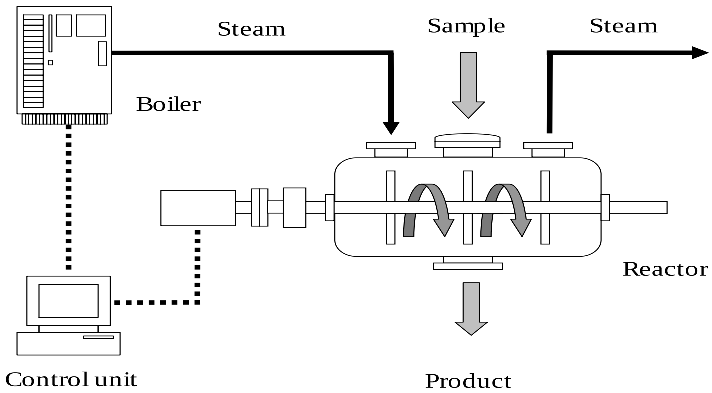

Figure 1.3: Hydrothermal process

1.2.2 Utilization of the hydrothermal treatment

Actually, not only for sewage sludge treatment, the hydrothermal treatment technology has been used in many fields for waste management. In recent years, using the hydrothermal treatment for converting organic wastes into more valuable substances has been investigated. According to the investigation about microalgae treated by the hydrothermal treatment at the temperature of 300◦C and 350◦C, an additional benefit 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[52]. The hydrothermal treatment was also demonstrated to be able to produce high yield of amino acid from chicken waste, hair and feather by controlling the reaction temperatures from 180◦C to 320◦C and the reaction pressures from 3 to 30 MPa[53]. Fish meat and silk fibroin can reportedly be converted into organic acids and amino acids by the hydrothermal treatment at 120◦C to 220◦C [54-55]. And the hydrothermal treatment were also be used as a new method of conversions of cellulose and disaccharides[56-59] and were also studied and had been found to be readily convertible into glucose and low-molecular-weight carboxylic acids[60]. We can see that the hydrothermal treatment has been widely investigated and developed as a technology for converting many kinds of biomass wastes into useful resources such as fuels and chemical components. And it can be inferred that from now on, much more investigation will be carried out for tapping more valuable products by the hydrothermal treatment technology.

1.3 Objective of this study

The hydrothermal treatment has been already applied to sewage sludge to improve their dewaterability and making the solid phase as solid fuel, however, the liquid phase is always treated as wastewater or discarded. Actually, during the hydrothermal process, a certain amount of nutrient in the sewage sludge can move into the liquid product, which shows a new possibility of the hydrothermal treatment. Some researchers use this technology for making solid fertilizer, but the liquid product associated with the hydrothermal process has not been well investigated. This study focuses on the possibility to utilize the liquid product produced by the hydrothermal process as a new organic liquid fertilizer.

The objective of this thesis is to investigate the possibility of liquid fertilizer production from sewage sludge by the hydrothermal treatment. The influences of process variables such as the reaction temperature and the reaction time are studied, and their effects on the yield and the quality of the nutrients are discussed. 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 are tested to investigate their variation trend during the hydrothermal process. Then the safety of the liquid product and its influence to the natural environment were evaluated, to confirm the feasibility of the liquid product to be used as fertilizer. Finally, plant growth experiment was carried out to prove the fertilizer effect to the plant.

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 the hydrothermal process. Therefore, the hydrothermal effect on the nutrient release of sewage sludge is gaining interest. The investigation on the nutrient solubilization is of great significance.

1.4 Thesis structure

This thesis aimed to investigate the possibility of liquid fertilizer production from sewage sludge by the hydrothermal treatment. By the lab scale hydrothermal treatment experiment, and analysis of the hydrothermal treatment process on the nutrient release, the law of nutrient solubilization was investigated, which can provide a basic evidence for extracting the nutrients, and find the optimum operating parameters to avoid the influence of the harmful toxicity components. Then the safety of the liquid product and its influence to the natural environment were evaluated, to confirm the feasibility of the liquid product to be used as fertilizer. Finally, plant growth experiment was carried out to prove the fertilizer effect to the plant.

The content of this study has been divided into five chapters as follows. In Chapter 1, the relationship of the global food crisis, energy, biomass waste and hydrothermal treatment was discussed. The basic mechanism of the hydrothermal treatment was reviewed and the previous works were presented, and the possibility of the hydrothermal treatment for biomass waste treatment and recycle is literature reviewed. The background of the hydrothermal treatment and its main principle is explained.

Chapter 2 discussed the effects of the hydrothermal process on the nutrient release of sewage sludge. This chapter will investigate the impact of the hydrothermal treatment on the solubilization of the nutrient component in sewage sludge and the characteristics of the liquid products. The influences of the process variables such as the reaction temperature and time will be studied. The influences of the process variables on the yield and the quality of the nutrient are discussed including the carbon balance and the nitrogen partitioning among 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 are tested to investigate their variation trend during the hydrothermal process.

Chapter 3 discusses the phytotoxicity and the biodegradation of the liquid product from the hydrothermal treatment. In this chapter, lab-scale organism decomposition system was used for testing the biodegradation of the liquid product. The cumulative emission of CO_2 in 50 days was calculated to determine the biodegradation of the liquid product. At the same time, the germination experiment was also done for testing the phytotoxicity of the liquid product obtained from hydrothermally treated sewage sludge.

The effects of the TOC concentration and the EC value on the seed germination were investigated together with the evaluation of the phytotoxicity and the safety of the liquid product.

In Chapter 4, the effect of the liquid product obtained by the hydrothermal treatment on the plant growth was discussed. In this chapter, to test the fertilizer effect of the liquid product, a six weeks plant growth experiment was carried out in a glass house. Komatsuna was used as the testing plant, and the liquid product was used as fertilizer. Depending on the different nutrient concentrations by different hydrothermal treatment parameters, the liquid product was mixed with chemical fertilizers in different ratio for testing, and two kinds of experiments were carried out and the experimental results were compared. By comparing and analyzing different planting parameters, the effect of the liquid product on the Komatsuna growth was discussed.

Chapter 5 summarizes the overall results. The main achievements in this research are summarized together with some recommendations for further improvement of this investigation.

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2 EFFECTS OF THE HYDROTHERMAL PROCESS ON THE NUTRIENT RELEASE OF SEWAGE SLUDGE

Abstract

In this chapter, the effects of the reaction temperature (160-240◦C), and the reaction time (30-90 minutes) were investigated, and both of solid and liquid products were analyzed individually to find out the law of the nutrient solubilization. The results showed that when the treatment temperature is higher than 180◦C, 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. At the same time, a certain amount of micro nutrients can also dissolved into the liquid product. The solubilization of the heavy metals are not only decided by the temperature, but also decided by the holding time. The hydrothermal treatment can effectively transport nutrient components in sewage sludge into the liquid product.

2.1 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, also 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, SO_2 and dioxins are also problems. Originally sewage sludge is a good agricultural fertilizer. Its nitrogen, phosphorus and potassium content are much higher than manure. But 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 2MPa) 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, the 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 pre-drying 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. And 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.

Based 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 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 organic acids and amino acid from fish meat or silk fibroin. Also, cellulose and disaccharides were also been found to be readily convertible into glucose and low-molecular-weight carboxylic acids by the hydrothermal treatment[5-12].

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 the 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 the reaction temperature and the 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 among 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 the hydrothermal process.

2.2 Experimental materials and methods

2.2.1 Material

In this research, the sewage sludge was obtained from a wastewater treatment facility located in Shimane prefecture of Japan. The nutritional value along with other properties of the sludge is provided in Table 2.1 and Table 2.2.

Table 2.1: Characteristics of sewage sludge

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

Table 2.2: Nutrient and heavy metal 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	−	−

2.2.2 Methods

2.2.2.1 Hydrothermal treatment

In this research, a bench-scale hydrothermal reactor with 0.5L capacity was utilized. The schematic view of the facility is shown in Fig.2.1. The reactor is a batch type (MMJ-500, Japan) which is equipped with an automated stirrer, a pressure sensor and a temperature controller. 60g of sludge (as received based) mixed with 60ml 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 the atmospheric. Then, the reactor was heated to the 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 90minutes) 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 minutes） 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 0.2μm pore size) before it was used for analytical measurements. As control, an experiment of 160◦C was also carried out to compare the effect of the hydrothermal treatment on the sewage sludge.

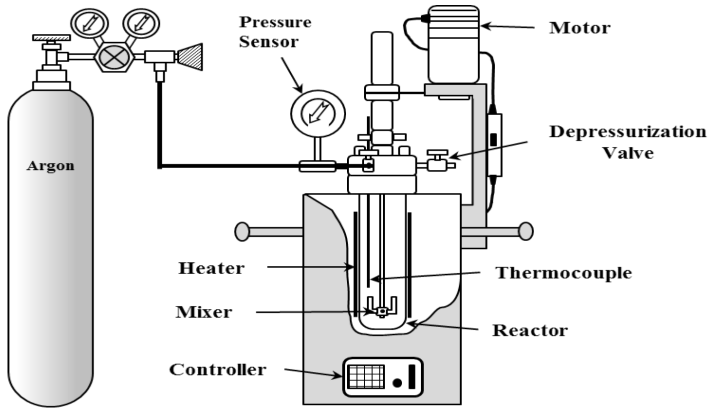

Figure 2.1: Schematic view of small-scale hydrothermal treatment reactor

2.2.2.2 Analysis

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 $HClO_4$ and HNO_3 solution by a Digi PREP 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), where the total organic carbon (TOC) is represented by the difference between TC and IC. The Total-N was measured using the Kjeldahl method, which involved acid digestion of the sludge followed by distillation and measurement of the released ammonia. The ammoniacal nitrogen (NH_4^+-N) was analyzed by employing the distillation procedure. The nitrate and nitrite were detected in negligible amount, and therefore omitted in this research. The difference between the Total-N and NH_4^+-N was then taken as the organic nitrogen (Org.-N).The potential of the hydrogen ion (pH) and the electrical conductivity(EC) values were measured using glass pH and EC electrodes(HORIBA,JAPAN).

In order to show the effect of the hydrothermal treatment on 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:

$$\text{Solubilization ratio}(\%) = \frac{\textit{content in initial sample} - \textit{content in treated sample}}{\textit{content in initial sample}} \times 100 \quad (2.1)$$

2.3 Results and discussion

2.3.1 Effects of the hydrothermal treatment on the solidsolubilization

The effects of the reaction temperature and the holding time on the reaction are demonstrated in Fig 2.2, which showed the solid solubilization ratio at various reaction temperatures ranging from 180◦C to 240◦C and the holding time from 30minutes to 90 minutes. As the control, the result at160◦C is also shown.

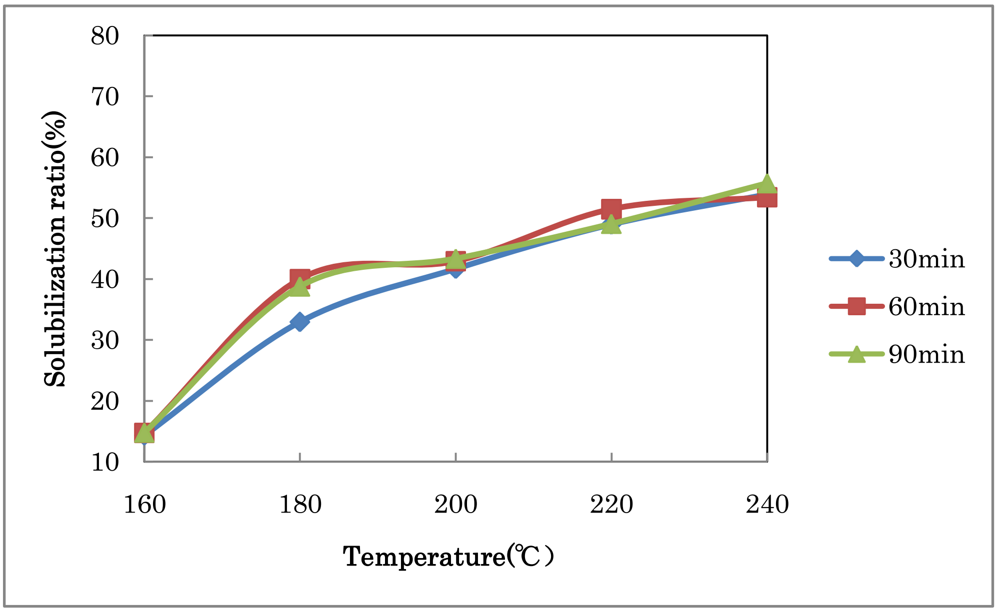

Figure 2.2: Solid solubilization ratio as functions of the reaction temperature and the holding time

We can see clearly that at the temperature of 160◦C, both the reaction temperature and the holding time showed almost no effect on the solid solubilization. The solubilization ratios were just about 15%. When it increased to 180◦C, 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 minutes holding time, only about 32% of the solid was dissolved; however, by increasing the holding time to 60 minutes, 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 Barlindhaug and Odegaard 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[15]. From many previous studies, it also showed that only when the reaction temperature is higher than 170◦C, the reaction will happen. In order to better understand 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.

2.3.2 Effects of hydrothermal treatment on the nutrient components of solid phase

2.3.2.1 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 macronutrients 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 the organic component.

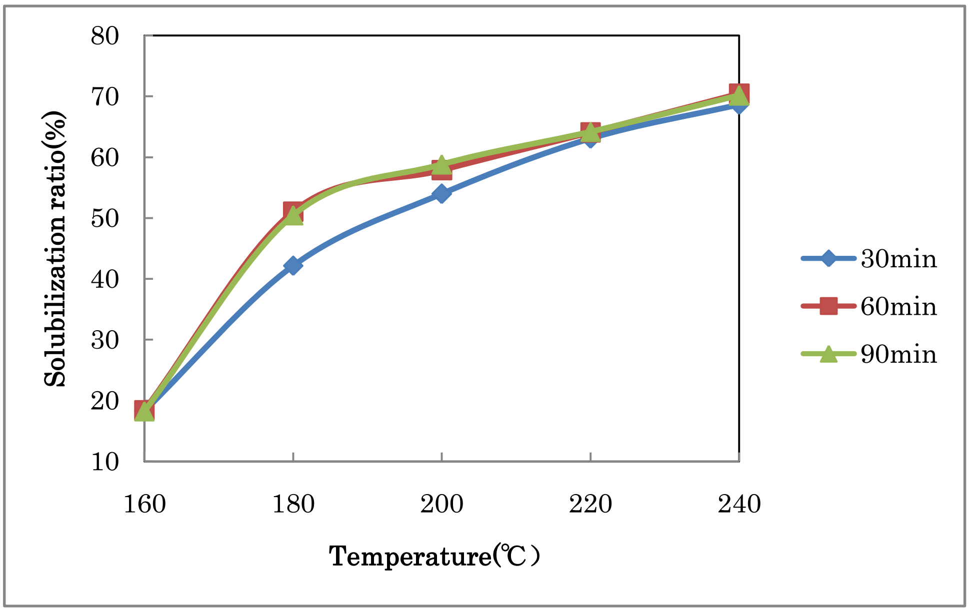

Figure 2.3: Nitrogen solubilization ratio as functions of the reaction temperature and the holding time

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(180◦C to 240◦C) and the 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 minutes to 60 minutes, the nitrogen solubilization ratio increased from 42% to 51%; but when the holding time was increased to 90 minutes, 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. As in the case of 160◦C, still the nitrogen solubilization is only about 20%, which showed a very low solubilization, and the holding time also showed no obvious effect.

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 macro molecular organic nitrogen in the solid phase of the sludge. During the 160◦C case, there was almost no reaction happened, the dissolved nitrogen mainly comes from the soluble component of the sewage 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 minutes made more protein dissolved, but further extension to 90 minutes 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 minutes). 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 (30minues) seem to be more suitable for large-scale application.

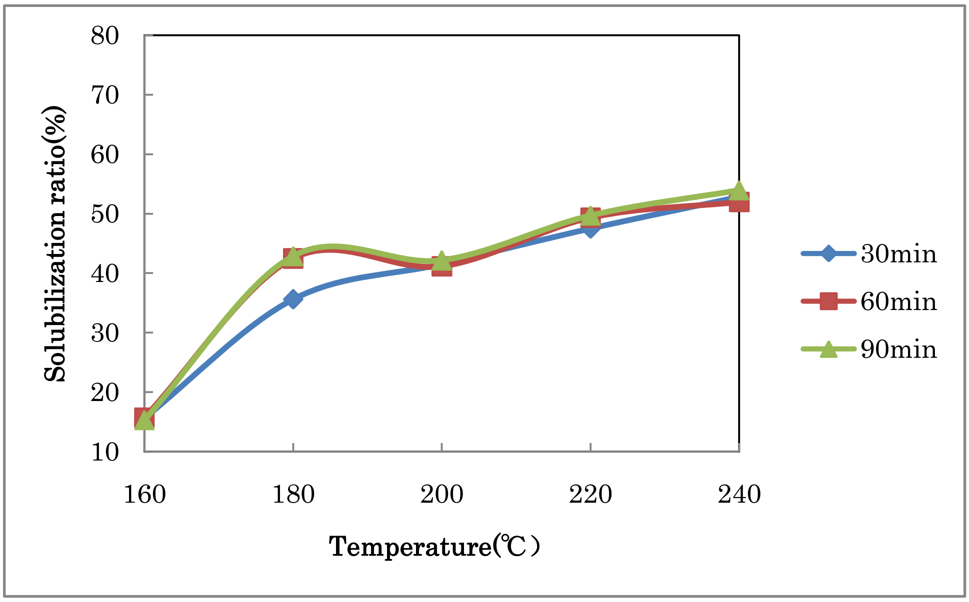

Figure 2.4: Carbon solubilization ratio as functions of the reaction temperature and the holding time

Figure 2.4 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. But for all the conditions tested, the holding time of 60 minutes and 90 minutes showed no difference. In the 160◦C case, the dissolved carbon was just only 15%, which can be seen as the soluble solid component. It is observable that at 180◦C, the solubilization ratio increased with the increase of the holding time from 30 minutes to 60 minutes 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 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[17]. So 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.

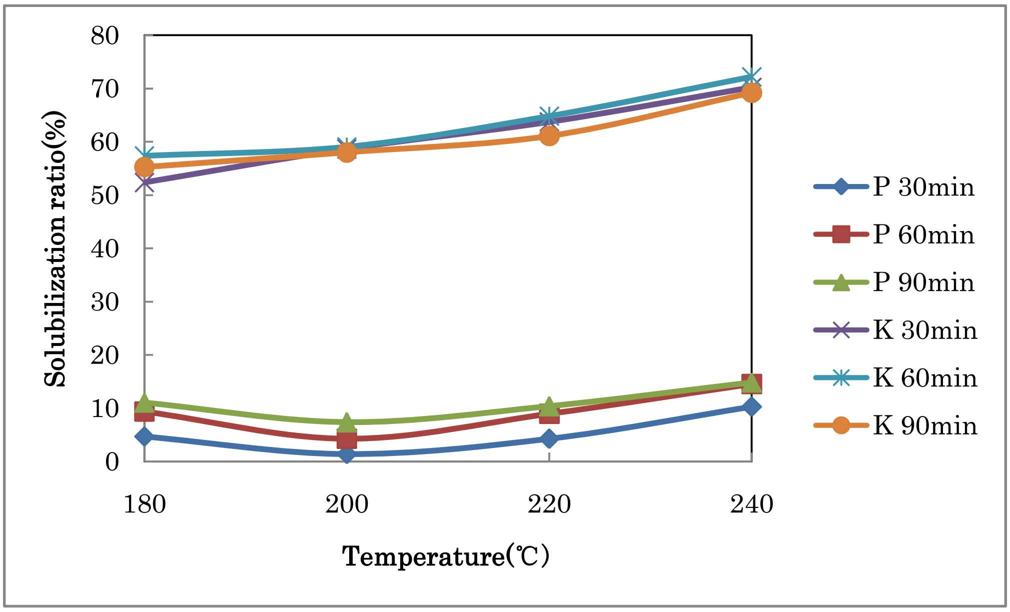

Figure 2.5: Phosphorus (P) and potassium (K) solubilization ratios as functions of the reaction temperature and the holding time

Figure 2.5 shows the solubilization of phosphorus (P) and potassium (K). As in the 160◦C case, the solubilized solid component was too low, and the solubilition of the largest quantity nutrient, nitrogen, is also very low, therefore it is not necessary to discuss the other nutrients as their concentrations were much more lower. Here just discuss the solubilition when the temperature was higher than 180◦C.

The solubilization of phosphorus does not show a significant increase by increasing the reaction temperature as well as extending the holding time. When the temperature increased up to higher than 170◦C, we can see the reaction happened. 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 2.2), it can be inferred that phosphorus was added as flocculants to the sludge, which is mainly in the form of insoluble $FePO_4$ precipitate. And 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 the organic matter.

2.3.2.2 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 2.3.

Table 2.3: Solubilization of the inorganic material and heavy metal

element		180℃			200℃			220℃			240℃		
		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

In Table 2.3, 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 minutes); however, for each reaction temperature, obvious decreasing trend can be seen when the holding time increased. By increasing the holding time from 30 minutes to 90 minutes, 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 minutes holding time), and the highest solubilization ratio decrease reached about 53% when the holding time was extended from 30 minutes to 90 minutes at the temperature of 180◦C. It is 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. And 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]. But in this study, the heavy metal contents are too low, and thus, the release ratio can only be seen as a reference.

2.3.3 Effects of the hydrothermal treatment on the liquid phase

2.3.3.1 pH and EC values

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 caramelize reaction or the 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 nucleophillically to lose H_2O 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 2.4 and 2.5. For the case of pH value, 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 minutes, 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 minutes, 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 comparatively low temperature(≤200◦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. As the temperature and pressure increased, the organic component in the sewage sludge reacted directly, which was hydrolyzd into micro molecule component, and the organic acid also decomposed into ammonia, CO_2 and so on, therefore the pH value increased when the temperature was increased to higher than 200◦C.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 also, as we had discussed before, metals, released into the liquid phase, also caused the EC value increase.

Table 2.4: The pH value of liquid products after each hydrothermal process

pH	30min	60min	90min
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 2.5: The EC value of liquid products after each hydrothermal process

EC(ms/cm)	30min	60min	90min
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

2.3.3.2 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 be degraded to become inorganic matters due to the decomposition. Some lectures also pointed that while the protein dissolves, it is also hydrolyzed to form multipeptide, 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 and form 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 NH_4^+-N concentrations were also measured. The degradation of protein was characterized by the percentage of Org-N and NH_4^+-N in the total nitrogen.

Table 2.6: The ratio of different kind of nitrogen in liquid phase

parameter	unit	180℃			200℃			220℃			240℃		
		30min	60min	90min	30min	60min	90min	30min	60min	90min	30min	60min	90min
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
NH_4^+-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

The result is presented in Table 2.6. The NH_4^+-N ratio increased and Org-N decreased with increasing the reaction temperature, demonstrating that a certain amount of Org-N in the liquid phase was decomposed to NH_4^+-N with increasing the reaction temperature. At the temperature of 180◦C, in the first 60 minutes holding time, the NH_4^+-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 minutes, the NH_4^+-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 NH_4^+-N ratio maintained constant levels in this temperature. At the temperatures of 220◦C and 240◦C, by changing the holding time from 30 minutes to 90 minutes, the NH_4^+-N ratio increased by 4.12% and 4.68%, respectively, which can also be considered to be maintained at the constant level. The NH_4^+-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, $NH_4^+$and CO_2 [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 minutes.

Referring to Table 2.5, it can be inferred that the pH change, not only depends on the production of NH_4^+-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. The pH value changed with the change of the carbon component form of liquid product.

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 the 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:

$$\text{TOC yield} = \frac{TOC\ concentration\ \times liquid\ phase\ volume}{dissolved\ carbon} \quad (2.2)$$

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

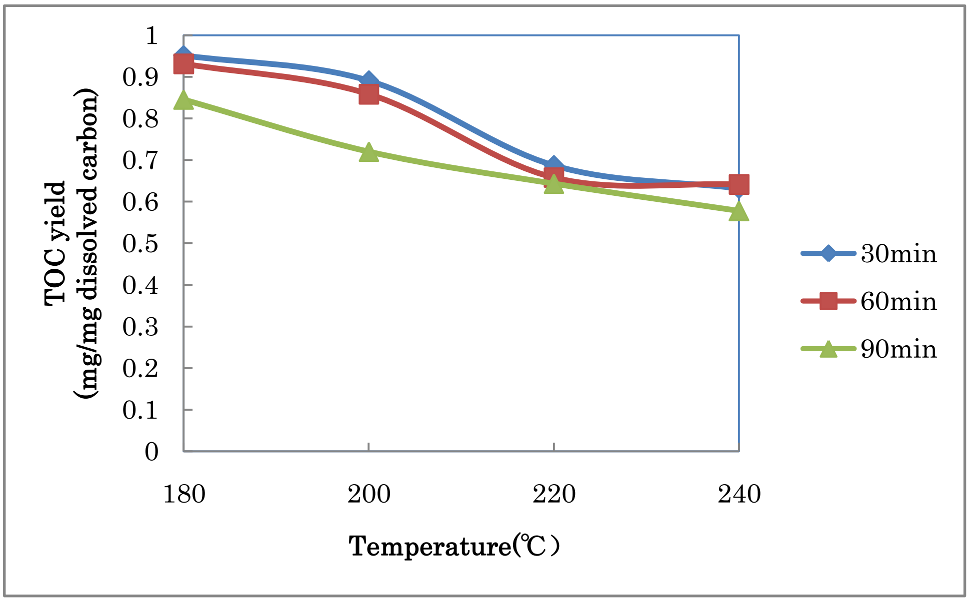

Figure 2.6: TOC yield as functions of the reaction temperature and the holding time

The TOC yield is shown in Fig.2.6. 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 minutes to 90 minutes. And 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 were also different. Generally speaking, the TOC yield decreased with increasing the reaction temperature, and for all the situations tested, the results for 30 minutes and 60 minutes holding times are almost identical; but at 180 ◦C and 200◦C, when the holding time was extended to 90 minutes, 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 is decomposed to gaseous products gradually, and most of the gaseous products were produced between 60 minutes and 90 minutes. As can be seen from Table 2.5, during the first 60 minutes 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 and 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, 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. Also, at this temperature, the pH value of the solution showed obvious increase trend, expressing the decomposition of the organic acid. By referring to Fig.2.6 and Table 2.5, this assumption could be demonstrated very well.

It is found that the hydrothermal treatment of sewage sludge at 190◦C and 2MPa can considerably enhance the dehydration performance of the slurry like product, 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.

2.4 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: 30tons/day
- Investment for full treatment plant:2 MUS$
- Moisture content of sewage sludge: 80 %
- Annual operation period: 330days
- Daily operation: 24 hours/day
- Daily solid fuel production (dry base): 6 tons/day (30tons/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

2.5 Conclusions

This chapter studied the application of moderate temperature hydrothermal treatment(160,180,200,220,240◦C) as a new treatment method of nutrient recycling from sewage sludge. It is observable that the hydrothermal treatment is effective to solubilize sludge. At the temperature of 160◦C, almost no reaction happened. When the temperature reached up to higher than 170◦C, obvious reaction happened. Both the reaction temperature and the holding time affect to the solubilization. At 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. And 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 CO_2, whose reaction rates are different. The EC value increased both according to the increase of the reaction temperature and also the holding time. Macro and micro nutrients solubilizations are dependent on different treatment parameters, therefore, by controlling the reaction temperature and the holding time, the quantity of the nutrients that dissolved into the liquid product can also be decided. On the other hand, as the reaction temperature and pressure were not so high as pyrolysis, the main reaction happened was hydrolysis, therefore, generally speaking, there is almost no toxic element in the compound. 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. Recovering the nutrient components from biomass by hydrothermal treatment is a convenient, clean and low cost technology, which can also be seen as a new method to be popularized.

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3 EVALUATION OF THE PHYTOTOXICITY AND BIODEGRADATION OF THE LIQUID PRODUCT FROM THE HYDROTHERMAL TREATMENT

Abstract

In this chapter, the germination experiment was conducted for testing the phytotoxicity of the liquid product. Also the effects of the TOC concentration and the EC value on the seed germination were investigated. At the same time, a lab-scale biodegradation system was used for testing the biodegradation of the liquid product. Certain amount of the liquid product was placed in the glass reactors, and the temperature was maintained at the room temperature. Then the inoculum from the common soil was used for biodegradation testing. The cumulative emission of CO_2 in 50 days was calculated to determine the biodegradation of the liquid product. The result showed that the hydrothermal reaction temperature determined the biodegradation rate of the liquid product, and the EC and TOC values of the liquid product also had effects on the germination rate of the plant. The organic acid produced during the hydrothermal process showed a positive effect on the root growth. The liquid product showed no obvious phytotoxicity, and it will be biodegraded by the natural microorganism in 50 days, which indicated that there is no accumulation in the soil, and will not cause organic pollution to the soil.

3.1 Introduction

In the last chapter, we have discussed the effect of the hydrothermal treatment on the solubilization of the elements in the sewage sludge. The application of moderate temperature hydrothermal treatment could be used as a new treatment method of nutrient recycling for sewage sludge. It is observable that the hydrothermal treatment is effective to solubilize sewage sludge and the nutrient components inside it. With different treatment parameters, different kinds of organic and inorganic nutrients are also produced; and organic components will be decomposed into acid first and finally into ammonia and CO_2, 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.

Sewage sludge, as a kind of biomass, contains high nutrient and organic contents.

As it is abandoned by the waste water factory and almost no cost, it is now being applied to the agricultural land in increasing amounts as a kind of fertilizer. Recycling sewage sludge into fertilizer for agricultural purposes may improve soil fertility by influencing the physical, chemical, and biological properties of the land. However, there is concern regarding elevated levels of heavy metals and pathogenic microorganisms, which may result from the use of untreated sewage sludge[1]. If we apply excessive sewage sludge to the soil, it will also introduce heavy metals to the soil. These heavy metals are not biodegradable, and will accumulate in the soil, and are subsequently causing the soil pollution. Therefore, the unprecedented growth of urban population has resulted in a vast buildup of sewage sludge throughout the world, and the improper handling and disposal of this sewage sludge has resulted in a major source of environmental pollution[2]. Effective pretreatment and monitoring by wastewater treatment facilities can ensure the sludge produced is low in potentially toxic contaminants, both organic and inorganic, and high in nutrients and humus, thus rendering sewage sludge an effective and cheap alternative to commercial fertilizer[3].

The traditional method for using the sewage sludge as fertilizer was sewage sludge compost. It is a solid fermentation biotechnology for the treatment of organic solid wastes, which can convert sewage sludge into fertilizer for bioremediation of soil[4]. During the compost process, the sewage sludge was affected under certain conditions by the action of microorganisms, and by degradation, the organic matter become constantly stable, and suitable for the production of a product for land using. And the use of sewage sludge in crop production is ideally favorable for a sustainable society, as it is a soil conditioner, which can recycle a substantial content of nutrients and organic matters[5]. Composting is generally divided into aerobic composting and anaerobic composting, but aerobic composting is more welcomed as compared with the anaerobic composting, because its energy efficiency is high and emits no odors. Composting has two major advantages: on one hand, it can put annoying waste into material easy to handle; on the other hand, it can create a valuable products. However, composting requires special conditions of humidity and ventilation to produce proper temperature. And composting often takes times, which is also facing a number of risks. Many researchers have reported the composting of the sewage sludge. The health and safety issues of using composted sludge have been raised by a number of researchers, since microorganisms inhabit raw and composted materials. The survival and dispersion of enteric bacteria and other potential pathogens have been reported[6-8].

By the hydrothermal treatment technology, as the reaction temperature is very high($\geq$180◦C), almost all of the pathogenic microorganisms will be killed, which resolves the threaten of the pathogenic. The nutrient can dissolve into the liquid product, and its solibilization can also be controlled by changing the reacting parameters. Moreover, most of the heavy metal can retain in the solid product, which means that the liquid product, almost can be seen as a kind of high quality fertilizer. However, the phytotoxic compounds can be present in this liquid product. And according to the research in the previous chapter, we have found that under all of the operating conditions, almost half of the nitrogen in the liquid product is organic nitrogen, and the organic carbon in the liquid product is also very high. Therefore, the liquid has a very high possibility to be used as a kind of organic fertilizer.

Even though the organic fertilizer has many advantages, such as can release nutrients at a slower and more consistent rate, increase physical and biological nutrient storage mechanisms in the soil, mitigate risks of over-fertilization, mobilize existing soil nutrients, help to retain soil moisture, reduce the stress due to temporary moisture stress, improving the soil structureand so on, still, as for liquid organic fertilizer, we have to pay attention to the components of it. There have been problems like the accumulation of NO_3^-in vegetables and increased soil EC concentration in organic farming caused by excessive application of animal manure and organic fertilizer[9][10].As the organic component in the liquid product was from thermo-chemical treatment processs, it is obvious that very complicate action happened during the hydrothermal process, and the products were also different based on the different treatment parameters. Therefore, if the organic component can not be degraded, it still can not be used as fertilizer. The safety of the liquid product generated during the hydrothermal process is also very important challenge as improper treatment leads to the pollution of the environment because it is probably that some of the constituents are toxic and potentially carcinogenic. On the other hand, the organic fertilizer, after being applied into the soil, only by the decomposition of the microorganisms that the organic molecular were broken into small scale nutrients, that it can be taken up by the plant. If it can not be decomposed by the microorganisms, not only still the plant can not use the nutrient, but also may result in the soil pollution. The liquid product from the hydrothermal process, which contains very complicate contents, and also its TOC concentration and EC value were very high, which may affect the plant growth and the environment. Therefore, if used as fertilizer, the liquid product is better diluted to avoid plant damage, but this automatically decreases its nutrient content so that it has to be combined with other fertilizers. Therefore, the evaluation of the liquid product's security is necessary.

The purpose of this study was to evaluate the phytotoxicity of the hydrothermal process liquid product, judging the optimum method of using the liquid product as fertilizer, and also evaluate the biodegradation of the liquid product from the hydrothermal process when was used as a kind of organic liquid fertilizer and evaluate its effect on the soil. In this study, the effects of the operating conditions of the hydrothermal treatment process on the biodegradation of the liquid product from sewage sludge were first investigated. Then, the phytotoxicity of varying degrees of organic matter concentrations were compared by the germination experiment

3.2 Experimental materials and methods

3.2.1 Characteristics of sludge

In this research, the sewage sludge was obtained from a wastewater treatment facility located in Shimane province, Japan. The nutritional value along with other properties of the sludge is provided in Table 3.1 and Table 3.2.

Table 3.1: Characteristics of sewage sludge

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

Table 3.2: Nutrient and heavy metal of sewage sludge

Raw	unit	P	K	S	Na	Mg	Ca	Fe	Al	Mn	Pb	Zn	Cu	Cd
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	−	−

3.2.2 Methods

3.2.2.1 Hydrothermal treatment

The bench-scale hydrothermal reactor with 0.5L capacity was still utilized. The schematic view of the facility is shown in Fig.3.1. The reactor is a batch type (MMJ-500, Japan) which is equipped with an automated stirrer, a pressure sensor and a temperature controller. 60g of sludge (as received base) mixed with 60ml 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 the atmospheric. Then, the reactor was heated to the target temperature (180, 200 and 220 ◦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 60 minutes. Once it 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 minutes）for getting the liquid phase. The liquid phase was filtered through sterile analytical filter units (with a membrane of 0.2μm pore size) and kept at 4 ◦C until analytical measurements.

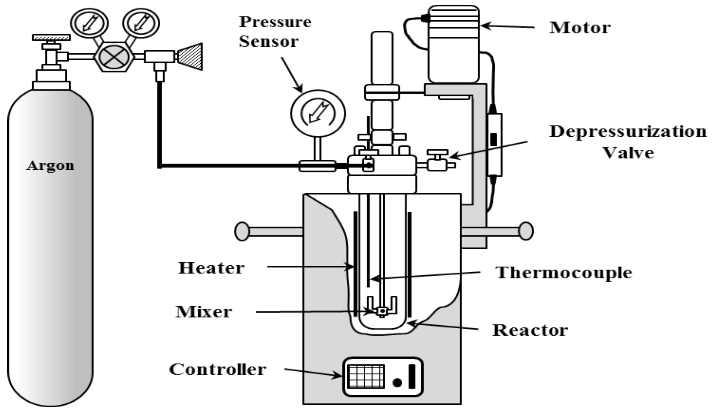


Figure 3.1: Schematic view of small-scale hydrothermal treatment reactor

3.2.2.2 Germination experiment

As the liquid product contains a lot of organic component useful for plants, an attractive application is to use it as a fertilizer; however, if it contains toxicity, it still can not be utilized, therefore, the phytotoxicity test is necessary. A germination experiment was carried out on the liquid product and compared with distilled water[11].Liquid product from different hydrothermal treatment parameters were diluted into different times, based on the TOC concentration and EC value, the detail is shown in Table 3.3. For tests of seed germination and root length measurement, 10 ml of filtrate was pipetted into a plastic sterile petri dish lined with Tanepita(FHK, JAPAN). Fifty Komatsuna (Brassica rapa var. peruviridis) seeds were evenly placed in each dish (three replicates for each sample) and the seeds were incubated at 25◦C in the dark at 75% of humidity. Distilled water was used as the control. Seed germination and root length in each plate were measured after 72 hours. The percentages of the seed germination ratio(SGR),the mean root length (MRL) and the germination index(GI)were calculated by the following formulas[12-14].

$$\mathrm{SGR}(\%) = \frac{Numbers\ of\ seeds\ germinated\ \ in\ the\ liquid\ product}{Number\ \ of\ all\ the\ seeds} \times 100 \quad (3.1)$$

$$MRL = \frac{Sum\ of\ all\ the\ root\ length\ in\ the\ liquid}{Number\ of\ all\ the\ germinated\ seeds} (3.2)$$

$$GI(\%) = \frac{\text{Mean of seed germination number} \times \text{Mean of root length of the treatment}}{\text{Mean of seed germination number} \times \text{Mean of root length of the control}} \times 100 (3.3)$$

Table 3.3: Diluted concentration (based on TOC and EC values)

TOC(ppm)	3500	1500	500	100
EC(ms/cm)	2.5	1.0	0.3	0.06

3.2.2.3 Preparation of inoculums

The inoculum was made from the soil which was taken from Japan university, Fujisawa campus. First of all, the impurities in the soil were removed, and then the pure soil was set into a desiccator whose bottom was set a petri dish filled with water for one week. After that, the dry soil was analyzed, and 10g dry soil was collected. Then the 10 g dry soil was put into 100 ml calcium chloride of 4.0mmoland shake for 30 minutes. After shaking, the mixture was centrifuged with the speed of 3000rpm for 15 minutes. The liquid supernatant was also filtered through a 0.2mm filter paper. Then, the inoculum (microbial extract) was finished.

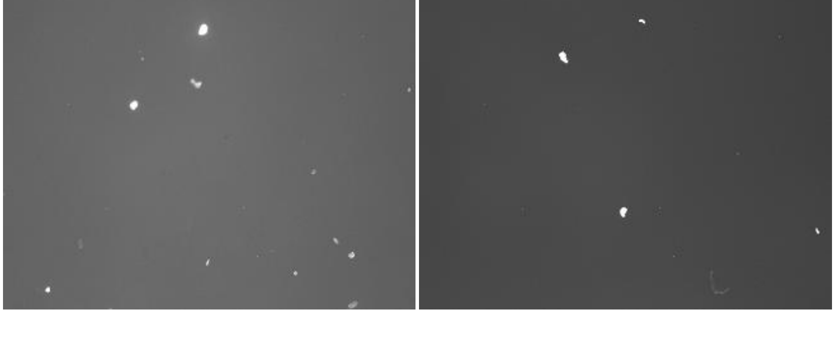
3.2.2.4 Biodegradation experiment

Biodegradation experiment was carried out in a small scale vial. The vial was made by glass, its volume was 123 ml, the height of which was 110 mm and the diameter was 40mm. First of all, 50 mg TOC were injected into the vials. The injected volumes were calculated according to the different TOC concentration of the different liquid products. To avoid the liquid product from staining on the inside wall of the vial that resulting to the errors, for every vial, 0.3g glass wool was also put into the vial as the base of the liquid product. Then the vials were heated in an autoclave for 15 minutes for sterilizing. After that, 0.1 ml inoculum was injected into the vials, and the vials were closed by spigot and sealed by an aluminum seal. These vials were set into the room temperature (25◦C) for 50 days’ cultivating. During the cultivation, a gas chromatography(GC) with thermal conductivity detector(TCD) was used to detect the CO_2 concentration, and the CO_2 concentration inside the vials was calculated. All of the tests were carried out for three times. When testing the CO_2 concentration each time, first of all, the spigot was opened and the air was introduced into the vial for about 1 minute, and the vial was sealed again. Then two days later, the same test was also done.

3.2.2.5 Analysis

The total-C (TC) and the inorganic carbon(IC) in the liquid phase was determined by the total organic carbon analyzer(TOC-5000,SHIMADZU), and the total organic carbon (TOC) was represented by the difference between TC and IC. The content of the organic nitrogen was measured using the Kjeldahl method, and the inorganic nitrogen in the liquid product was determined by using the Bremner's MgO method. The nitrate and nitrite were detected in negligible amount, and therefore omitted in this research. The pH and EC (Electrical Conductivity)values were measured using glass pH and EC electrodes(HORIBA,JAPAN).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 nitrogen (Total-N) contents in the dried plant samples and soil were measured using an automatic high sensitive analyzer (Sumigraph NC-220F, SCAS, Japan). The macro and micro nutrients were analyzed using the same method with the liquid product. Analytical precision was checked against a certified standard material and most samples fell within±10% of the certified value.

Viable cell count was carried out in a petri dish with the diameter of 170 mm. The area of the filter was 226.865mm². As the moisture content was3.794ml in every 10g of soil, 7.5bacteria were observed when the average view field was 10^{-4} m^2, therefore, there were 1701.49 bacteria in the petri dish. Totally, there are 17×10^6 bacteria in the 10g dry soil. Then there were 17×10^4 in 0.1 ml inoculums. The number of the bacteria was detected by a fluorescence microscope, and the result is shown in Fig.3.2.



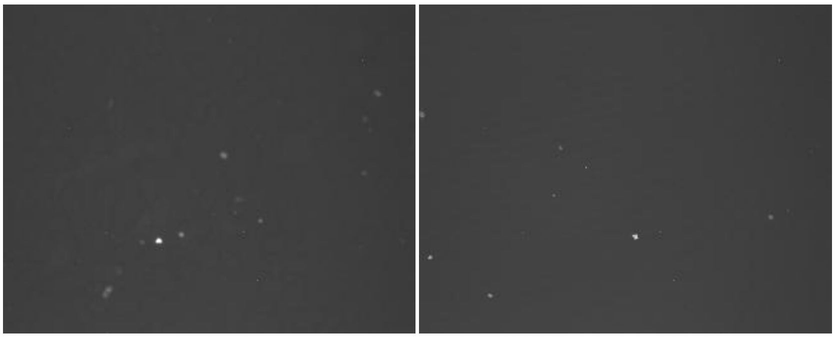


Figure 3.2: The number of the bacteria in a fluorescence microscope

The CO_2 concentration was analyzed by a gas chromatograph manufactured by Shimadzu(GC-8A). During the course of the composting experiment, the CO_2 evolution rate, which is defined as the molar CO_2 evolution per unit day per unit dry solid weight of composting material, and the cumulative emission of carbon was calculated.

Pressure(P):hPa×100=Pa(3.4)
Volume(V):m^3=1×10^{-6}(3.5)
Mole(n):CO_2ml=volume of the vial(ml)×CO_2(ppm)×10^{-6}(3.6)
Temperature(T)=273+Celsius degree(25∘C)(3.7)
Mole number of CO_2=P (pressure)÷V(volume)×n(mole)÷(8.3144×T(temperature)(3.8)
CO_2 weight(mg)=mole number of CO_2×44.01(molar mass) ×1000(3.9)
Carbon weight(mg)=CO_2 weight (mg)COm÷44(3.10)

3.3 Results and discussion

3.3.1 Effects of the hydrothermal treatment on the release of nutrient

In this section, the release of nitrogen(N), phosphorus(P), and potassium(K)were investigated. N, P, and K are the three major macronutrients for fertilizer production. Therefore, the investigation of the effectiveness of the hydrothermal treatment for the dissolutions of the three components to the liquid phase is essential. On the other hand, the organic carbon component, which is solubilized into the liquid product are also detected to evaluate the fertilizer effect. As the pH value and the EC value are also very important indexes for the liquid fertilizer, which will also decide the fertilizer effect, they are also analyzed. The result is presented in Table 3.4 and Table 3.5.

Table 3.4: Basic parameters of the liquid product

Temperature	TOC(ppm)	TN(ppm)	NH_4^+(ppm)	TP(ppm)	TK(ppm)	pH	EC(ms/cm)
180℃	14000	4204	2125	282	656	6.68	6.87
200℃	13500	4483	2392	205	638	5.92	7.32
220℃	10960	4428	2290	126	460	7.29	9.42

Table 3.5: Micronutrient concentrations in the liquid product

Element		180℃	200℃	220℃
Na		25.1	27.7	25.65
Mg		2.06	2.13	2.59
Ca		11.49	12.00	13.47
Fe		100.5	122.5	74
Al	(mg/l)	5.45	6.00	2.49
Pb		0.276	0.224	0.184
S		339	363	328
Zn		_	_	_
Mn		_	_	_

Table 3.4 and Table 3.5 show the effect of the hydrothermal treatment on the nutrient and heavy metal concentrations in the liquid product. In general, the concentration of the total organic carbon is the highest, and the nitrogen concentration also showed very superiority in the liquid product. The nitrogen concentration significantly increased with the temperature increase, while when the temperature was 220◦C, the total nitrogen concentration showed a little decreasing trend, which indicated that for the same treatment time, higher reaction temperature seem to able to transfer more nitrogen content from the solid phase to the liquid phase. But when the temperature was higher than 200◦C, accompanied with the polysaccharide dissolve and solvolysis[15], a certain amount of celluloses, hemicelluloses or lignin in the solid phase also dissolved. Thus the volume of the liquid product increased, which also diluted the nitrogen concentration. Some previous studies also had been demonstrated that for the biomass conversion process in hot-compressed water, the temperature was the most critical parameter for the solubilization[16][17].

The solubilization of phosphorus and potassium showed increase trend by increasing the reaction temperature, but not so obvious, similar to those of nitrogen and carbon. In addition, it is obvious that the concentration of potassium far exceeds the concentration of phosphorus. From the high phosphorus initial content together with the presence of high Fe initial content, it can be inferred that phosphorus was added as flocculants to the sludge, and was mainly in the form of insoluble $FePO_4$ precipitate. 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. The concentrations of the micronutrients and heavy metals showed very low levels entirely. So, even though the liquid product contains many kinds of elements, including heavy metals, their concentrations are too low to cause harmful effect to the plant. Also, it is well studied that the main composition of sewage sludge is complex organic compounds, and Barlindhaug and Odegaard[18] 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. This also explained why the liquid product showed different pH values by changing the hydrothermal reaction temperature. The concentrations of N, P and K were around 4000 ppm, 200 ppm and 600 ppm, respectively. The nitrogen concentration was similar to the commercial fertilizers, while the concentrations of P and K were much lower. However, the concentrations of heavy metals were lower than commercial fertilizer, and after dilution, it can be inferred that the concentration will become more lower, which showed more safety to the plant. Particularly, As, Cd, Cu and Ni were not detected, and the concentration of Pb component was also very low. The ratio of NH_4^+also showed that only about half of the nitrogen content is small molecule nitrogen which can be absorbed easily by the plant. However, the huge amount of organic nitrogen also showed a new possibility of use of the liquid product as organic fertilizer.

3.3.2 Germination experiment of the liquid product

Figures 3.3and 3.4 showed the germination experiment based on the EC concentration and TOC concentration. As the color of the original liquid product was brown, from these figures we can see that, with adding more water, the color became lighter and lighter. And also, we can see the concentration change clearly by judging the liquid color. Wherever, for the same EC value, it is also shown that the higher the reaction temperature was, the lighter the color was, which also showed different reaction during different treatment, and the product showed different properties too. Even though the liquid was diluted to 2.5ms/cm, the color was still dense. Only be diluted for more than 30 times that the color can not be recognized.

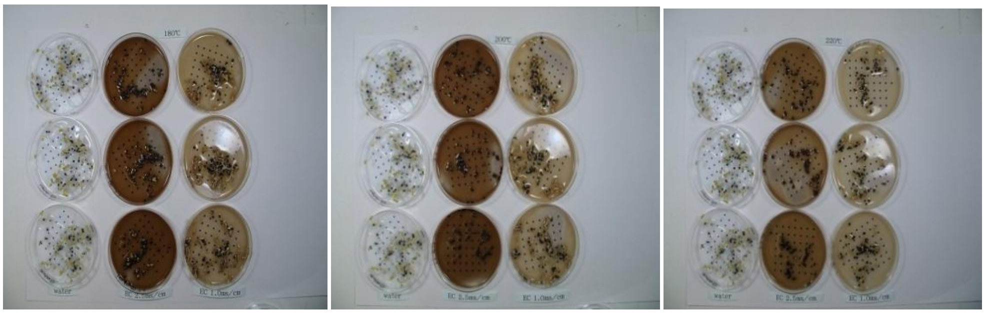


Figure 3.3: The germination experiment based on the EC concentration

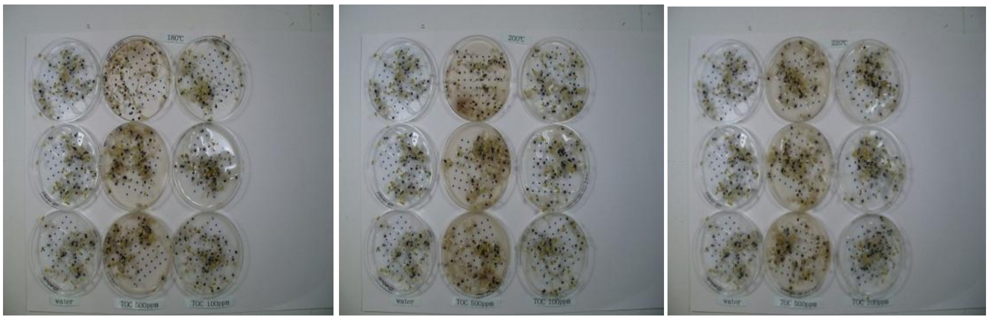


Figure 3.4: The germination experiment based on the TOC concentration

Figure 3.5 shows the germination ratio and Figure 3.6 shows the root length depending on the different TOC concentration and EC value, and Figure 3.7 shows the GI calculation result. Generally speaking, both of the germination ratio and the root length tended to increase with increased dilution. The germination ratio in the distilled water is 98% and most of all the seeds germinated. In regards to the germination ratio, it showed that the lower the EC value is, the higher the germination ratio is. When the EC value was 2.5 ms/cm, all of the seeds could not germinate. When it is diluted to 1.0 ms/cm, under all of the reaction temperature, about half of the seeds geminated. In the 180◦C and 200◦C group, the germination ratios were 61% and 59%, and in the 220◦C group it was 48%, which showed that even if the EC values were the same, the germination ratio were still not the same. Because the EC value increased with the increase of the reaction temperature, it is obvious that the reaction temperature also determined the components inside the liquid product, which also caused the different germination ratio. A relatively higher reaction temperature will cause more complex chemical reactions and more ion dissolutions, and these dissolved ions are that we did not measure because the composition of the sludge itself is very complex. When the EC value was diluted to 0.3ms/cm, all of the germination ratios increased to about 90%.When the liquid product was diluted to lower than 0.1ms/cm, there is no obvious difference between all of the three kinds of liquid product. And we can also see that the liquid produced obtained at the temperature of 220◦C showed more harmful effect than those obtained at 180◦C and 200◦C. On the other hand, the TOC value also decreased with the dilution of the liquid product, so at the same time, we can also see that too high TOC concentration is harmful to the seed germination.

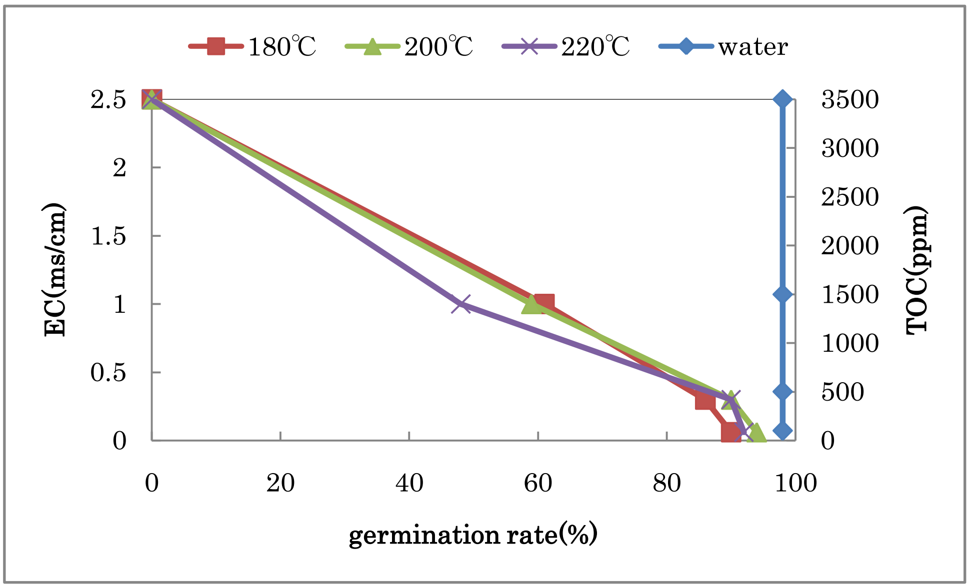


Figure 3.5: The effect of TOC and EC on the germination ratio

The root length also indicated the effect of the liquid product on the plant growth. Similar with the germination ratio, the root length also increased with the dilution. Particularly, when the TOC concentration was 500 ppm, nearly all of the average root lengths were the same. When it is diluted to lower than 750 ppm, the three kinds of liquid products showed almost the same effect on the root length. The average root length of the distilled water group was 28 mm, from the figure still we can see that higher EC value or TOC concentration were harmful to the root length, but when the TOC concentration was diluted to lower than 100 ppm, the liquid product showed promotion effect on the root growth than the distilled water, which means that the micronutrient may improve the growth of the root. Especially, the 200◦C, TOC concentration 100 ppm group showed more obvious promotion effect than the others.

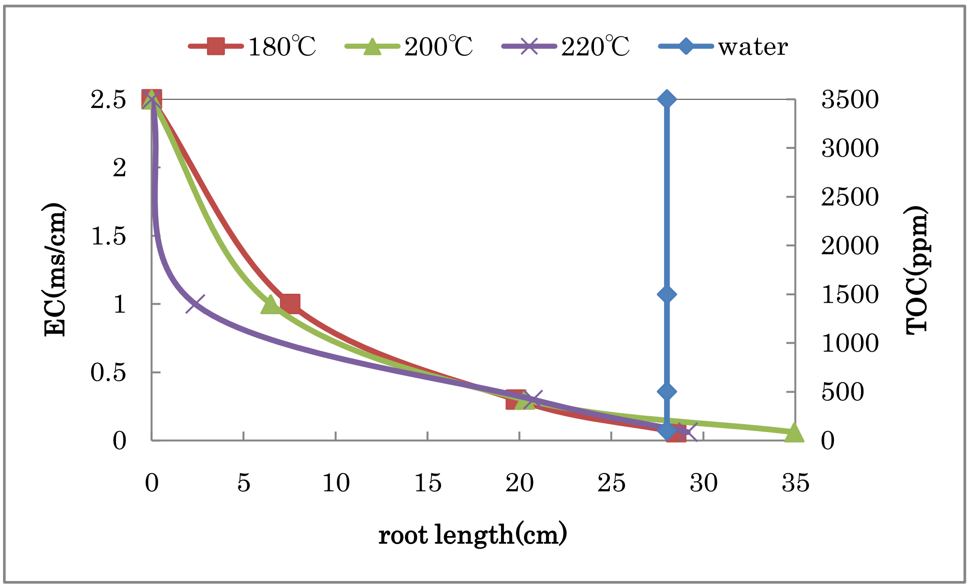


Figure 3.6: The effect of TOC and EC on the root length

The concentrations of heavy metals in the liquid products were almost 0, thus it was feasible and safe for the application. GI analysis was carried out to study the phytotoxicity on seed germination of different dilutions of the liquid product and the results are given in Fig.3.7. For all of the liquid products, the GI value increased with the increasing dilution rate, and for the 200◦C group, when the EC value was 0.06 ms/cm, it reached about120%. Phytotoxicity is the degree to which a chemicalor compound is toxic to the plants. A GI over 50% has been considered to be phytotoxin-free[12]. According to this GI criterion, the liquid product required an at least more than 20 times dilution to reach stabilization of nutrients.

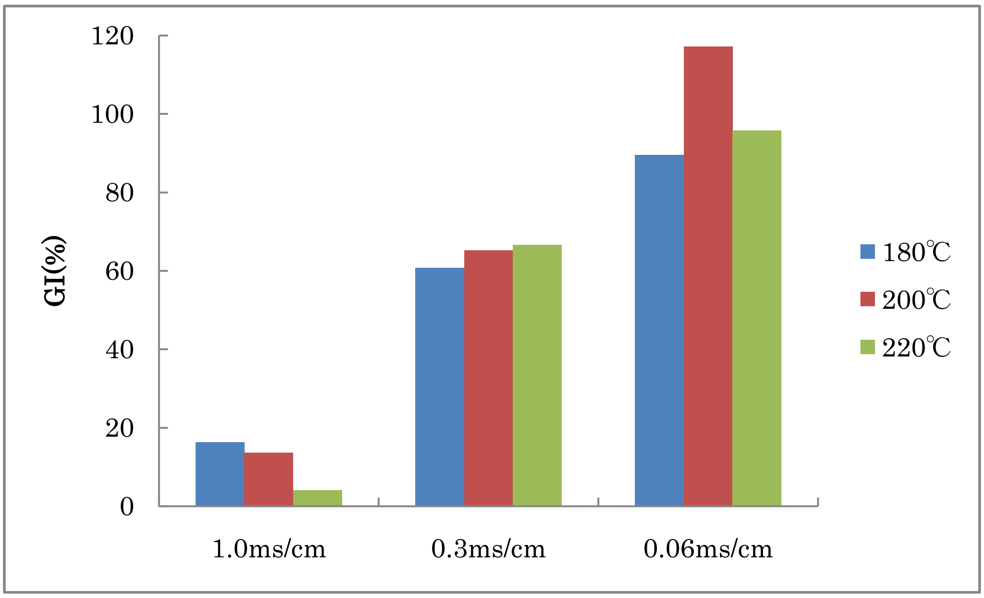


Figure 3.7: The effect of TOC and EC on the root length

The low germination ratio indicated an adverse effect on root growth of Komatsuna, which is possibly due to the high concentrations of TOC and high EC value[19][20] that are known to impact the plant[21]. According to this germination experiment criterion, the liquid product required more than 10 times dilution to reach stabilization of the organic matter to decrease the harmful effect on the plant. At 30 times dilution, the germination ratio was found to be over 80%. On the other hand, the 200◦C group phenomenon indicated that proper low nutrient and organic acid concentrations will promote the root growth. So, if being used as liquid fertilizer, the liquid dilution times and the components concentration modulation are also very important.

It has been reported that protein, carbohydrate and lipid are the main constituents of domestic sludge[22]. Sewage sludge was reported to be used as the protein source, because its main constituents are protein and carbohydrate[23]. In this research, the nitrogen concentration of the raw sample is 7.2%, thus, protein was the largest constituent of the sewage sludge. During the hydrothermal process, the concentrations of the protein and carbohydrate in the liquid phase fluctuated with the increase of the reaction temperature. The reason was that soluble protein and carbohydrate were the result of a net balance between competing rates of release and degradation. With the increase of the reaction temperature, the degradation rate exceeded the release, and the concentration was observed to decrease[23]. The technology of using sewage sludge as resource for extracting the bacteria proteins, and then using chemical methods for generating the AACTE fertilizer was also investigated[24]. During anaerobic bio-digestion or thermal processes, propionic acid, formic acid, acetic acid, and other kinds of volatile acids can also be produced[25]. Therefore, in this research, as the reaction happened, the protein and carbohydrate components also dissolved into the liquid product. With increasing the reaction temperature and the holding time, the hydrolysis reaction happened, which caused the change of the composition and the pH value. During the reaction, with the hydrolysis of the protein, more amino acid was produced, which lead the pH value of the liquid product becomes lower. But it is obvious that a higher temperature also caused a further degradation of the amino acid, which resulted in the pH value increasing and the higher ammonium concentration. It is well known that amino acid can promote the plant growth. In this experiment, it is obvious that this amino acid could also promote the root growth. It has been reported that humic acids increase the number of roots thereby stimulating nutrient uptake and plant development[26].

3.3.3 Biodegradation experiment of the liquid product

CO_2 is the main product generated when the organic component is completely degraded in the biodegradation processes. Therefore, the rate of CO_2 production, which is also called as the respiration rate, was measured as an indicator for biodegradation. Typically, the container was opened once daily for reaeration and to measure the evolved CO_2, as described previously. The effect of different operational parameters on the decomposition of organic component in the hydrothermal process liquid was quantitatively examined. The final values of the cumulated CO_2 ratio and the rate of CO_2 production during the biodegradation experiment with various reaction temperatures and holding times are shown in Fig. 3.8- Fig.3.10.

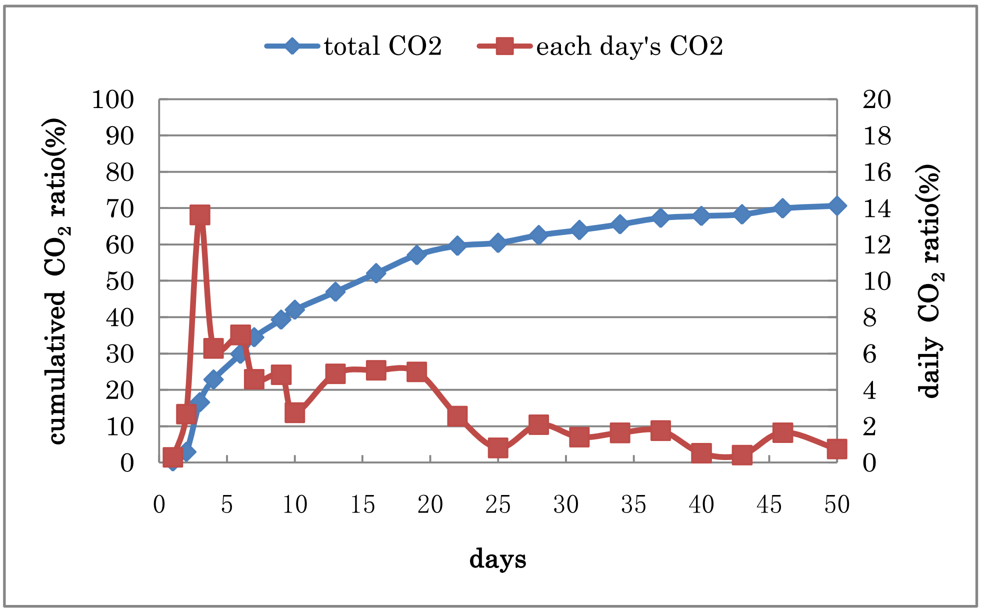


Figure 3.8: Biodegradation with the reaction temperature of 180℃

During the biodegradation proceed, different treatment parameters showed obvious differences. In the case of 180◦C, in the first week, the liquid product showed very good biodegradation. From the very beginning, it can be degraded very well, especially when it reached the third day, the rate of CO_2 production reached about 14%, which means about 14% total carbon in the liquid product was degraded by the microorganisms in the inoculums. And from the fourth day, it kept a rate of about 5% each day's biodegradation rate until the 20th day. We can clearly see that during the first 3 weeks, about 60% of the organic carbon was decomposed. Then the biodegradation rate became lower than before, which turned to lower than 2% each two days. Until the 50th day, about 70% organic carbon was decomposed by the microorganisms in the inoculums. Generally speaking, the biodegradation can be separated into two stages, the first stage was in the first 3 weeks, when it showed very good microbial activity and biodegradation efficiency; and the second stage was after the third week, the biodegradation efficiency decreased quickly and the cumulative emission of CO_2 was also less than 10%.

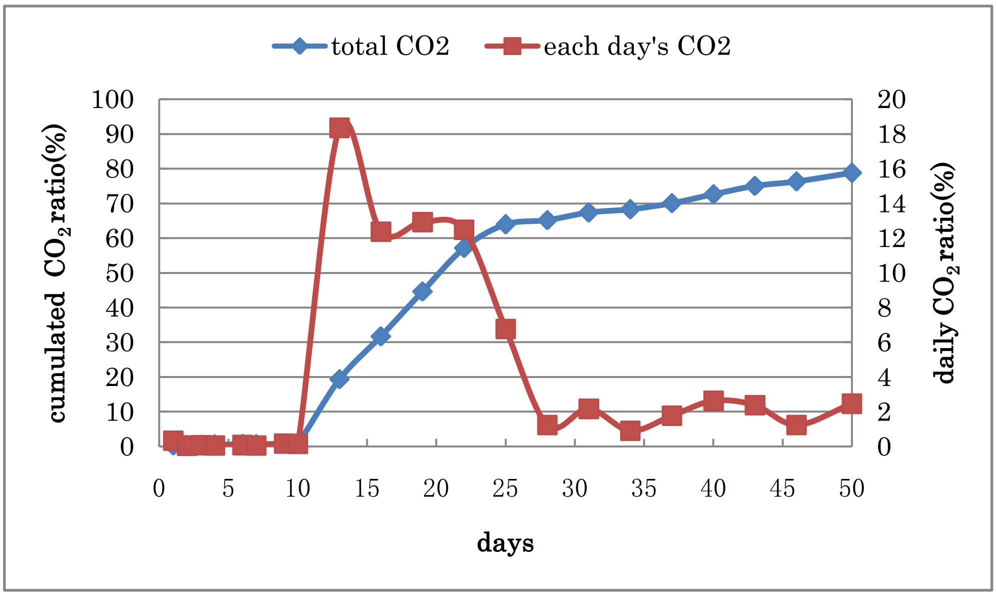


Figure 3.9: Biodegradation with the reaction temperature of 200℃

In the case of 200◦C, it showed obvious difference with the case of 180◦C. In the first 2 weeks, the curve is almost a straight line, parallel with the lateral axis. It means during these ten days time, the microbial activity was very low, and almost no CO_2 was produced. While when it turned to the 12^{th} day, the CO_2 production showed a retaliatory rebound, which reached about 18% each day. And in the following 10 days, it kept the high biodegradation rate of about 13% each day. When it reached the 25^{th} day, about 67% of the organic carbon was decomposed. Since that, similar with the case of 180◦C, the biodegradation rate decreased to about 3% each two days. Then until the 50^{th} day, about 80% organic carbon was decomposed by the microorganisms in the inoculums. From Fig.3.8 we can see an obvious lag phase duration. The lag phase duration means the time where the degradation by microorganism was slow. Comparing with the case of 180◦C, there is a ten days lag phase duration. And almost 80% of the decomposed carbon was released in 12 days. In this case, the biodegradation can be separated into three stages, the first stage was in the first 2 weeks, when it showed almost no biodegradation efficiency; since the 12^{th} day, very good microbial activity and biodegradation efficiency were shown by the huge amount of CO_2 production; and the third stage was after the 25^{th} day, the biodegradation efficiency decreased quickly and the cumulated CO_2 ratio was about 13%.

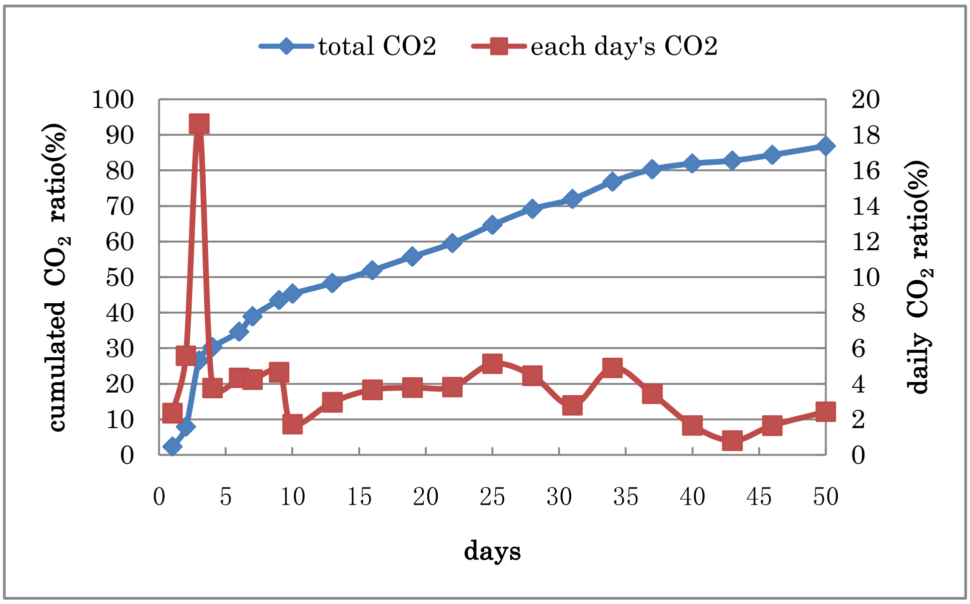


Figure 3.10: Biodegradation with the reaction temperature of 220℃

In the case of 220◦C, significant differences from the case of 180◦C and 200◦Cwere observed. Similar with the case of 180◦C, in the first week, the liquid product showed very good biodegradation. In the third day, the rate of CO_2 production reached about 18%. After the daily respiration values peaked approximately at the third day, it decreased rapidly, reached about 5% each two days. While the microbial cultures degraded the organic carbon for a longer time period, resulting in a higher cumulative CO_2 production with the others by the end of the 50^{th} day, was about 90%. It seems that it is so difficult to separate the biodegradation stage, as after the third day, the biodegradation rate became almost the same.

Comparing the three figures it can be seen that all of the cumulated CO_2 value of the liquid product were very high, showing that a large amount of easily degradable organic matter was present in the liquid product, since the easily degradable fractions would be consumed during the biodegradation process. While comparing the biodegradation rate, large differences were observed. The large difference in the degradation rate can be partially explained by the chemical structure differences between the liquid products obtained with different hydrothermal operating parameters. We can see that the higher the temperature was, the easier the degradation was, and consequently showed a larger cumulative CO_2 production. In most cases, cumulative CO_2 production and the daily respiration peaks were highest and earliest when inoculum of microbes that were already adapted to the respective contaminant were added[26]. Therefore, we can infer that the liquid product from hydrothermal treatment process can be easily decomposed by the microorganisms in the common soil, which also means the microbes in the nature can adapted to the liquid products very well, especially in the case of 180◦C and 220◦C. In the case of 200◦C, a ten days' lag duration appeared, which mostly probably due to the pH value change. From Table 3.4, we can see that the pH of the liquid product was lower than 6, showing faint acidic. We have discussed that during the hydrothermal process, together with the increase of the reaction temperature, the big molecular component, just like protein, was decomposed into organic acid firstly, and then amino acid, finally decomposed into ammonia, water and CO_2. The 200◦C case proved that it was the amino acid duration, when huge amount of organic acid not only reduced the pH value of the liquid, but also inhibit the microbial activity. After about ten days lag duration, with the degradation of the amino acid itself and the increasing of the microorganisms, the microorganisms also adopted to the new environment, then the retaliatory rebound happened. However, in either case, more than 60% organic component could be decomposed in about 25 days. So, when it is applied into the soil, even if it could not be utilized by the plant, the microorganisms still can decompose it, which could prevent the accumulation of the organic component in the soil, shows a security to the soil.

3.4 Conclusions

In this chapter, the characteristics of the component in the liquid product were investigated. The organic component concentration was very high, and huge amount of nitrogen was dissolved into the liquid product, and about half of the nitrogen was inorganic nitrogen. The potassium solubilization was high but the concentration in the liquid product was low. Even though a certain amount of heavy metals were also dissolved into the liquid phase, the concentrations were too low to result in harmful influence. The germination experiment was conducted for testing the phytotoxicity of the liquid product, and the effects of the TOC concentration and the EC value on the seed germination were investigated. The result showed that the high TOC and EC values were harmful to the plant, but if the liquid product was diluted to the appropriate times, the germination will increase to the common level, therefore, no obvious phytotoxicity was found. The organic acid, which was produced during the hydrothermal process, can promote the growth of the plant root.

The biodegradation of the products obtained with different operation parameters were compared. All of the products proved the characteristic that can be biodegraded and also provided with environmentally friendly option. All of the products can be biodegraded by more than 70% in 50 days. The 200◦C liquid product degradation showed the longest lag phases, but reached higher mineralization levels at the end of the experiment. The hydrothermal treatment can remove the nutrient from the solid phase to the liquid phase, and compositions of the products were different due to the different operation parameters. The biodegradation rate increased together with the treatment temperature, mainly because of the different chemical structure of the component in the liquid product.

The liquid product obtained from the hydrothermal treatment showed abundant nutrient content and excellent biodegradation, showing a new evident and possibility for using as a kind of liquid fertilizer. By proper diluting, the liquid product can be used directly to the seed without any pretreatment or agent, and not only can promote the root growth, but also will not cause soil pollution.

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4 EFFECTS OF LIQUID FERTILIZER PRODUCED FROM SEWAGE SLUDGE BY THE HYDROTHERMAL PROCESS ON THE GROWTH OF KOMATSUNA

Abstract

In this chapter, to test the fertilizer effect of the liquid product, the plant growth experiment was carried out in a glass house. This experiment lasted for about 7 weeks, under the natural light and the controlled temperature and moisture. Komatsuna was planted on two kinds of different soil collected from different places, and the fertilizer applications were also different. After harvesting, the yield of Komatsuna, the basic growth parameters, and the ratio of the nutrient uptakes were determined. By analyzing these parameters, the effect of the liquid product on the Komatsuna growth was discussed. The result showed that the liquid product can promote the growth of plant effectively, the uptake of nitrogen depend on the liquid application. The uptakes of potassium and phosphorus are low, showing no obvious difference from the chemical fertilizer. The liquid product can be used as a fertilizer, and considering the different requirement of nutrient by different kinds of plants, the addition of appropriate amount of chemical fertilizer is recommended.

4.1 Introduction

Excess use of chemical fertilizers will greatly reduce the content of organic matter in soils, which directly produces impact on physical, chemical and biological properties and results in risks of degradation of soil[1]. Therefore, organic fertilizer is necessary for agriculture production. Sewage sludge is often used as fertilizer after compost. As a kind of biomass originate organic fertilizer, it has many advantages, such as providing a whole array of nutrients for soil [2-6], preventing soil erosion, increasing beneficial soil organisms, reducing the need for fertilizers and pesticides, improving physical and biological properties of soil, and keeping organic wastes out of landfills and so on. So, it can promote biomass production and quality of crops. However, comparing with the chemical fertilizer, composts' nutrients level is lower, and heavy metals accumulation in the plants also becomes problem. Moreover, the heavy metals can be washed into aquifers and may result in risks to crop seed germination, food safety, and so on[7].

On the other hand, in recent years, the liquid fertilizer is gaining attention year by year. Compared with the solid fertilizer, liquid fertilizer showed more advantages. First of all, it can be mixed more regularly. Compared with the solid fertilizer, liquid fertilizer can be mixed with various fertilizer, pesticide, herbicide and pesticides. If we take any drop of the solution, it will contain all the effective consistent. Since the consistency of the solution, as long as one parameter is measured, the other parameters can be quickly identified. Second, its recipe is very easy to adjust, which showed easier precisive fertilization. For different soils and crops, the special preparations of fertilizer are often needed. To produce a unique formula of solid fertilizers is much more complicated than the production of liquid fertilizer process. If we want to add trace elements, small amount of trace elements was added into a certain volume of the solid fertilizer first, and then mixed with general fertilizer. But in the case of liquid fertilizer, just add the trace elements and stir are enough. And the organic fertilizer combined with chemical fertilizer is an important approach to maintain and improve the soil fertility, and increase the fertilizer use efficiency[8]. Third, it is very easy to add other agrochemicals. Usually, the amount of insecticide and fungicide are very little. To mix a small amount of them in a large amount of fertilizer, it is obvious that liquid fertilizer is easier to do it than the solid fertilizer as it is difficult to achieve uniform mixing in the solid fertilizer. Liquid fertilizers can be seen as very good carrier of herbicides, insecticides, fungicides, plant growth regulators, rare earth and some natural active substances such as fulvic acids, amino acids and so on. If these substances are administered together, not only can save time and labor, but also can realize the versatility of liquid fertilizer. And finally, liquid fertilizer production showed low cost and low energy consumption, the production process without any emission. Therefore, in many foreign countries, liquid fertilizer factories are built in the farm or near the cropland.

In view of the above advantages, liquid fertilizer was rapidly developed in some high labor cost countries. In U.S, the liquid fertilizer takes 55% of the total fertilizer, liquid fertilizer factories are more than 2800. France, Romania, Spain, United Kingdom, Australia, Canada, the Netherlands, Denmark, Norway, Israel, New Zealand, Mexico, Colombia and other countries are large-scale application of liquid fertilizer countries. In Israel, more than 90% crops are using liquid fertilizer through irrigation systems.

In the previous chapters, we had found that the nutrient components in the sewage sludge, can be removed into the liquid phase by the hydrothermal treatment, where the quantity depends on the operating parameters. Even though a certain amount of harmful heavy metal can also be removed into the liquid product, the amounts are very low, and we can also control the movement of some kinds of heavy metals by changing the holding time. Therefore, the liquid product from the hydrothermal treatment can be used as a kind of liquid fertilizer. However, as the TOC and nitrogen concentration in the liquid product are very high, and the EC value are also very high, if be used directly, it will cause harmful effect to the root, so when be used, the liquid should be diluted. On the other hand, we have found that about half of the nitrogen in the liquid is ammonia nitrogen, which can be used direct by the plants, while the other organic nitrogen in the liquid product, if can be used or not is still need to be investigated. Also, a certain amount of potassium and phosphorus are also dissolved into the liquid product, even though the solubilization of the potassium looks as high as about 70%, due to the low original concentration in the sewage sludge, and the low solubilization of phosphorus, actually the concentrations of these two kinds of nutrients are very low. As everyone knows that the quantities of the potassium and phosphorus also decided the yield of the plants, if it is necessary to solve the problem and how to solve the problem need to be investigated.

Many researchers had investigated the effects of the compost product for different plants growth [9][10], and the possibility of reutilization of biodegraded wastes as liquid fertilizers[11], but no one had detected the effect of the hydrothermal process liquid to the plant. Therefore, the aim of this chapter is to investigate the effects of the hydrothermal process liquid product on the growth of Komatsuna. This chapter will investigate on the characteristics of nutrient uptake and nitrogen use efficiency under application of the hydrothermal process liquid by Komatsuna growth experiment. Two kinds of different plant growth experiments was carried out, the application of liquid product on the alluvial soil and loam soil were investigated to clearly distinguish the relationship between the degree of plant growth and liquid product application. These results would provide a theoretical basis for the sustainable utilization of the liquid product as fertilizer.

4.2 Experimental materials and methods

4.2.1 Hydrothermal treatment

In this experiment, the bench-scale hydrothermal reactor with 0.5L capacity was utilized. The reactor is a batch type (MMJ-500, Japan) which is equipped with an automated stirrer, a pressure sensor and a temperature controller. 100g of sludge (as received base) mixed with 100ml 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. The initial pressure inside was set to near the atmospheric. Then, the reactor was heated to the target temperature (180, 200 and 220 ◦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 60 minutes. Once it 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 minutes）for getting the liquid phase. The liquid phase was filtered through sterile analytical filter units (with a membrane of 0.2μm pore size) and kept at 4 ◦C until analytical measurements. As for plant growth experiment, because large amount of liquid product is necessary, the quantity of the raw material was increased, but the ratio of sludge to water was not changed, and the hydrothermal experiment was done for many times. Then the liquid product under the same parameters was mixed together as the feedstock for the plant growth experiments.

4.2.2 Plant growth experiment

Nitrogen component is the hugest nutrient component in the liquid product, and half of the nitrogen is organic nitrogen, so the liquid product is inferred that can be used as a kind of organic nitrogen fertilizer. Therefore, the nitrogen effect on the plant can also be seen as the most important parameter to evaluate the fertilizer value of the liquid product. Komatsuna is a kind of plant which is similar with cress, sensitive to nitrogen treatment and very easy to cultivate in the laboratory. In this experiment, Komatuna was used for evaluate the fertilizer effect of the liquid product. As different fertilizer applications will also affect the growth of Komatsuna, the experiment was set into different groups with different fertilizer quantity to investigate the optimum application.

4.2.2.1 Plant growth experiment in alluvial soil

In this experiment, the alluvial soil was taken from Hiratsuka city, Japan, and was sieved through a 2mm sieve before using. Alluvium soil is loose, unconsolidated soil or sediments, which has been eroded, reshaped by water in some form, and redeposited in a non-marine setting. Alluvium soil is typically made up of a variety of materials, including fine particles of silt and clay and larger particles of sand and gravel. In this experiment, after screen, the main component is clay. And it almost contains no nutrient. Its maximum moisture, water-holding capacity (based on 1000g dry weight of soil), pH (1:2.5, H_2O), EC (Electrical Conductivity) (1:5, H_2O) were 8.76%, 396g, 6.75 and 0.08ms/cm, respectively. The nitrogen content is almost 0 in the soil. Therefore, this kind of soil can be seen as an ideal soil for investigating the nutrient uptakes. To prevent wash-away of the growth test nutrients, the growth of Komatsuna was carried out in Neubauer pots, and by the addition of water to maintain the moisture content of the pots. The quantity of the water added to the plant was 50% to 60% of the maximum water-holding volume. In this experiment, 400g soil was prepared and different volume of the liquid product were mixed with soil and put into Neubauer pots. Every pot was added total nitrogen, total phosphorus, and total potassium as 100mg respectively, which is the best proportion and quantity of fertilizer for planting Komatsuna in the Neubauer pots. The three kinds of nutrients were obtained from the liquid product by the hydrothermal treatment, the applied volume was calculated depending on the nutrient concentration. As the phosphorus and potassium concentrations in the liquid product were very low, to avoid the effect by different phosphorus and potassium level, calcium superphosphate and potassium chloride were also used for additional supply.

Also, to evaluate the organic nitrogen component fertility, the nitrogen applications were also divided into 1 time, 2 times and 4 times groups. In the 1 time group, only 25 mg nitrogen was from the liquid product, the other 75 mg was added by ammonium sulfate. In the case of the 2 times group, 50mg nitrogen component was from the liquid product, and in the case of 4 times group, all the nitrogen component was from the liquid product. All the experiments were triplicated. Twenty seeds of Komatsuna were sown in each pot and allowed to germinate and grow under the natural sunlight in a glasshouse and at a controlled temperature of 25±3°C. Fifty days after sowing, the length of the stem and the width of the leaf were measured for every pot, then the tops of plants were harvested and their fresh weights were measured. The weight of the roots was ignored because it was negligibly small compared with the tops. And then the plants were dried at 60°C to a constant weight. For comparison, experiment as controls was also conducted, all of the fertilizer added was chemical fertilizer, containing calcium superphosphate, ammonium sulfate and potassium chloride, respectively. Finally, the nutrient quantity in the dry plant and soil were also analyzed, and the nutrient distribution was evaluated. The nutrient arrangement is shown in Table 4.1.

Table 4.1: The nutrient arrangement of the plant growth experiment with chemical fertilizer

Liquid product		Added component(mg/pot)			
		volume(ml)	TN	TP	TK
basic as control		------------	100	100	100
180℃	1 time	5.95	25+75	1.68+98.32	3.9+96.1
	2 time	11.9	50+50	3.35+96.75	7.8+92.2
	4 time	23.8	100+0	6.71+93.29	15.6+84.4
200℃	1 time	5.58	100	1.14+98.86	3.55+96.45
	2 time	11.15	25+75	2.28+97.71	7.12+92.88
	4 time	22.31	50+50	4.57+95.43	14.23+85.77
220℃	1 time	5.65	100	0.71+99.29	2.6+97.4
	2 time	11.29	25+75	1.42+98.58	5.2+94.8
	4 time	22.58	50+50	2.85+97.15	10.4+89.6

4.2.2.2 Plant growth experiment in volcanic soil

For testing the fertility of the liquid product in the common soil, the experiment using volcanic soil was also carried out. The soil used in this experiment was taken from Japan University, Fujizawa city, Japan, which is a kind of volcanic soil. Volcanic soil is formed from volcanic ash and cinder deposits. It largely consists of non-crystalline minerals, such as allophone and imogolite, which can form strong bonds with organic matter. As a result, organic matter generally accumulates in the volcanic soil. In addition to organic matter, volcanic soils may also contain high amounts of volcanic glass material with the possibility of amorphous iron and aluminum minerals. Therefore, volcanic soil is typically very fertile soils. In this experiment, its maximum moisture, water-holding capacity (based on 1000g dry weight of soil), pH (1:2.5, H_2O), EC (Electrical Conductivity)(1:5, H_2O) were 74.8%, 427g, 6.7 and 44.39ms/cm, respectively. The nitrogen content is 0.7829%. In this kind of volcanic soil, there are a lot of micronutrient, and as in the past 3 years the sample area was used as cultivation land, its phosphorus content is very high, which is about 726mg/kg. Same as the experiment in alluvial soil, the growth experiment of Komatsuna was also carried out in Neubauer pots, and by the addition of water to maintain the moisture content of the pots. The quantity of the water added to the plant was 50% to 60% of the maximum water-holding volume. 400g soil was also prepared and different volume of the liquid product were mixed with soil and put into Neubauer pots. The total nitrogen contents were separated to 25mg, 50 mg and 100mg respectively, and all of them were from the liquid product. The applied volume was calculated depending on the nutrient concentration. In the 1 time group, only 25 mg nitrogen from the liquid product was added. In the case of the 2 times group, 50mg nitrogen component from the liquid product was added, and in the case of 4 times group, 100mg nitrogen component from the liquid product was added. No chemical fertilizer was added. All the experiments were triplicated. The experiment process was the same as the experiment in alluvial soil. For comparison, experiment as controls was also carried out. In this experiment, the controls with nothing added (blank), the controls with only chemical fertilizer(basic), the controls with only nitrogen fertilizer(N) were carried out respectively. Finally, the nutrient quantity in the dry plant and soil were also analyzed, and the nutrient concentrations were evaluated. The nutrient arrangement is shown in Table 4.2.

Table 4.2: The nutrient arrangement of the plant growth experiment without adding chemical fertilizer

Liquid product		Added component(mg/pot)			
		volum(ml)	TN	TP	TK
basic		------------	100	100	100
blank		------------	0	0	0
nitrogen		------------	100	0	0
180℃	1 time	calculation	25	0	0
200℃	2 time		50	0	0
220℃	4 time		100	0	0

4.2.3 Analysis

The total-C (TC) and the inorganic carbon(IC) in the 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 content of the organic nitrogen was measured using the Kjeldahl method, and inorganic nitrogen in the liquid product was determined by using the Bremner's MgO method. The nitrate and nitrite were detected in negligible amount, and therefore omitted in this research. The pH and EC (Electrical Conductivity)values were measured using glass pH and EC electrodes(HORIBA, JAPAN).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 nitrogen (Total-N) contents in the dried plant samples and soil were measured using an automatic high sensitive analyzer (Sumigraph NC-220F, SCAS, Japan). The macro and micro nutrients were analyzed using the same method with the liquid product. Analytical precision was checked against a certified standard material and the most samples fell within±10% of the certified value.

4.3 Results and discussion

4.3.1 Nitrogen uptakes in the alluvial soil

Since the growth of plants and their quality are mainly a function of the quantity of fertilizer, to improve the utilization of the fertilizer nutrients is also very important. Organic matter affects crop growth and yield directly by supplying nutrient[12], and also can apply a delayed nutrient release. Combined use of organic and inorganic sources of nutrients is essential to augment the efficiency of nutrients[13]. In this section, the yield change of the plant with the different fertilizer application was discussed and the uptakes of the three primary nutrients, N, P, and K were also analyzed and compared with chemical fertilizers. Figure 4.1 showed the condition of the plant growth experiment.

Figure 4.1: The plant growth experiment

Figure 4.2 showed the fresh weight of the plant after the harvest. The control group was added with chemical fertilizer, the others were added with the mixture of both liquid product and chemical fertilizer. We can see clearly that for every pot, the fresh weight of the plant showed difference even though it is not so obvious. The control group showed the average plant weight of about 33.2g/pot, which means the common chemical fertilizer can result in such a yield. For the 180°C groups, different liquid product ratio were applied, and showed different fertilizer effect. When it was used as 1 time, which means only a quarter of the added fertilizer was the liquid product from the hydrothermal treatment, the fresh weight of the plant was lower than the control group. When it turned to the 180°C, 2 times group, the fresh weight showed almost the same value with the control group. And when we added the liquid product as 4 times, which means all of the nitrogen component was from the liquid product and no chemical fertilizer was added, it also showed a lower yield than the control group. In the case of 200°C group, we can also see the similar trend of the yield, the 2 times group still showed superiority than the other times. The 220°C groups also showed the similar trend with the other groups, even though in this case, 4 times group showed the lowest yield. In the case of different treatment temperatures, the same liquid product application time also showed similar yield, the difference was not so obvious. The 200°C, 2 time group showed the best yield in all the groups, and comparing with the control group, it showed almost the same yield.

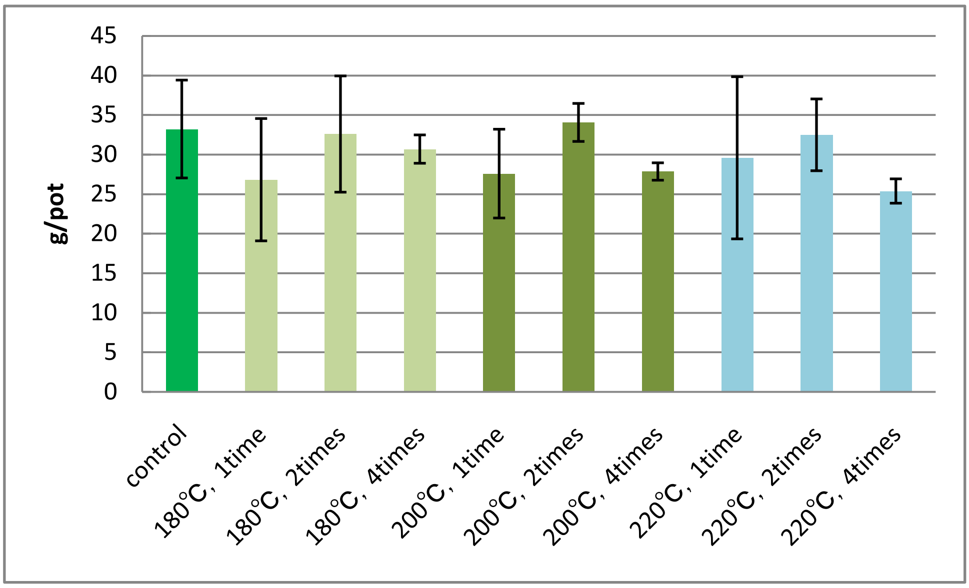

Figure 4.2: Fresh weight of the plant

For the same amount of fertilizer application, the plant showed different yields. That’s because the plant growth experiment was carried out in the Neubauer pot, which can prevent wash-away of the nutrient, but cannot prevent the nutrient loss from volatilization. Therefore, the nutrient uptakes were also analyzed. The nutrient uptakes were shown in Figures4.3 to 4.5.

Figure 4.3 showed the nitrogen uptakes. The control group showed that only about 60% of the nitrogen could be absorbed by the plant and the other 20% still remained in the soil, and about 20% was lost. As the nitrogen added into the control group was ammonium sulfate, which was a chemical fertilizer that can be took up easily by the plant, a certain amount of the ammonia, after the application, will also volatilized into the environment.

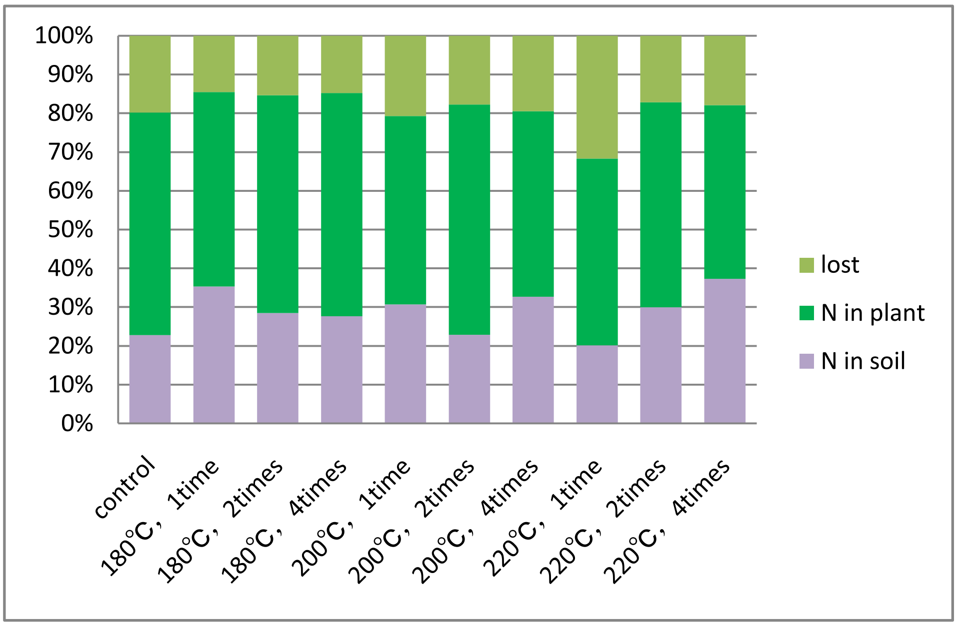

Figure 4.3: Nitrogen uptakes of the plant

In different test group, the nitrogen quantity remained in the soil showed different value. In the case of the 180◦C group, 1 time application, the remained nitrogen quantity was higher than the control group, which showed that a certain amount of organic nitrogen remained in the soil. On the other hand, when we only used chemical fertilizer, only about 60% nitrogen can be taken up by the plant also proved that not all of the nitrogen applied can be used. Usually, plant will take up the inorganic nitrogen first, then when the organic nitrogen was decomposed into low molecular nitrogen that can be used by the plant. While with the increasing of the liquid product application, the lost nitrogen did not change obvious, and also, the taken-up nitrogen quantity increased a little. This phenomenon proved that the combined organic and inorganic nutrients can promote the efficiency of nutrients take-up. In the case of 200◦C groups, 2 times application showed obvious uptakes. And in the 220◦C groups, it also showed the similar trends.

The growth of the plant is not only influenced by the sunlight, water, air, fertilizer and so on, but also, the characteristics of the fertilizer are also affecting it. The nutrient take up is greatly affected by environmental factors and other growth conditions[14]. The interactions between ions in the fertilizer also play an essential role. For some kind of plant, the uptake of total N and K depends on N form applied, and the uptake of P, K, Ca and Mg were affected by the pH value. In different parts of the plant, the uptake is also different[15]. The fertilizer we used for the test was obtained from the hydrothermal process, where the pH, the EC value and the composition are also different, which affected the plant growth. For the 180◦C groups, the liquid fertilizer we used showed a relatively neutral pH, and the EC value was also lower than the other groups, therefore, the organic component inside the liquid product mainly comes from the dissolution of the big organic molecular. It seems that the organic component can be decomposed and taken up by the plant. For the 200◦C and 220◦C groups, still 2 times application showed good uptakes, which means 2 times mixing ratio is the best choice for Komatsuna growth. For all of the 4 times application, it showed obvious inhibiting effect compared with the other times, which may due to the high EC values. If we applied 4 times quantity to the plant, it means that we should add more liquid volume, and the water we used for watering every day was decided, which indicated that the more quantity we used, the higher the EC value would become. Too high EC value is not only harmful to the plant, but also influencing the activity of the microorganism inside the soil, which also influence the decomposition of the organic component. On the other hand, some kinds of microorganism are also very sensitive to the pH value. In this test, the liquid product used in the 200◦C group and 220◦C groups are also different, not only the EC value, but also the pH value and the components are not the same. For different kinds of plant, the EC value of the surround environment influences the plant growth very well. As in different group, the volume of the liquid product we added were also different, therefore the EC value were also different. It is obvious that higher liquid product application will cause the increase of the EC value. Therefore, in the case of 1 time group, even though its EC value was lower, most of the nitrogen was in the form of ammonia, which is very easy to volatilize into the air, causing the lack of nitrogen uptake; in the 2 times group, the EC value increased to the appropriate value, which can promote the plant growth; in the 4 times group, the EC value was too high, which caused not only harmful effect to the root, but also inhibited the microorganism activities, therefore it showed lower production. These differences decided the different decomposition rate, which also decided the different nutrient uptake. From the test result it seems that all of the tests for phosphorus and potassium uptakes showed no obvious difference. This is not a bad phenomenon because at least we can infer that the phosphorus and potassium from sewage sludge did not take harmful effect to the plant. It appears that the components in the liquid product, such as humic acids and plant growth regulators, stimulated the plant growth. The liquid product also contains micro-nutrients that might stimulate plant growth. During the hydrothermal treatment, a lot of labile nutrients are also produced and dissolved into the liquid product. The labile nutrients of the liquid product would be easily released into the soil and consumed by the microbes, thereby stimulating the growth of the plants.

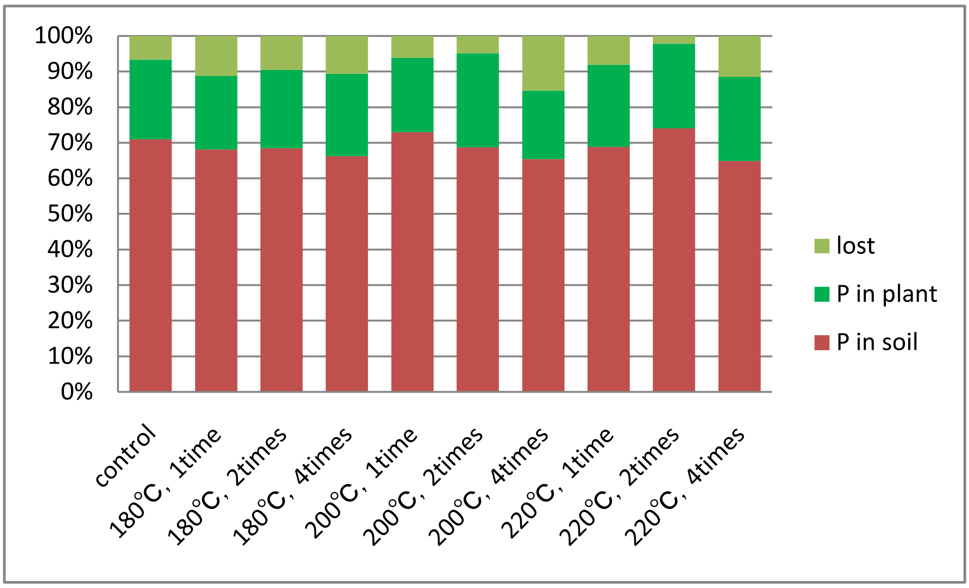

Figure 4.4: Phosphorus uptakes of the plant

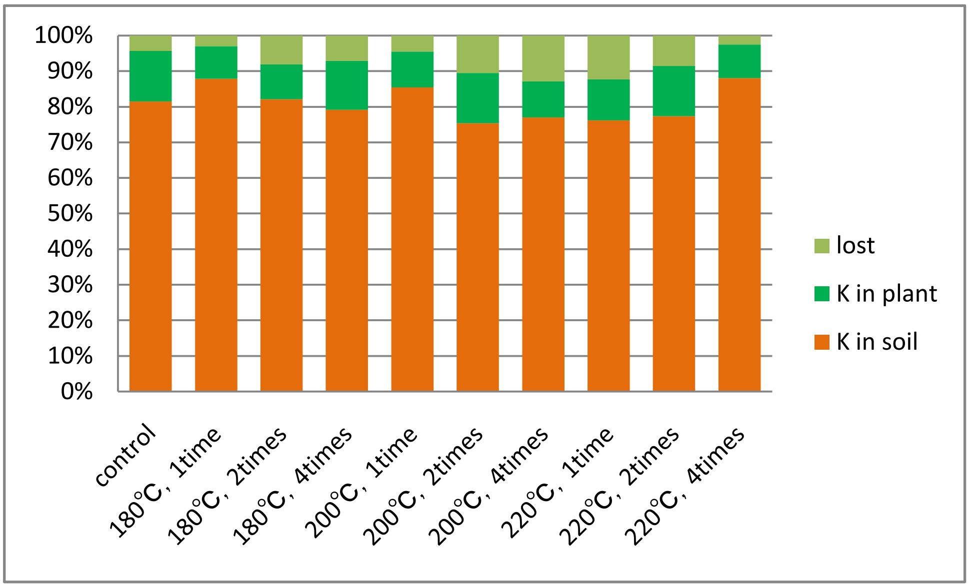

Figure 4.5: Potassium uptakes of the plant

4.3.2 Fertilizing value of the liquid product without chemical fertilizer

If there is enough nitrogen for microorganism demand, the inorganic nitrogen will increase through mineralization of organic matter, where nitrogen is seldom immobilized when organic material with high nitrogen mass fraction is applied to soil[16]. The importance of N，P and K fertilizer to the plant is well known[17], and their application was the factor that most explained the variation in plant growth experiment. In this experiment, as there is no chemical fertilizer was added in the liquid product, the yield of the plant growth experiment was conducted for investigating the fertility of the organic nitrogen component in the liquid product. The result was also compared with the control group and the group with only chemical nitrogen fertilizer.

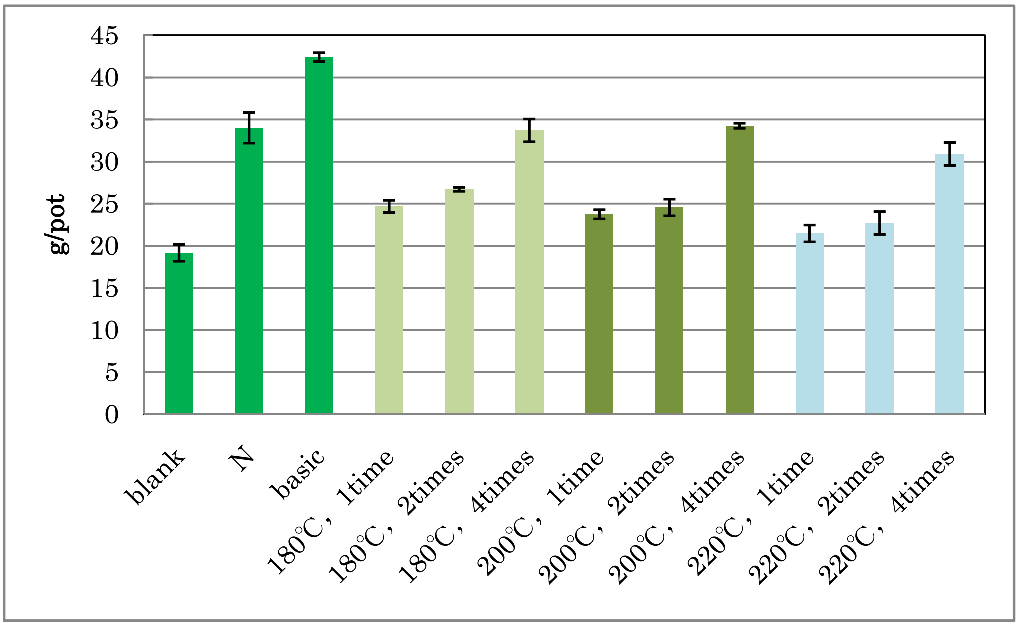

Figure 4.6: Fresh weight of the plant

Figure 4.6 showed that the weight of the plants after 7 weeks growth was significantly affected by the liquid product, with the highest weight of about 34 g found in the 200◦C, 4 times group, and the lowest of about 18 g in the blank group. Actually, from Fig. 4.6, we can see clearly that for all of the 4 times groups, the plant showed similar yield, which means the quantity of the liquid product is the most important factor for the plant growth. Even though the high EC value are the same with the last experiment, for the yield, different from the mixed chemical fertilizer experiment, the 4 times group still showed very good effect to the plant. The highest yield in this experiment is the basic group, in which we added 100mg N, P and K respectively. This phenomenon also explained that the nutrient balance is the determining factor for the plant growth. The insufficiency of P and K application will cause the diminished output. Comparing the blank group and the basic group, more than two times difference can be recognized. For the basic group, the three kinds of nutrients are enough, that the yield is the highest. The nitrogen group, whose yield is not so high as the basic group, can be explained by the lack of phosphorus and potassium. However, comparing all of the 4 times groups, the 220◦C group showed lower yield than the other groups, which also can be explained that too high EC value still will inhibit the plant growth. For all the tested experiments, 4 times groups showed higher yield than the 1 time and 2 times groups. For the same treatment temperature, the 1 time and 2 times groups showed no obvious difference as the nitrogen application are not enough. For comparison we also did plant growth experiment added with only chemical nitrogen fertilizer. From the figure we can see clearly that the liquid product obtained from the hydrothermal process showed almost the same yield with the chemical nitrogen fertilizer group. Therefore, it means that the organic nitrogen component in the liquid product, after being decomposed by the microbes in the soil, can be absorbed easily by the plant, and have no obvious harmful result.

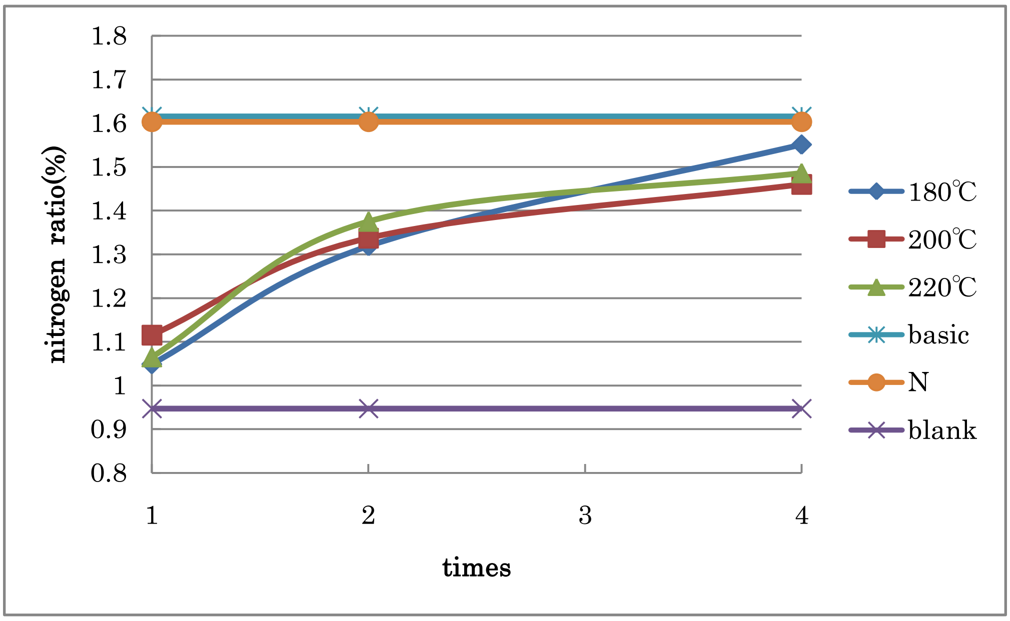

Figure 4.7: Nitrogen ratio in the plant

We also detected the nitrogen ratio in the plant. The result is shown in Fig 4.7. Here we can clearly see that the nitrogen uptake increased together with the application increasing. Comparing the basic group and the nitrogen group, the nitrogen ratio showed almost the same level, reaching about 1.6%. In Fig 4.6, we have already seen that the yields of the two groups are different. It seems that the phosphorus and potassium contents in the fertilizer also affect the yield. And for the same kind of liquid product, the higher quantity the liquid applied, the higher nitrogen ratio could be detected, which also showed the importance of the nitrogen fertilizer to the plant. The interesting thing is that all the same times application also showed similar nitrogen ratio, which offered the evidence that all of the liquids can be absorbed by the similar amount. The liquid product obtained at different reaction temperatures did not show obvious difference to the plant growth. Even though the 1 time and 2 times groups showed no obvious difference in the yield, the nitrogen ratio showed obvious difference.

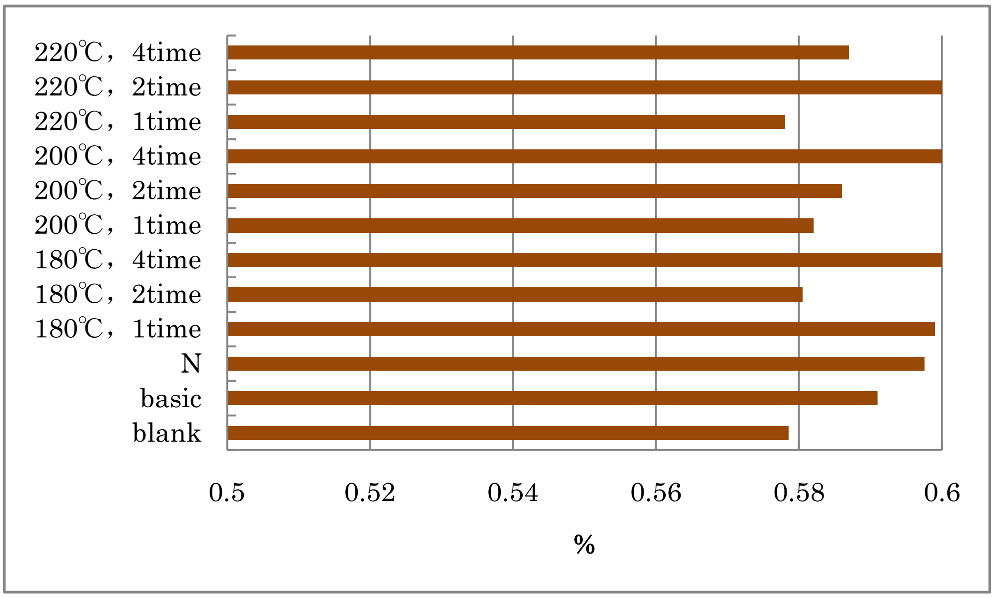

Figure 4.8: Nitrogen ratio in the soil

After plant growth experiment, the nitrogen ratio in the soil was also analyzed. The soil we used in this experiment itself contains a certain amount of nitrogen, but from the yield of the blank group we can see that the content is not enough. After the application of the liquid product, the nitrogen remained in the soil are shown in Fig 4.8. Here we can see the nitrogen ratio, increased to different levels, but the value is not so high and all of them are concentrated from 0.57% to 0.6%. Therefore, the nitrogen concentration in the soil can be seen as almost no change. On one hand, it showed that most of the nitrogen applied to the soil was absorbed by the plant and the efficiency of the nitrogen can be ensured; on the other hand, no more nitrogen was remained in the soil, which also showed the safety of the liquid product because it will not cause the soil pollution by the excessive nitrogen application.

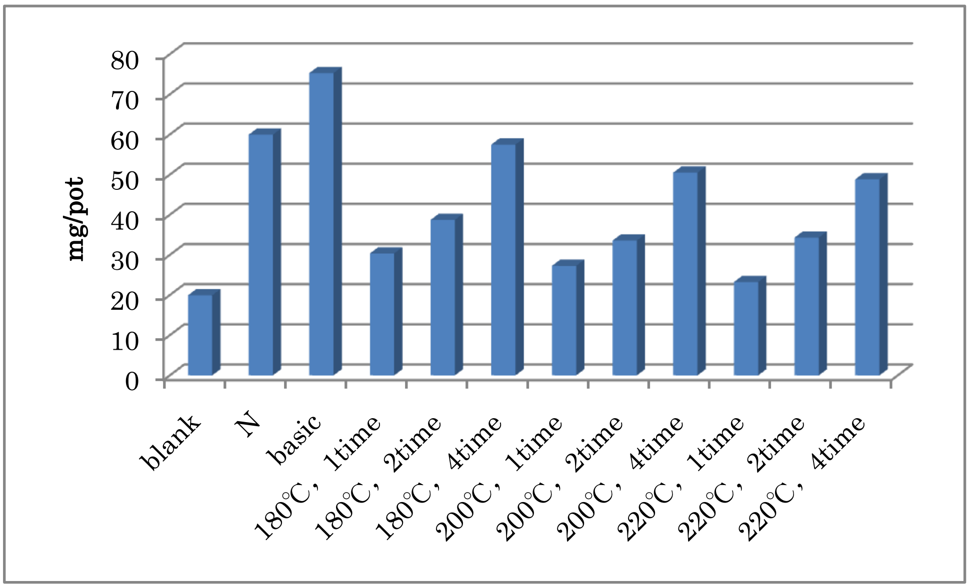

Figure 4.9: Nitrogen content in the plant

The total nitrogen content in the plant is calculated and the result is shown in Fig 4.9. Generally speaking, the trend is similar with the plant yield. The highest yield group also showed the highest nitrogen uptake. It seems that the nitrogen content in the soil decided the nitrogen uptake. For the 1 time and 2 times groups, the nitrogen uptake showed different levels, while from Fig 4.6we had discovered that there was no obvious difference between the two groups on the yield. A possible reason of this phenomenon is the different micronutrient concentrations in the soil. Some papers reported that the micronutrient will provide the plant's ability of nitrogen uptake. Therefore, when it turns to the 4 times groups, we can see very obvious difference on the yield. However, on one hand, larger application of the liquid product will increase the concentrations of the micronutrient in the soil, which finally will improve the nitrogen uptake; on the other hand, large application also increased the liquid EC value. The result is similar with the experiment with chemical fertilizer, where higher EC value inhibited the plant growth and the activity of the microorganisms. By comparing the nitrogen uptake of the basic and all the 4 times groups, we can see that the higher the treatment temperature was, the lower the nitrogen uptake was. Therefore, it does not mean that the larger the application is, the better the yield is. To find the right total application and dilution times are also another challenge.

Table 4.3: The concentrations of K and P in the plant

element	K（mg/g）			P(mg/g)		
	1time	2times	4times	1time	2times	4times
blank		20.57±0.33			8.63±0.46	
N		20.68±0.58			8.25±0.37	
basic		22.71±0.19			11.69±0.25	
180℃	18.68±1.42	18.38±0.73	19.34±1.21	8.77±0.92	9.24±0.12	8.49±1.57
200℃	19.03±0.54	17.28±1.89	20.47±0.33	9.12±0.27	9.57±0.31	8.63±0.66
220℃	20.83±0.13	19.89±0.64	19.35±0.46	8.7±0.95	7.71±1.63	8.82±1.97

Table 4.3 showed the potassium and phosphorus concentrations in the plant. From the table we can see that the liquid product did not show obvious effect on the potassium and phosphorus concentrations. The basic groups, which were added with 100 mg of potassium and phosphorus, were different from the uptake of the nitrogen. Even though the concentrations were higher, the uptakes of the potassium and phosphorus did not increase with the increase of the nitrogen concentration. Therefore, the result showed the same with the experiment in the alluvial soil. The potassium concentration in the blank group was about 20mg/g, and the concentration of the basic group plant was about 22mg/g, which showed not so much difference. According to the increase of the liquid product application, the concentration of the potassium in the plant did not increase and all of the concentrations were kept at a similar level. In the case of phosphorus, it also showed similar level with the blank group, which was about 8 mg/g.

Comparing the two experiments, we can see that the liquid product can be used as a kind of nitrogen liquid fertilizer successfully as it showed wonderful fertilizer effect to the plant growth. However, during the experiment, we also discovered that even though it also contains many other kinds of micronutrients, the concentrations of the micronutrients are too low, therefore, when using this kind of liquid product as fertilizer, mixing with chemical fertilizer is recommended. The yield of the plant by different applications also showed the importance of mixing with chemical fertilizer. The liquid product can be used as a kind of organic fertilizer and the use of chemical fertilizer combined with organic fertilizer could maintain the soil nutrients balance, amend soil physical and chemical properties, increase the soil organic matter and nutrient availability, decrease fertilizer loss rate, and then enhance soil fertility and ecosystem productivity[18-20]. The soil with organic fertilizer continually applied is also reported that had lower bulk density and higher porosity values, porous and buffering capacities[21], therefore, using this byproduct as a kind of organic fertilizer is also practicable.

The liquid product from sewage sludge by the hydrothermal treatment contains abundant organic substance and nitrogen nutrients, while the concentrations of phosphorus and potassium as well as some microelements that are essential for the growth of crops are very low. Even though the heavy metals in the sludge were a big concern for their risks, the contents of heavy metals in liquid product were too low to cause harmful results, which showed the high safety of the liquid product be used as fertilizer.

4.4 Conclusions

Using the liquid product from sewage sludge by the hydrothermal treatment as fertilizer is a good way for treating and reusing the sewage sludge treatment byproduct. After the treatment, most of the heavy metals in the sewage sludge would remain in the solid product, and the concentrations of them in the liquid are very low, therefore, after diluting, the concentration become much more lower that will not cause harmful effect to the plant. The addition of the liquid product to the soil can promote the soil fertility properties significantly. From the plant growth experiment, we found that the yield of Komatsuna increases with the increase of addition of the liquid product from 25 mg to 100mg per pot in comparison with the blank group which has no addition of liquid product to the soil. However, no obvious difference appeared with the increase addition of the liquid product from 25mg to 50mg per pot, while obvious difference appeared when the application increased to 100mg/pot. So the optimal amount of the application of the liquid product to the soil was 250mg nitrogen/kg soil. The results of the uptake of nitrogen component by Komatsuna show that the growth of the plant is not only dependent on the nitrogen amount but also dependent on the other kinds of nutrients, therefore the nutrient balance is very important for the plant growth. The addition of the chemical fertilizer into the liquid product is recommended. The contents of the nitrogen component in the soil increased with increasing the amount of liquid product added, but showed no large value, therefore the liquid product will not cause the soil pollution. The liquid product obtained by the hydrothermal process from sewage sludge showed its wonderful effects on the plants growth and nutrients cycle. Using the liquid product to fertilizers is proposed to be appropriate way to reduce environmental damage and use resources effectively. The successful application of the hydrothermal process liquid product as liquid fertilizer here suggested a potential management of residues from biomass waste by the hydrothermal treatment in industry and provided an efficient fertilizer source for agricultural use.

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5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

This thesis aimed to investigate the possibility of liquid fertilizer production from sewage sludge by the hydrothermal treatment. By the lab scale hydrothermal treatment experiment and analysis of the hydrothermal treatment process on the nutrient release, the law of nutrient solubilization was investigated, which can provide a basic evidence for extracting the nutrients, and find the optimum operating parameters to avoid the influence of the harmful toxicity components. Then the germination experiment was conducted for testing the phytotoxicity of the liquid product, the effects of the TOC concentration and the EC value on the seed germination were investigated. At the same time, a lab-scale biodegradation system was used for testing the biodegradation of the liquid product to test the safety of the liquid product and its influence to the natural environment. To confirm the effect of the liquid product to be used as fertilizer, finally, plant growth experiment was carried out to prove the fertilizer effect on the plant. Komatsuna was planted on two kinds of different soil collected from different place, and the liquid product was added as a fertilizer. After harvesting, the yield of Komatsuna, the basic growth parameters, and the ratio of the nutrient absorption were determined. By comparing and analyzing these parameters, the effect of the liquid product on the Komatsuna growth was discussed. The results obtained from these studies allow drawing the following major conclusions.

The application of moderate temperature hydrothermal treatment (180,200,220,240◦C) as a new treatment method of nutrient recycling from sewage sludge was proved to be effective to solubilize sludge. For the reaction 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. And 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 acids first and finally into ammonia and CO_2, with different reaction rates.

In the liquid product, the organic component concentration was very high, and huge amount of nitrogen and potassium were also dissolved. As macronutrient, about half of the nitrogen dissolved was inorganic nitrogen. Even though the liquid product also contains a certain amount of heavy metals, the concentrations were too low to result in harmful influence. According to the germination experiment, the phytotoxicity of the liquid product was investigated. The high TOC and EC values were harmful to the plant, but if diluted to the appropriate times, the germination will increase to the common level, and the liquid product can also promote the growth of the plant root. By the biodegradation experiment, the cumulative emission of CO_2 in 50 days was calculated. The result showed that the hydrothermal reaction temperature determined the biodegradation rate of the liquid product. It can be inferred that when be used as fertilizer, as high EC value will cause harmful effect to the plant, the pre-dilution is necessary. The organic acid produced during the hydrothermal process showed a positive effect on the root growth. The liquid product showed no obvious phytotoxicity, and it will be biodegraded by the natural microorganism in 50 days. The product was proved to be environmentally friendly option.

During the plant growth experiment, different amount of liquid product were added to the soil for testing the fertilizer effect. The contents of the nitrogen component in the soil increased with the amount of liquid product added. The application of the liquid product to the soil can improve soil fertility properties significantly. The yield of Komatsuna in the experiments increased with the amount of liquid product added to the soil and the optimal amount of the application of the liquid product to the common soil was 250mgnitrogen/kg soil. Compared with the blank experiment that did not add the liquid product, the yield of Komatsuna increased 78-89%. The uptake of the nitrogen component by Komatsuna showed that the growth of the plant is not only dependent on the nitrogen amount but also dependent on the other kinds of nutrients. The result showed that the liquid product can promote the growth of plant effectively and the uptake of nitrogen depends on the liquid application. The uptake of potassium and phosphorus was low, showing no obvious difference from the chemical fertilizer. The liquid product can be used as a fertilizer, and considering the different requirement of nutrient by different kinds of plants, the addition of appropriate amount of chemical fertilizer is recommended.

In this study, the liquid product from sewage sludge by the hydrothermal treatment was successfully used as a kind of liquid organic fertilizer. The GI value of the germination experiment was satisfactory. Plant growth experiments demonstrated that the application of the liquid product effectively promoted plant growth and was safe for the soil. According to all the results, we can see that the liquid product by the hydrothermal process from sewage sludge showed its wonderful effects on the plants growth and nutrients cycle. Using the liquid product as fertilizer is proposed to be a promising way to reduce environmental damage and use resources effectively. The successful application of the liquid product from the hydrothermal process as liquid fertilizer here suggested a potential management of residues from biomass waste by the hydrothermal treatment in industry and provided an efficient fertilizer source for agricultural use. Therefore, this study provides a new way of high value utilization of sewage sludge by producing low cost but high quality liquid product. The hydrothermal treatment technology uses water as clean medium and free sewage sludge as raw material. So it can effectively reduce the costs of sludge treatment and avoid the secondary environmental pollution if extensively applied in big scale production. However, the efficiency of the big scale production and the direct effects of the liquid products in the field experiment should be further studied.

5.2 Recommendations for future research

This research is focusing on the possibility of using the liquid byproduct from sewage sludge by the hydrothermal treatment process as liquid fertilizer, and our experiment is just confined in the lab scale investigation, thus there is still a lot of necessary work to do in the future.

The cost effectiveness was calculated in Chapter 2, which showed that using the hydrothermal treatment for recovering the nutrient in the sewage sludge is a low cost and high profit method for treating sewage sludge. However, our experiment is just carried out in a small scale experiment, therefore the calculation is just under an ideal situation. To investigate the real cost-effectiveness situation and the mass balance in the industry, the big scale experiment should also be considered as the future work.

It is obvious that a certain amount of organic component in the sewage sludge can be converted into organic acid under the temperature of 200℃, and this kind of acid can improve the root length of the plant. Because of the analysis condition limited, the complicate composition of the organic acid can not be recognized accurately. If we can distinguish them, it will show very practical significance.

In the case of biodegradation experiment, the accumulated CO_2 quantity was tested in a sealed system. Since during the degrading process, organic nitrogen, as a kind of important component in the liquid product, can also be decomposed by the organisms in the soil. Therefore, the decomposition of the organic nitrogen component should also be conducted.

As for the plant growth experiment, it showed that the liquid can be used as a good kind of nitrogen fertilizer. However, the test plant we used in the experiment is just Komatsuna. Whether this kind of fertilizer can be used and get the similar good result on the other kind of plant is still needed to be discussed. The amount of the liquid fertilizer we used for application is proved that 100mg nitrogen equivalent weight is the best application. Considering that the high EC value will decrease the yield, more volume experiment was not carried out. Therefore, the higher application of the liquid product should also be tested. On the other hand, the liquid product we got from sewage sludge is lack of P and K, so that the mixing of chemical elements is recommended. According to our previous research, the chicken manure contains huge amount of K. So if the hydrothermal treatment can remove K into the liquid product and mix it together with the liquid product from sewage sludge, it is a new challenge and interesting investigation.