LEACHING OF TRACE-POLLUTANTS FROM WASTEWATER SLUDGE THROUGH THE ULTRASONIC TREATMENT

Joo-Yeon Oh

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Joo-Yeon Oh

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Major Advisor
Sung-Deuk Choi

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This certifies that the thesis of Joo-Yeon Oh is approved.

11. 04. 2013

Thesis supervisor: Sung-Deuk Choi

Changha Lee: Thesis Committee Member #1

Changsoo Lee: Thesis Committee Member #2

Abstract

The generation amount of sludge has increased along economic growth. In accordance with the London Convention and the Marine Environment Management Act, dumping sewage sludge and live stock manure in the ocean was banned since 2012. Ultrasonic treatment has been mainly used among various reduction techniques because of low expenses and high efficiency. Sludge is decomposed and a lot of pollutants in sludge were leached by using ultrasonic treatment. When trace-pollutants were leached from the sludge sediment, they can cause contamination on supernatant. Also, trace-pollutants such as heavy metals and PAHs (polycyclic aromatic hydrocarbons) can have a significant impact. However, the fate of trace-pollutants in supernatant and sediment of sludge after being treated using ultrasonic treatment has been rarely reported.

In this study, wastewater sludge was collected from chemical plants in Ulsan, Korea, and the effect of ultrasonic treatment on sludge reduction and leaching of trace-pollutants was investigated. Sludge samples were irradiated at 600 W for 5-30 min by ultrasonicaters and centrifuged at 3,000 rpm for 30 min. To confirm the effect on the reduction of sludge, we investigated microorganism flocs in the sludge due to ultrasonic irradiation times using microscope. Volume change of sediment in the sludge and TSS (Total Suspended Solid) were also analyzed. To confirm concentration of heavy metals in supernatant and sediment, the samples were analyzed using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-OES, 720-ES, Varian, USA) after the stage of acid treatment. We also analyzed the concentration of PAHs in supernatant and sediment using Gas chromatograph-mass spectrometer (GC/MS, Agilent 7890A, Agilent, USA) and calculated the fate of PAHs.

Changes of microorganism in sludge were observed using a microscope. The cell walls and flocs of microorganism were disintegrated by increasing irradiation time. According to these results, it was expected that the ultrasonic treatment have a great effect on the leaching of trace-pollutants and the disintegration of microorganism. The TSS concentration was increased by increasing irradiation times because suspended materials can be increased by decreasing size of flocs. While the concentration of heavy metals and PAHs decreased in the sediment, the concentration of heavy metals and PAHs increased in the supernatant according to the result. The reason for the leaching of heavy metals and PAHs was the disintegration of cell walls of microorganism. Therefore, it was expected that the treatment has great effect on leaching of trace-pollutants and reducing sludge by increasing irradiation times and irradiation intensity.

According to these results, leached trace-pollutants in supernatants were possible to be the source of sludge treatment in WWTP (wastewater treatment plant). Therefore, treatment of supernatant after

ultrasonic treatment should be considered appropriately. On the other hand, the sediment in sludge was able to be used more safely by leaching trace-pollutants in it using ultrasonic treatment. Therefore, ultrasonic treatment which has effect on both reducing sludge and recycling it safely should be developed by carrying out continuous monitoring of the effect on the sludge.

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Chapter 1. Introduction

I. Research background

Sludge is the precipitate which is formed in the process of purifying using sewage treatment. It can be classified into organic and inorganic matter and is made up of less than 85% water content (above 15% solid content). The amount of the sludge has increased with economic growth. According to 『The National Waste Generation and Treatment』, wastewater occupied 53% of the total sludge which accounted for the largest portion (Figure 1).

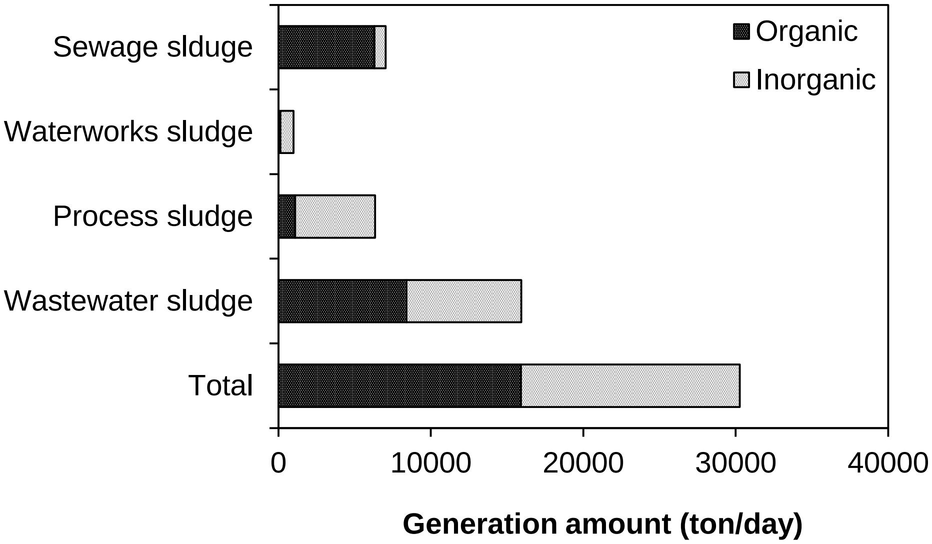


Figure 1: The generation amount of sludge

The generation amount of the wastewater sludge represents a tendency to increase every year until 2009. The amount was about 39,171 ton/day in 2009 and increased about 30 times when compared to the amount of 2002 (sludge amount: 28,112 ton/day). However, the generation amount of wastewater sludge decreased by 24% compared to the amount of 2009 (sludge amount: 30,200 ton/day). This tendency was created by the law; The ocean dumping of sewage sludge and livestock manure was banned since 2012 and the ocean dumping of food waste leachates sludge and human waste sludge was prohibited since 2013. Thus, the interest in reduction of sludge generation and recycling it has increased.

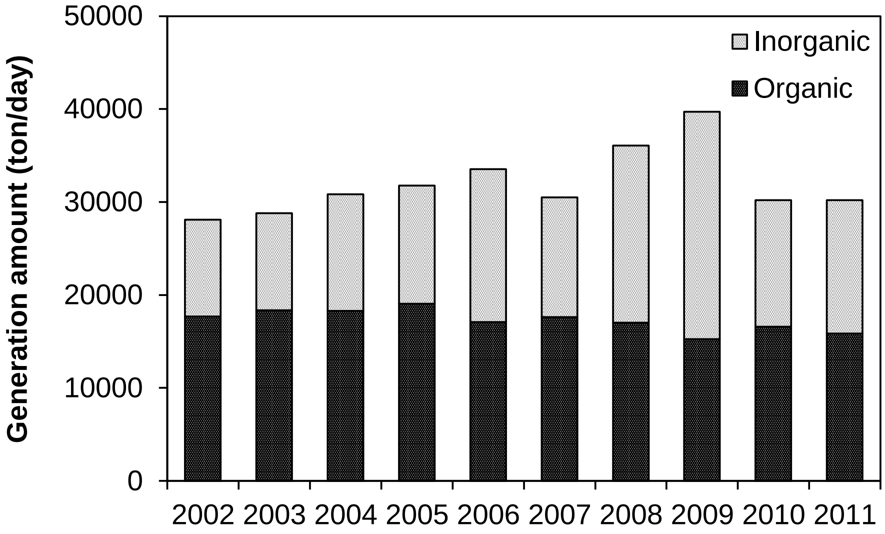


Figure 2: The trend of generation amount of wastewater sludge

There are a variety of method to reduce the sludge like mechanical treatment,[1] electrical treatment,[2] thermal treatment,[3,4] ozone oxidation,[5,6] and ultrasonic treatment.[7,8,9,10] Ultrasonic treatment is most widely used among them because the treatment has relatively high effect of reduction.[11] Studies were also carried out to increase the effectiveness of sludge reduction using a combination of multiple technologies.[12,13] For example, when sludge was handled by continuous processing using biological methods, more than 80% of COD (Chemical Oxygen Demand) was reduced by sludge reduction, and methane production was increased by 64% during anaerobic digestion.[14] Generally, sludge treatments have been used on the low-frequency 20-40 kHz.[15,16,17] Sludge reduction according to frequency changes of ultrasounds was observed in some studies.[8,18,19,20] In addition, many studies have been conducted about sludge reduction consistency with changes of the ultrasonic irradiation time or irradiation intensity.[7,18,21,22]

In order to handle wastewater sludge, various methods have been used. They are categorized into reclamation, incineration, recycling, and ocean dumping (Figure 3). The recycling has been mainly used on wastewater sludge. In the early 2000s, the treatment amount using recycling and ocean dumping increased while the treatment amount using reclamation and incineration decreased. In the mid-2000s, the treatment amount using reclamation and incineration has increased while the treatment amount using ocean dumping has decreased gradually. In the late 2000s, the amount using reclamation, incineration, and recycling has increased because of reinforced regulation about ocean dumping. Other methods instead of ocean dumping, especially recycling were widely used.

The management of trace-pollutants in sludge is very important for recycling sludge. The trace-pollutants can have a harmful effect on human and environment. Also, this is very important to the regulation and management. In other countries, the standards of trace-pollutants in water, soil, and sediment were handled strictly. However, the standard of trace-pollutants, especially organic pollutants, was not included in Korea. Therefore, the appropriate criteria for Korea should be established for managing sludge safely.

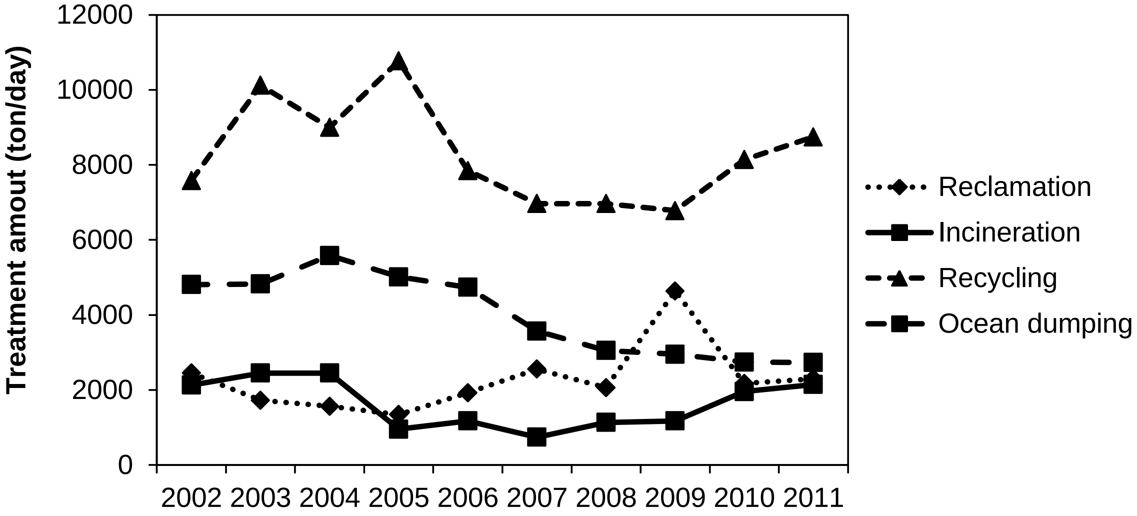


Figure 3: The trend of treatment amount of wastewater sludge

The previous studies about ultrasonic treatment focused only on the reduction of sludge. Some studies have reported that some decrease in concentration and removal of heavy metals in sediment was caused by leaching effect of ultrasonic treatment.[23,24,25] These studies explained the phenomenon representing disintegration of cell walls and flocs in sludge. Also, some studies reported the concentrations of PAHs and heavy metals in the sludge is decreased according to the ultrasonic treatment.[19,22,26,27,28] However, most of studies on pollutants such as PAHs (polycyclic aromatic hydrocarbons) and heavy metals in sludge have been performed without separating supernatant and sediment. In these cases, exact identification about the fate of sludge is very difficult. In order to handle sludge safely, it is important to carry out studies about not only reducing sludge but also concentration them and following the fate of trace-pollutants. Thus the concentration of trace-pollutants should be analyzed in both supernatant and sediment due to ultrasonic treatment.

II. The types of sludge

Sludge is divided into two groups, organic which contains more than 40% of organic matter and inorganic sludge which contains less than 40% of organic matter. Most of the sludge belongs to the organic group. In addition, the organic group can be classified as sewage treatment sludge, wastewater treatment sludge, excreta treatment sludge and livestock wastewater treatment sludge. Types of sludge are subdivided depending on the process of treatment plant as shown in Table 1.

Table 1. Characteristics by the type of sludge

Types of sludge	Characteristics
Raw sludge (primary sludge)	Precipitated solids settling in the primary clarifiers Easily Corruption due to approximately 65% of the organic matter content Gray and severe odor
Activated sludge (secondary sludge)	Precipitated sludge in the secondary clarifiers by aeration Digestible by either alone or mixed with the primary sludge Brown and soil odor
Digested sludge (Aerobic)	Easy to dehydration If digested properly Brown or dark brown and none odor
Digested sludge (Anaerobic)	Oder is caused less after digestion, dry sludge can be used as good quality soil Dark brown, contains a large amount of gas
Chemical sludge	Sludge has a bit of a sticky and becomes gelatinous if the addition of iron or aluminum hydrate. Large amount of gas discharged and sludge specific gravity increased when stored for a long time.
Tricking filter sludge	Decomposition proceeding is slower than undigested sludge Brown and less odor

III. Ultrasound treatment

3.1. The basic theory

Ultrasound is sound waves with frequencies above 16,000Hz which cannot be heard by humans. Frequency are classified into two groups, infrasonic frequencies and ultrasonic frequencies according to intensity. Frequency that humans can hear varies from 16 Hz to 16 kHz. Infrasonic frequency has 16 Hz or lower and ultrasonic has 16 kHz or higher. In addition, ultrasound can be distinguished depending whether it has low-frequency or high-frequency. Low frequency has a shorter wavelength but good directivity. Phase gap arises due to density variations occurring in medium. Bubbles are generated by hydraulic pressure when the ultrasonic waves through the medium. This phenomenon is called cavitation. High frequency generates high accelerations of 100,000 G so cavitations do not occur due to high linearity. Cavitation phenomena can be categorized into transient cavitations and stable cavitations according to the ultrasound intensity. When ultrasonic intensity is greater than 10 W/cm^2, transition cavitations occur. Cavitations exist during one cycle or multiple cycles and the limited size of bubbles created by them are completely destroyed. By this, a large quantity of energy is generated. However, cavitations are stably generated only when ultrasonic intensity is lower than 1～3 W/cm^2. Generated bubbles cannot be destroyed completely but only split into smaller bubbles. This is used as the nucleus for generating new cavitations. Condensation heat occurs when cavitations are destroyed. Reaction takes place in a very short period of time which is not enough for passing around the generated heat. At this time, hot-spots are generated and the temperature of them reaches thousands of degrees. The molecular motion becomes active and the reaction time gets faster because of the large kinetic energy of reactant particles made by the high temperature.

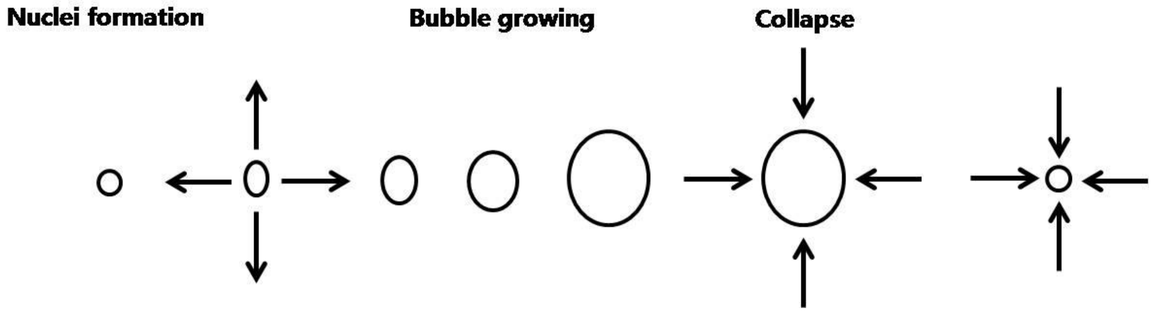


Figure 4: Cavitation bubbles occur within a homogeneous medium

3.2.Affecting factors of ultrasound reaction

3.2.1. Frequency of ultrasonic

The frequency and intensity of ultrasound is related to causing cavitation phenomenon. The sludge is destroyed effectively by the frequencies less than 40 kHz. Generally, cavitation phenomenon occurs easily at low frequencies. Cavitation phenomenon is less likely to occur at 1 MHz because it is not enough time to grow bubbles. Also, cavitations increasingly occur depend on the increasing ultrasound intensity.

3.2.2. pH

OH^- concentration of the aqueous solution increased in accordance with the increase of pH of reactants. The reaction rate gets higher according to the increase in the generation rate of radials. In contrast, OH^- concentration of the aqueous solution decreased in accordance with the decrease of pH of reactants. Oxidative Decomposition is facilitated by an increase of HO_2 radicals.

3.2.3. Reaction temperature

Generally, most of the people expect that chemical reaction rate caused by ultrasound will increase when the temperature rises. However, reaction rate decreases when the temperature of reactor rises. Also, when the temperature increases, the cavitation intensity weakens and the number of bubbles increases. If maximum energy is emitted, bubbles inside become empty and pressure increases. When the bubbles collapse, emitted energy is reduced by a decrease of the pressure which makes the difference between inside and outside of the bubbles.

3.2.4. Surface tension

Theoretically, surface tension has an inverse relationship with cavitations. Frequency generated in micro bubbles is greater than cohesion between each of the liquid molecules. Cavitations do not occur when the surface tension grows.

3.2.5. Duration of the pulse

Preparation steps are required in order to generate cavitations. Short pulses are less likely to create cavitation phenomenon because cavitations need a large vibrations. Bubbles do not vibrate during one cycle and grow size that can be resonant during vibration several times. Usually, the pulse width was kept equivalent.

IV. Objective of this study

There are various methods for the reduction of sludge and ultrasonic treatment has been widely used because of low expense and high effectiveness. Concentration of trace-pollutants by ultrasonic treatment in sludge also was studied. Some previous studies explained the trace-pollutants including sediment leached and disintegration of cell walls and flocs of microorganism after treating them with ultrasonic treatment. However the study about concentration in both supernatant and sediment according to ultrasonic treatment has been rarely performed. Thus, the effect on the fate of trace-pollutants in sludge using ultrasonic treatment should be investigated in order to manage sludge safely.

Therefore, this study observed cell walls and flocs of microorganism in sludge using microscopes to identify sludge reduction and analyzed the concentration of TSS (total suspended solid) and VSS (volatile suspended solid). We also analyzed the concentration of trace-pollutants (heavy metals and PAHs) in supernatant and sediment of sludge. Based on the results, we investigated the fate of PAHs after treated with ultrasonic treatment using mass balance of PAHs in sludge. Finally, we will present basic data for selection of concentrated trace-pollutants in Korea in order to handle sludge effectively.

Chapter 2. Reduction of sludge

I. Research background of sludge reduction

Sludge pretreatment is classified by physical treatment, chemical treatment, and biological treatment, significantly and can also be classified as mechanical pretreatment, electrical pretreatment, thermal pretreatment, thermal-biological pretreatment, chemical pretreatment, biological pretreatment, and acoustic pretreatment.

Table 2. Classification of the sludge reduction technologies

Classification	Pretreatment
Mechanical pretreatment	Ball milling High pressure homogenization Shear gap homogenization Lysate centrifugation
Electrical pretreatment	Electron beam irradiation Electro impulse discharge
Thermal pretreatment	Freezing•Thawing Pyrolysis
Thermal-biological pretreatment	Aerobic digestion
Chemical pretreatment	Acid/base reactions Ozone oxidation
Biological pretreatment	Addition of enzymes
Acoustic pretreatment	Cavitation/sonochemical reactions

1.1.Mechanical pretreatment

Mechanical pretreatment is a method that facilitates the intracellular organics elution of intracellular organisms through the cell wall destruction using physical force such as high-energy tension, pressure, and rotation. This method uses crushing, wet mill, jet spray.

1.2.Electrical pretreatment

Electrical pretreatment destroys the cell of organisms in sludge using high-energy electron beam. This method has effects on the extinction of the sludge cell walls, as well as on pathogenic bacteria by generating reactive radicals.

1.3.Thermal pretreatment

Thermal pretreatment is the way that heats sludge from 15 to 60 minutes at a temperature of 60～250˚C. This method has been used by anaerobic pretreatment method of activated sludge. It was developed to improve dehydration and stabilization.

1.4.Freezing and thawing pretreatment

Through this method, sludge from sewage treatment plants can be dewatered and freezed using the process of fusion effectively. This process improves the solid-liquid separation and change structure of the activated sludge. Freezing rate of organic matter in sludge is related to elution. When freezing rate decreases, leached organic matter and the amount of fusion of protein increases. However, this method requires a lot of energy to freeze sludge and has some disadvantages on facility issues including large crystals.

1.5.Chemical pretreatment

Chemical pretreatment improves the hydrolysis of organic matter using acid or alkali. The principle of this process is that the cell walls of microbes disintegrate by the sudden change of pH with addition of strong alkaline, after keeping low pH using strong acid. Chemicals such as NaOH, KOH, $Mg(OH)_2$, and $Ca(OH)_2$ are used in this process. NaOH is most effective when it comes to sludge solubilization and bio degradation.

1.6.Ozone oxidation pretreatment

Ozone pretreatment oxidizes the cell walls of microbes using radical reactions caused by microorganism processing with strong oxidation of ozone. When underwater decomposition of ozone, OH radicals damage the cell walls and it can be changed from polysaccharide to low molecular weight substances. The advantage of this method is that it does not require the process of dehydration from the disposal of the sludge. Also it is safe and hygienic due to death of pathogenic microorganisms. Odor control is especially easy because of the death of the fungi generated from sewage treatment plants. Also, it can improve dewatering ability of sludge and homogenization of particles.

1.7.Biological pretreatment

Biological pretreatment treats sludge using microorganisms. When nutrients to help grow are supplied to a cell, this method can be applied from the aerobic and the anaerobic digestion process. In addition, this way the decomposition of organic substances is facilitated and odor can be handled.

1.8.Ultrasound pretreatment

Ultrasound pretreatment destroys the microorganism cells with instantaneous high temperature and high pressure caused by ultrasonic cavitation phenomenon. At this time, more than 95% of the cells are destroyed. Removal efficiency of untreated volatile solids comes to approximately 60%. Anaerobic digestion requires 15 – 20 days to be processed. If treated sludge increases digestion efficiency and gas conversion, residence time in digestion reactor can be decreased to 2.5 day. Generally, material which has low biodegradation rate is converted into methane with ease.

1.9.Combined pretreatment

Combined pretreatment handles sludge with combination of more than one way. For example, combinations of ways such as ozone + ultrasound treatment, heat + alkaline treatment, ultrasound + alkaline treatment are used. These are used to complement disadvantage of each treatment and to improve solubilization rate of organic matter.

II. Sludge sampling and ultrasonic treatment

2.1.Sludge sampling

We collected sludge samples from a WWTP of Chemical Plant in Ulsan, Korea, on March 2011. The plant had a flow rate of 150 tons a day. The collected sludge was immediately transferred to the lab and stored in opaque glasses for shorter than 24 h at 4˚C. In order to minimize the impact of corruption and microorganism proliferation in sludge, all experiments were completed within 7 days after sampling and the exposure to the room temperature of the samples was minimized.

Figure 5: Sludge sampling for analysis of sludge reduction

Figure 6: Basic shape of sludge samples

2.2.Ultrasound treatment

Changes of the volume and weight of the sludge were measured by changing the irradiation intensity and irradiation time to observe the relationship between ultrasound treatment and sludge reduction. In order to choose the ultrasonic instrument, horn type and bath type of ultrasound equipment were used. 20 kHz ultrasound machine (sonosmasher, ULH-700S, Sibata, Japan) was used ultrasonic irradiation time was changed from 0.5 to 30 minutes and ultrasound intensity was changed from 100W to 600 W.

42 individual samples (600 mL) inserted in beakers (1,000 mL) was treated by ultrasound treatment. In order to measure changes in the volume of sludge, treated sludge was measured by the volume of sediment via centrifugation.

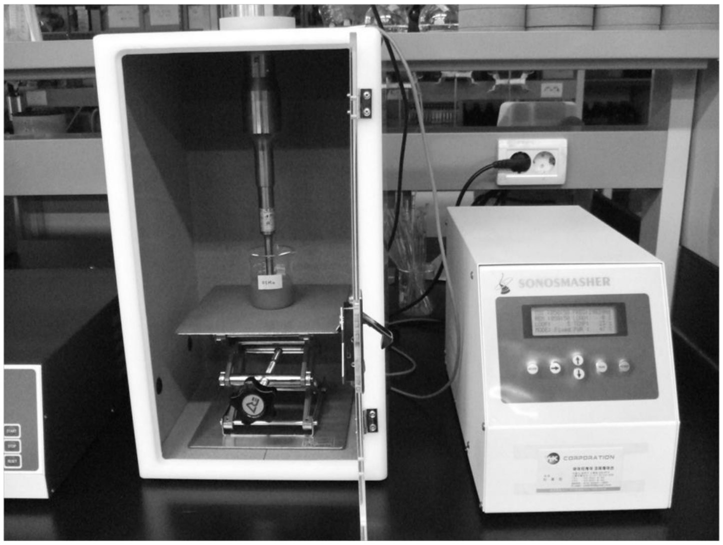


Figure 7: The reduction of sludge using ultrasonicator

III. Experiment for reduction of sludge due to ultrasonic treatment

3.1. Analysis for basic properties

3.1.1. Analysis of elemental

Analyzed samples were dried using an electric oven (WOR-105, DAIHAN Scientific, Korea) at temperatures above 120˚C for 24 hours. The dried samples were made into the form of powder by Muller and mortar. Then, approximately 1.5 g was analyzed using an elemental analyzer (Flash 2000, Thermo, USA) carbon, hydrogen, oxygen, nitrogen, and sulfur.

3.1.2. Measurement of pH and moisture content measurements

The sludge was measured using a pH meter and the sludge cake was measured in the same manner as measuring PH of soil. The soil pH measurement methods were based on 25 g of samples which was added to 50 mL of water after one hour or more specifically to be eluted composition in samples with water. Each sample was measured three times.

The electric oven and moisture meters were used to measure moisture content. These devices were used selectively and measured the same sample using repeated analysis. As a result, the moisture content of the same sample showed a difference of 3 - 5%.

Figure 8: The measurement process of pH and moisture content

3.2.The observation of microorganism cell walls in sludge resulted in ultrasonic treatment

The sludge samples are observed using optical microscope (Axio Scope, Carl Zeiss, Germany) to identify the change on cell walls of microorganism in sludge immediately after sonication. For examination of disintegration of microorganism cell walls, flocs in sludge, they are magnified 50-1000 times bigger than the original one.

3.3.Measurement of volume of sediment in sludge due to ultrasonic treatment

In order to measure the changes of sludge solids by ultrasound treatment, sludge volume change and weight change was observed using a conical tube (Palcon, bioscience, USA). Fifty mL of ultrasonically treated sludge was filled into conical tubes and it was separated into supernatant and sediment using centrifuge (Combi 514R, Hanil, Science Industrial, Korea) for 30 min at 3000 rpm. Sludge reduction by the presence or absence of ultrasonic was confirmed by the volume of sediment, and then sediments were dried. Sludge reduction results could be obtained by measuring the weight using the ultrasound.

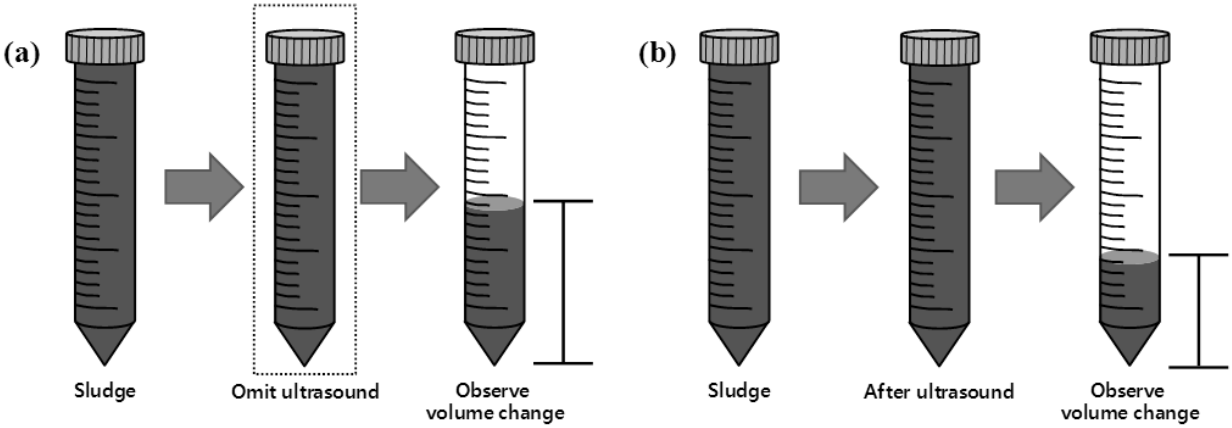


Figure 9: Observation for volume change of sludge

(a) Omitted ultrasound, (b) Treated ultrasonic

3.4.Analysis of TSS and VSS concentration by ultrasonic treatment

5 mL of sludge was filtered using glass fiber filter papers (pore size: 0.45 μm and a diameter of 47 mm). Generally, the filter which are used to analyze VSS, is the filter with pore size of 1.2 μm and a diameter of 47 mm.[29] However, we used the filter with pore size of 0.45 μm in this study to compare the concentration of TSS and VSS with the concentration of PAHs. Filtered suspended solids are dried and ignited subsequently. The concentration of suspended solids were calculated by the difference the weight of the untreated and treated suspended solids. Before the experiment, filter paper used in the experiments were ignited for 15 min at 450˚C in order to prevent contamination of organic matter as much as possible. To obtain the TSS concentration, 5 mL of the sludge was filtered using filter paper and it was dried for 2 hours at 110˚C in an electrical oven. The dried filter papers were cooled down for 30 minutes in desiccators. In order to measure the amount of VSS filter papers measuring total suspended solids were ignited for 15 min at 450˚C. Then, weight of the filter paper after ignition was measured in desiccators for 30 minutes.

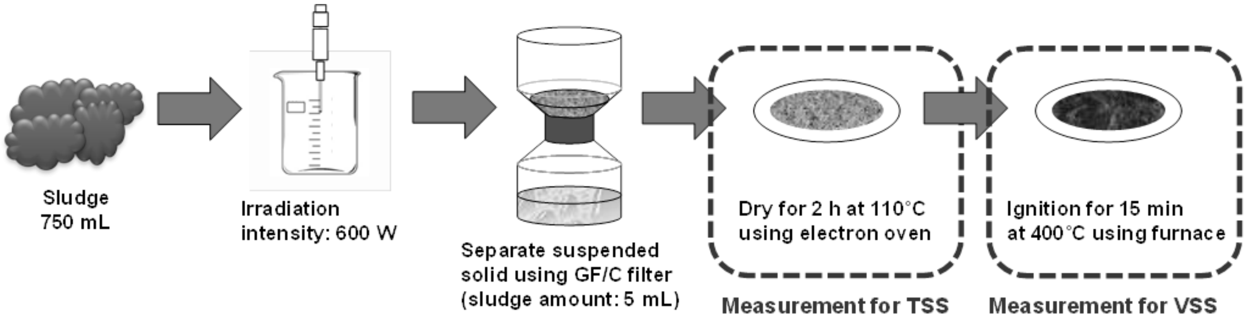


Figure 10: The measurement process of TSS and VSS

IV. Results of sludge reduction due to ultrasonic treatment

4.1. Properties of sludge

4.1.1. Results of element analysis

The analysis of the composition of the sludge using elemental analyzer is presented in table 2. The definite composition of sludge contained carbon (39.1%), hydrogen (6.0%), nitrogen (5.9%), sulfur (0.8%), oxygen (29.8%), and other (18.4%). This value is similar sludge composition ratio reported in previous studies.

Table 3. Element analysis of sludge

Element(%)	C	H	N	O	S	The other
sludge	36.03	5.61	5.40	0.77	29.67	22.52

4.1.2. Results of pH and moisture content measurements

pH of concentrated sludge (6.8), coherent sludge (7.0), and sludge cake (7.6) was measured. These values are included in the general scope. The average pH of the sludge is 6.8 (n=3) and this value belonged to the normal pH range (5.0-8.0).

Measured moisture content of concentrated sludge (98.9%), coherent sludge (98.6%), and sludge cake (89.1%) was measured using electric oven. They all contained high level of moisture.

4.1.3. Microscopy for confirmation the status of the sludge

The sludge was observed at a magnification of 400 (10×40) using an optical microscope (Axio Scope, Carl Zeiss, Germany). As a result, more or 2 μm microorganisms were observed (Figure 11). To determine the size, color, shape characteristics of these microorganisms, the microbes estimated were various algae (Anacystis, Gomphospaeria, Anabaena, etc.) and motile protozoa. When considering the configuration of typical sludge microorganisms, it can be assumed that the sludge contains a variety of bacteria and fungi.

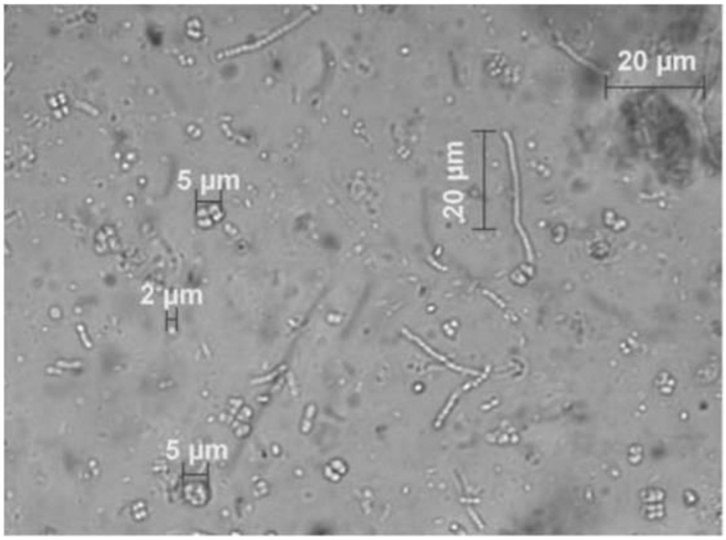
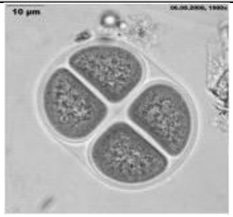
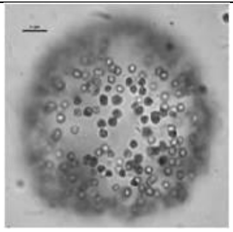
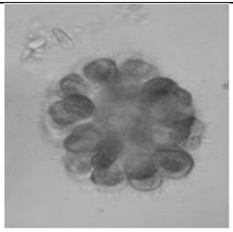
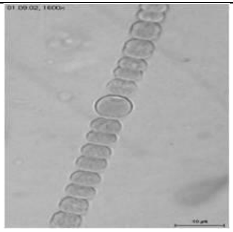


Figure 11: Observation of microorganism in sludge

Table 4. Types and characteristics of microorganisms from sludge

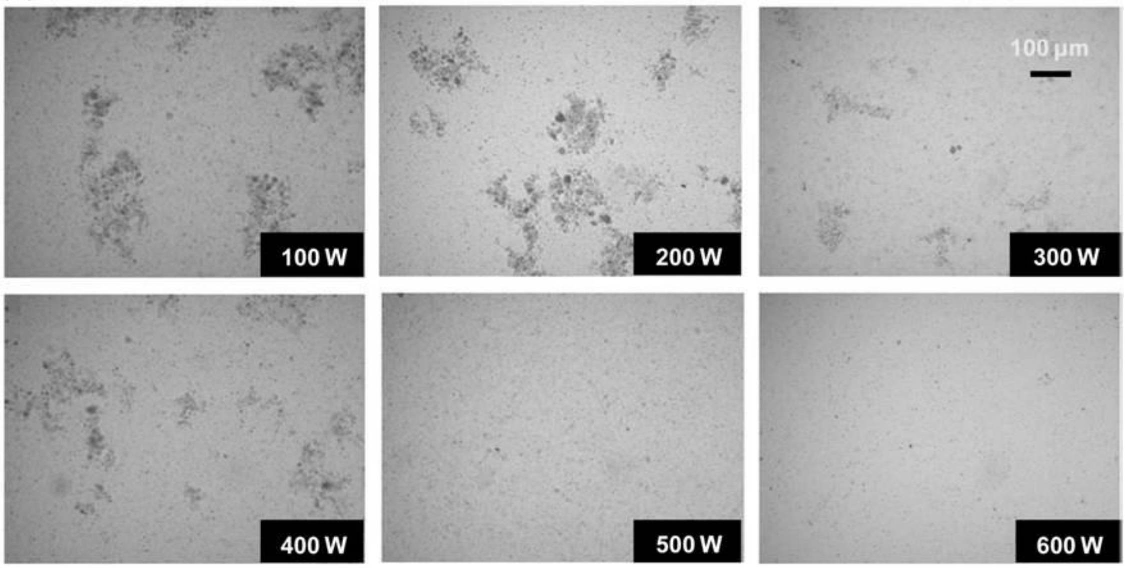
Classification (genus)	Shape	Size	Features
Anacystis		5 µm	• Algae of family like Chroococcus • 2-4 cells size of about 1 µm formed a group • Some variants are swimming
Gomphospaeria (Coelosphaerium type)		2-20 µm	• Phytoplankton • Circular or oval cell division in the center • Mucinous stem does not exist
Gomphospaeria (Phytoplankton)		2-20 µm	• Phytoplankton • When thrive, potential toxicity is increased • It is increased by direct sunlight and warm temperatures
Anabaena		40 µm	• Algae of family like cyanobacteria • It had the ability of nitrogen fixation • It is used as a natural fertilizer

4.2.Results of the change of microorganism cell walls by ultrasound treatment

The sludge samples which are treated with ultrasonic intensity of 100-600 W were identified using an optical microscope to observe the relationship ultrasonic intensity and changes in the cell walls of microorganisms. The result is shown in Figure 12 (a); cell walls of the sludge were destroyed by the increased ultrasonic intensity. Microscope magnification was 100 (10×10), and ultrasound time was applied condition equivalent to 30 min. according to the previous studies, flocs of microorganisms are distributed and microorganism cell walls were destroyed by increased ultrasonic irradiation intensity.[30,31]

Irradiation time was adjusted every 0.5, 1, 5, 10, 15, 30 minutes to observe the relationship between ultrasonic time and changes of cell walls of microorganisms. Intensity of ultrasound was kept 600 W. As a result, cell walls were destroyed with the increase of the time ultrasound applied. In particular, the biggest change occurred between 5-10 minutes.

(a) Irradiation time = 30 min



(b) Irradiation intensity = 600 W

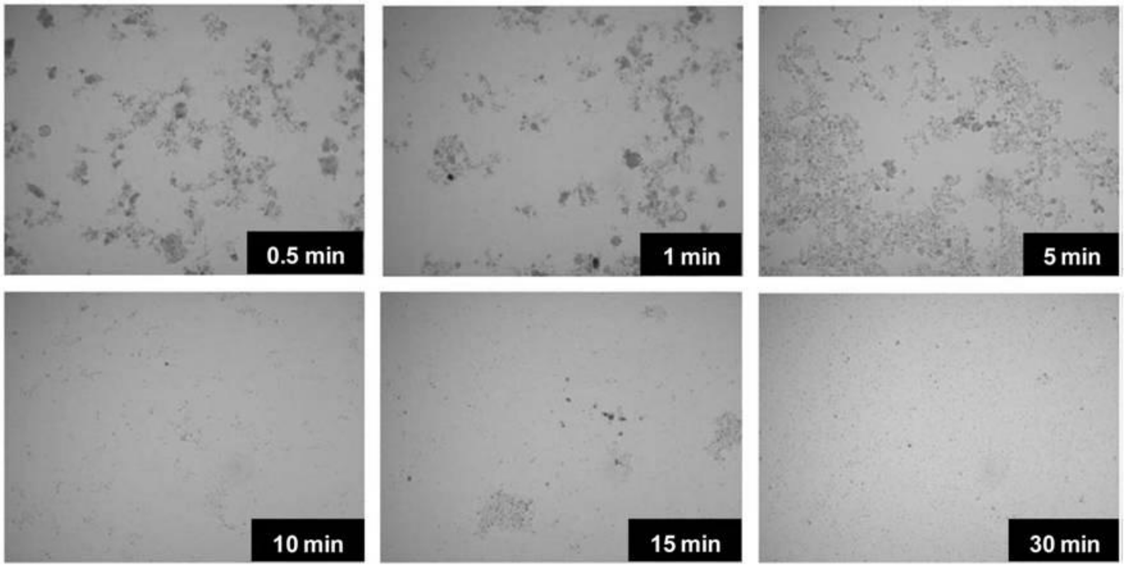


Figure 12: Change of microorganism flocs in the sludge samples according to ultrasonic treatment.

4.3.Results of volume of sediment in sludge due to ultrasonic treatment

Each of the sludge samples treated by ultrasonic treatment was centrifuged (3,000 rpm, 30 min). The volume of the sediment separated from supernatant was measured. The sediment of sludge samples that was not treated by ultrasound was 6 mL. Increasing ultrasound intensity and processing time, the volume of the sediment decreased.

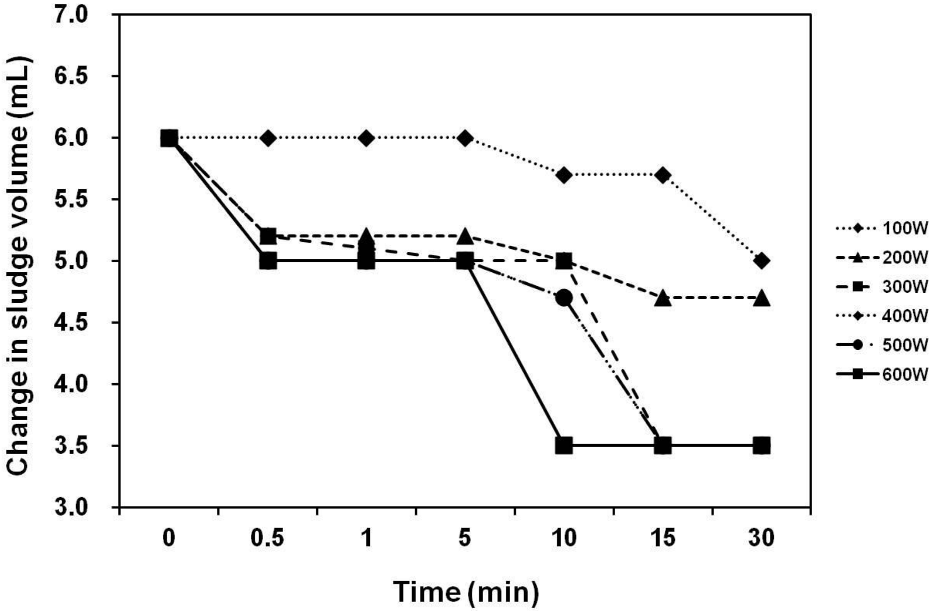


Figure 13: Change of volume on sludge depends on change of intensity on ultrasonic wave and irradiation time of ultrasonic wave

The colors of supernatant were changed dramatically from transparent to brown and the viscosity of the sludge weakened when it was handled with higher than 400 W. This is because the microbes inside the cell material were leaked to supernatant due to the destruction of the cell wall of microorganisms by ultrasound. When Sludge was treated with 600 W of ultrasonic irradiation intensity for more than 10 minutes, the most of the sediment decreased (42%). The amount of sediment was not reduced from the most of the samples before being given 5 minutes of sonication. After irradiated for more than ten min, the amount of sediment decreased rapidly with intensity of 300W or higher. Therefore, the optimum conditions of ultrasonic intensity and processing time to destroy the microorganism cell walls should be identified for the economical processing.

Table 5. Change of volume on sludge depend on change of intensity on ultrasonic wave and irradiation time of ultrasonic wave (%)

Concentrated sludge (after centrifuged)						
	0.5 min	1 min	5 min	10 min	15 min	30 min
100 W	0.0	0.0	0.0	5.0	5.0	16.6
200 W	13.3	13.3	13.3	16.6	21.6	21.6
300 W	13.3	15.0	16.6	16.6	**41.6**	**41.6**
400 W	16.6	16.6	16.6	21.6	**41.6**	**41.6**
500 W	16.6	16.6	16.6	21.6	**41.6**	**41.6**
600 W	16.6	16.6	16.6	**41.6**	**41.6**	**41.6**

4.4.Time trend of TSS (Total suspended solid) and VSS(volatile suspended solids) concentration due to ultrasonic treatment

In order to confirm sludge reduction using TSS and VSS, the concentration of TSS and VSS treated at 600 W by ultrasonic treatment had to be analyzed. The concentration of TSS and VSS decreased the largest from 15 min to 20 min. Suspended solids increased according to the disintegration of cell walls and the flocs of microorganisms.[32,33] Some previous studies also selected these methods to reduce sludge and the results were reported that the more the ultrasonic energy increased, the higher the concentration of TSS and VSS became.

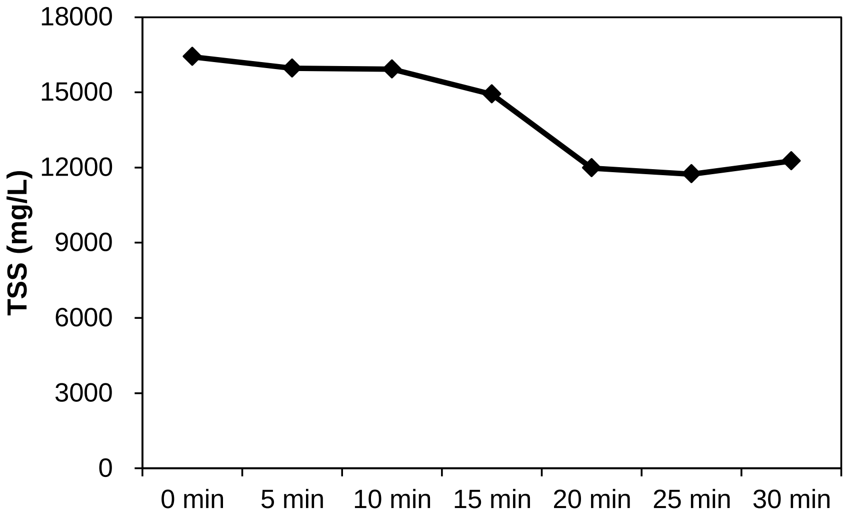


Figure 14: The concentration of TSS according to ultrasonic irradiation times

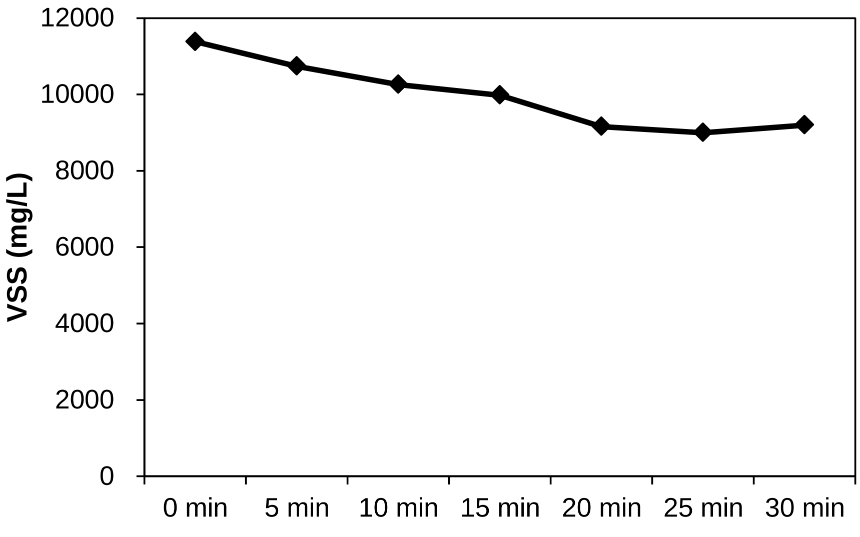


Figure 15: The concentration of VSS according to ultrasonic irradiation times

Chapter 3. Heavy metals

I. Research background of heavy metals

1.1.Definition

Heavy metals are metal elements such as antimony(Sb), lead(Pb), mercury(Hg), zinc(Zn), cadmium(Cd), chrome(Cr), nickel(Ni), and cobalt(Co).whose weights are over four. It is mandatory for plants, animals and humans to ingest small amount of some of the elements. However, when ingested too much or other hardly broke heavy metals are ingested, they can be accumulated in the body and do harm for them.

1.2.Physical and chemical properties

Heavy metals are widely used in industrial fields in many different forms and they exist in water or dirt in different forms. Table describes physical-chemical properties of heavy metals. Most of them are non-soluble in water but soluble in acid. Thus, acid rain can leach heavy metal into water, dirt, and ground waters in mine area and other heavy metal pollution sources.

Table 6. Physical and chemical properties of heavy metals

Metal	CAS No.	Weight (g)	Boiling point (˚C)	Melting point(˚C)	At room temperature	Density (as 25˚C)	Vapor pressure
Antimony	7440-36-0	121.75	1635	630	Silver-white	6.68	1 mmHg as 886˚C
Chromium	7440-47-3	51.99	1900	2642	Steel-gray	7.14	1 mmHg as 1616˚C
Cadmium	7440-43-9	112.41	321	321	Silver-gray	8.66	1 mmHg as 394˚C
Zinc	7440-66-6	65.37	419.5	908	White	-	1 mmHg as 487˚C
Nickel	7440-02-0	58.70	1455	1455	Silver	8.90	1 mmHg as 1810˚C
Copper	7440-50-8	63.55	1083	2567	Red	8.94	1 mmHg as 1628˚C
Mercury	7439-97-6	200.59	356.73	-38.87	Silver-white	13.53	0.002 mmHg as 25˚C
Arsenic	7440-38-2	74.92	817	817 at 28 atm	Silver-gray	5.73	1 mmHg as 372˚C
Lead	7439-92-1	207.20	324.4	1740	Bluish-white	11.34	1.77 mmHg as 1000˚C

1.3.Type of heavy metals

3.3.1. Cadmium (Cd)

Since Cadmium has a property of rust-proof, it is used to plate instruments precisely, build ships and make anti-rust additives for cleaning instruments. It also used with Cu, Ag, Bi to make alloy which can be made into shafts or silver solders.

It can be ingested through digestion system or respiration system. After ingested, it will flow into blood and accumulated in kidneys, livers and bowels. Lethal dose of cadmium for human was not clarified, but effects of cadmium over ingestion are diabetes, albuminuria and aminoaciduria.

3.3.2. Arsenic (As)

Arsenic is widely distributed in natural, and trace amount of arsenic is contained in most of food. It is often used in murder, because it does not have taste, color and smell. However, when exposed for a long time, it can be accumulated in kidney, muscle, skin, hair, nail and bones.

Vomiting, diarrhea, listless, convulsion, dysphasia, arrhythmia, eczema and even death can caused by Acute poisoning, when it is ingested 70~200 mg. Chronic poisoning occurs when 3~6mg/L is ingested for a long time, and it causes infection on mucous membrane, muscle weakness, loss of appetite, black pigment on skin, cornification, and hair loss.

3.3.3. Chromium (Cr)

Chromium is used as additives to stainless steel and nichrome wire, and fire-proof additives. Hexavalent chromium is used in chrome plating, battery, picture printing, and dye. Because of its oxidizing power, it is used as oxidizer of dye, catalyst, leather and industrial chemicals.

Ingestion of hexavalent chromium in the form of powder generates acute poisoning which represents symptoms of infection on skin, lung, and organ. Also, a chronic poisoning represents the symptom of hepatitis.

3.3.4. Copper (Cu)

As a metal, Copper in dried air in stable in modern temperature, but in moist air which contains CO_2, SO_2 or salt, it forms basic salt that cover it with bright green.

Toxicity of copper is very low for mammals, but for birds or algae its toxicity has great impact. Ingestion of 1~2gof cooper a day cause stomach disease, but it shows low accumulate rate so a chronic poisoning happens very rarely.

3.3.5. Zinc (Zn)

For human being, defection of zinc causes lack of growth, malfunction of blood clotting and have bad effect on recovery. It is relatively light metal which has low melting point and high machinility so it can be widely used to make alloy.

50 mg/L of ingestion of Zinc can cause acute poisoning with diarrhea, stomachache, convulsion on stomach. But chronic poisoning of zinc does not exist.

3.3.6. Lead (Pb)

Lead usually is leaked from lead mine or recycled metals from factories, and burning gasoline in the form of gas.

Lead attaches to hemoglobin to decrease its function, cause anemia, and to be accumulated in blood, nervous system and kidney. An acute lead poisoning causes fatigue, brain damage, while a chronic lead poisoning causes weight loss, weakness, headache, falling of sight, and loss of appetite.

3.3.7. Nickel (Ni)

A large amount of Nickel could be found in wasted water of plating, casting, or machine-processing factories. Risk of it is not known, but when exposed through dermal and respiratory system it acts like a carcinogen and cause nose cancer or lung cancer if it is ingested in the form of nickel-carbonyl. A chronic poisoning of nickel affects nervous, respiratory and dermal system.

II. Sludge sampling and ultrasonic treatment for analysis of heavy metals

2.1.Sludge sampling for analysis of heavy metals

We collected sludge samples from a WWTP, on October 2011. The shape and color of the sludge in the thickener seems to be kept to same status but the color of sludge in settled tank appeared green. The collected sludge samples were transferred to the lab immediately and stored for shorter than 24 h at 4˚C. We immediately conducted experiments to minimize the impact of corruption and microorganism proliferation in sludge.

Figure 16: Sludge sampling for analysis of heavy metals

2.2.Ultrasonic treatment for analysis of heavy metals

In order to identify the result of concentration of heavy metals, we performed ultrasonic treatment. 750 mL of the sludge samples were irradiated for 5 to 30 min. We also selected the irradiation intensity of 600 W because 600 W was the maximum for the instruments. Thus, we collected all of the samples and applied irradiation intensity of 600 W. The sludge samples treated by ultrasonic wave were centrifuged for 30 min at 3000 rpm.

III. Analysis of heavy metals

3.1.Analysis of heavy metals for supernatant in sludge

In order to analyze sludge-eluted heavy metals, we collected sample supernatant through centrifugation. 5 mL of supernatant and 12 ml of aqua regia (HCl : HNO3 = 3:1 in volume) was put in decomposition container (BaekDuTM, ODLAB, Korea) of Graphite digestion system (ODLAB, Korea), and we decomposed them thermally at 200℃ for 120 minutes. Decomposed samples ware cooled down for 30 minutes, filtered through 5A filters (ADVANTEC, Japan), washed thoroughly and mixed with remains. The volume of the treated sample was 50 mL.

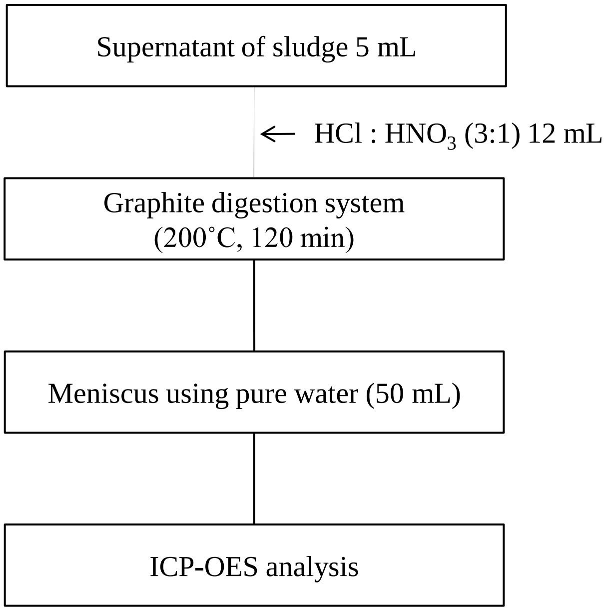


Figure 17: Analytical procedures of heavy metal concentration in supernatant of sludge

3.2.Analysis of heavy metals for sediment in sludge

The samples were collected in the sediment of the sludge after centrifugation for 30 min and dried for 24 h at 110℃. The dried sediment samples (0.2 g) and 12 ml of aqua regia (HCl : HNO3 = 3:1 in volume) was put in decomposition container of Graphite digestion system, and decomposed thermally for 120 min at 200℃. The decomposed samples were cooled down for 30 min and filtered through 5A filters. Finally, the volume was 50 mL. Distilled water in the containers used and mixed remained.

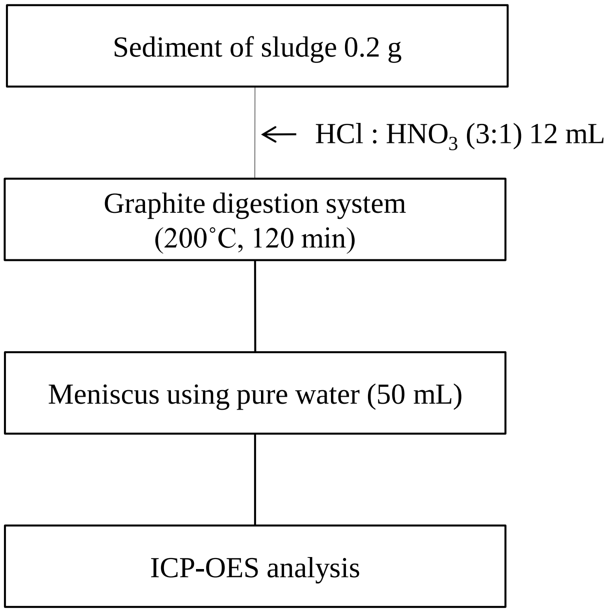


Figure 18: Analytical procedures of heavy metal concentration in sediment of sludge

3.3.Instrumental analysis of heavy metals

We analyzed four different kinds of heavy metals (Cd, Cu, Pb, Zn) using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-OES, 720-ES, Varian, USA). The condition for the experiment was set up as: Plasma flow=15 L/min, Auxiliary flow=1.5 L/min, Nebulizer flow=0.7 L/min, Radio Frequency generator power=1,200W, Measurement time=5 sec, Replicate measurements=3. Coefficient of determination (R^2) was over 0.999 for all the samples, and value of analysis was corrected by comparison with laboratory blank. LOQ (Limit of quantification) was determined as ten times standard deviation of values of lab blanks that analyzed for seven times. To find out recovery, samples were checked and blended in 5ml of diluted water and 0.1 ml standard (1,000 mg/L). Analyzing these samples with same method which was used for the supernatant samples, the rate of recovery of heavy metals was resulted in 99~105%. To minimize contamination in experiments, lab instruments that were made of metal or glasses were never used and all the instruments were washed in 5M of HCl for 24 hours. To increase accuracy, all samples were analyzed for 3 times and RSD (Relative Standard Deviation) was kept under 30% for every sample.

Figure 19: ICP-OES for analysis of heavy metals

IV. Results and discussion of heavy metals

4.1.Leaching of heavy metals in supernatant due to ultrasonic treatment

Changes of concentration of heavy metals (Cd, Pb, Cu, Zn) in the sludge supernatant after treated by ultrasonic wave treatment is shown on Figure 5. Before treatment (0 min), concentration of heavy metals in the sludge supernatant was not detected. Thirty minutes later it was under 5%. Since concentration of heavy metals was proportional to treatment time, it can be said that ultrasonic wave broke microorganism cell walls and agglomerates and attached heavy metals were moved toward the supernatant. After being treated for 30 minutes, zinc showed highest concentration (2,190 μg/L) and cadmium showed lowest concentration (0.78 μg/L). Copper (156 μg/L) and lead (52 μg/L) showed moderate concentration. Comparing these concentration with emission regulation for uncontaminated area mentioned『Water Quality and Ecosystem Conservation Act』(Cadmium: 20 μg/L, Lead: 100 μg/L, Zinc: 1,000 μg/L, Copper: 1,000 μg/L), only zinc concentration exceeded the regulation. Concentration of other heavy metals was below the regulation (5,000 μg/L) of other area ((A), (b), Exception). Calculating emissions by zinc concentration (2,190 μg/L) and sludge capacity of target sewage plants (150 ton/day), 330 g/day of zinc would be leach from sludge. Considering that actual sludge treatment uses high-power ultrasonic generators and treat much more sludge, total amount of heavy metals that comes out from sludge would larger than expected. Without proper treatment of these eluted liquid of sludge that emitted from certain water system, it would damage ecosystem. Thus, clear result figure for this treatment should be prepared.

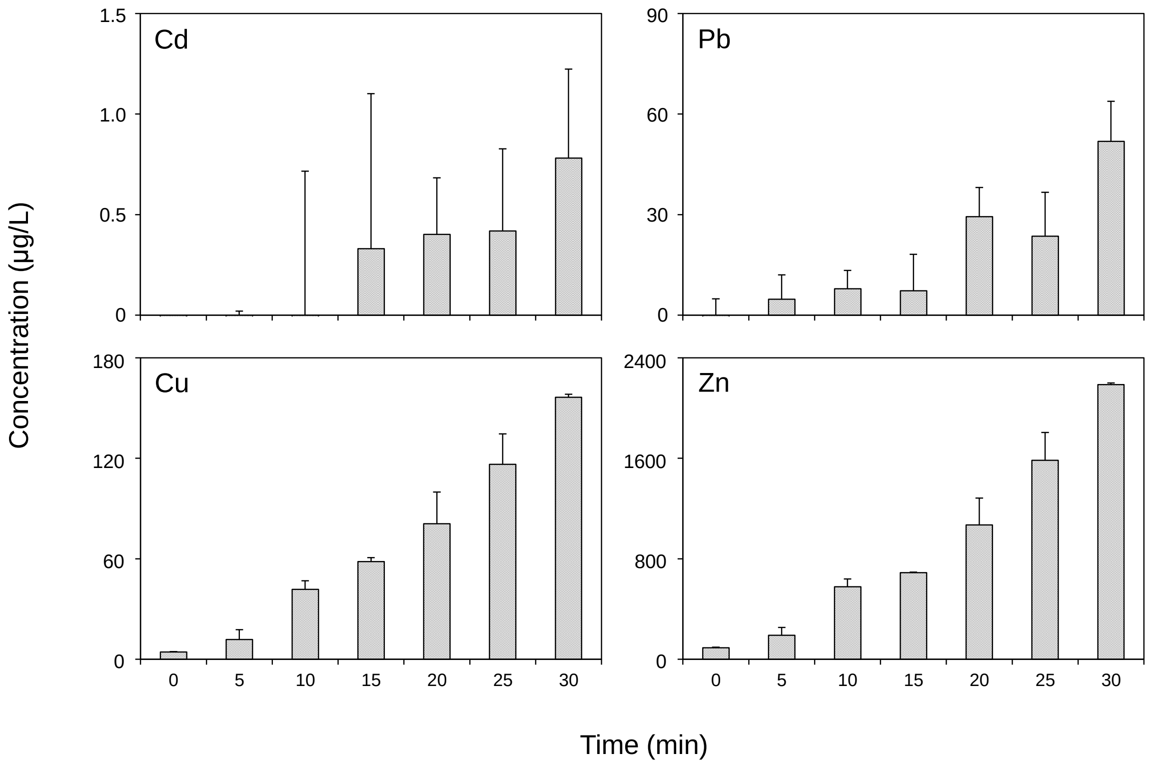


Figure 20: Time trends of heavy metals in sludge supernatant after the ultrasonic treatment

4.2.Changes of heavy metals in sediment due to ultrasonic treatment

The concentration of four heavy metals in the sediment being treated by ultrasonic treatment was investigated (Figure 21). When comparing those amounts of concentration before treatment (0min) and after treatment (30 min), the gap was lower than 20%. As a result of the concentration of heavy metals in the supernatant after treated for 30 minutes shows that zinc showed the highest concentration (521 mg/kg), and cadmium showed the lowest concentration (0.57 mg/kg). Copper (21 mg/kg) and lead (12 mg/kg) showed moderate concentration. The heavy metal concentrations in the sediment of sludge decreased from 0 min to 25 min due to the disintegration of cell walls and flocs of microorganisms in sludge. However, the concentration after treated for 30 min showed increased figure. Thus, we should study about this phenomenon additionally.

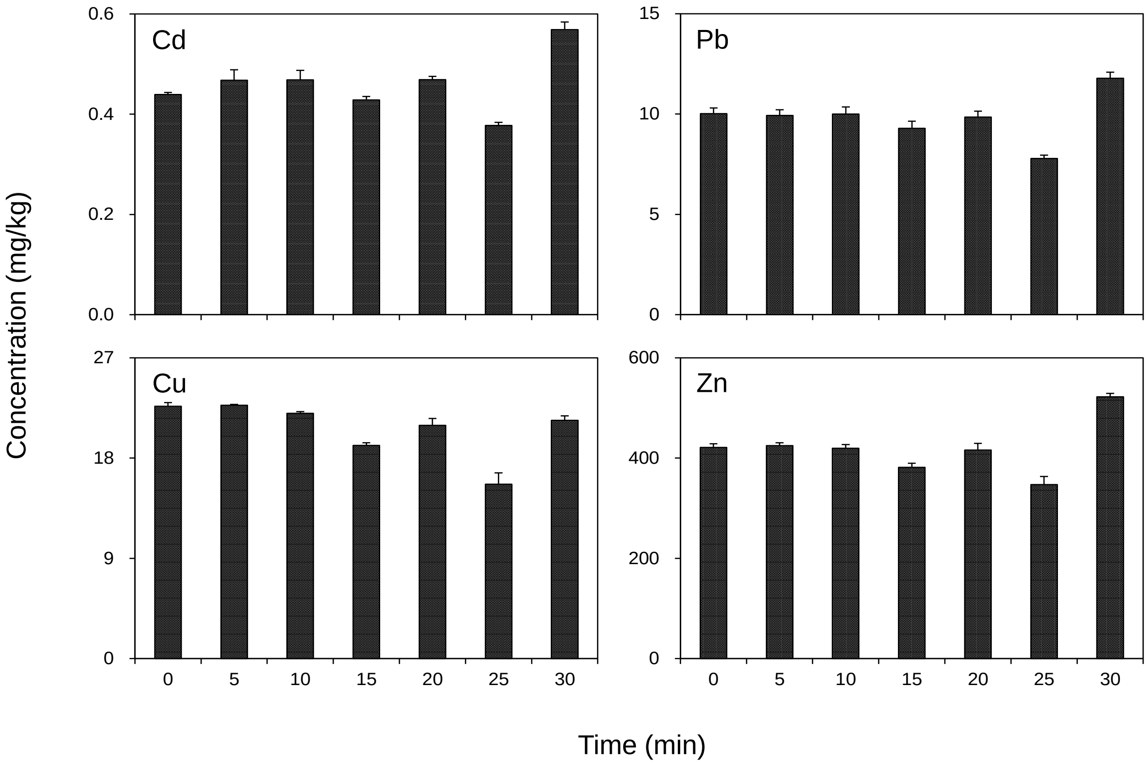


Figure 21: Time trends of heavy metals in sludge sediment after the ultrasonic treatment

Most of the concentration of heavy metals in this study was lower than concentration provided in Soil Conservation Act (Table 7). The soil was divided into three parts according to the standard of soil pollutant. Zone 1 includes the region such as orchard, ranch land, fish farm, park, and cemetery. Zone 2 includes the region such as woods and fields, salt pond, and stream. Zone 3 includes factory lot, parking lot, road, railroad area, and military facilities. The concentration of zinc which was highest level among it of other heavy metals was similar to the level of Zone 2. While the other compound was lower than the level of Zone 1. The ultrasonic treatment has great effect on reduction and recycling of sludge sediment according to decreased concentration of heavy metals in sediment.

Table 7. The standard of soil pollution (Unit: mg/kg)

	Concern level of soil pollution			Countermeasure level of soil pollution		
	Zone 1	Zone 2	Zone 3	Zone 1	Zone 2	Zone 3
Cd	4	10	60	12	30	180
Pb	200	400	700	600	1,200	2,100
Cu	150	500	200	450	1,500	6,000
Zn	300	600	2,000	900	1,800	5,000

Chapter 4. PAHs

I. Research background of PAHs

1.1.Definition

PAHs (Polycyclic aromatic hydrocarbons) are hydrocarbons that contain at least two or more connected benzene rings. Material with 2～4 benzene rings is adsorbed in the form of gas and particulate matter, and material with five or more benzene rings is adsorbed by most particulate matter. PAHs belong to POPs (Persistent organic pollutants) and the basic properties of the POPs are toxicity, persistency, bioaccumulation, multimedia fate, and long-range transport. PAHs have a little solubility in water, low degradation ability but high affinity for the material. Therefore, PAHs are very stable. US Environment Protection Agency designated 16 priority PAHs. Chemical structures of those PAHs are shown on Figure 22.

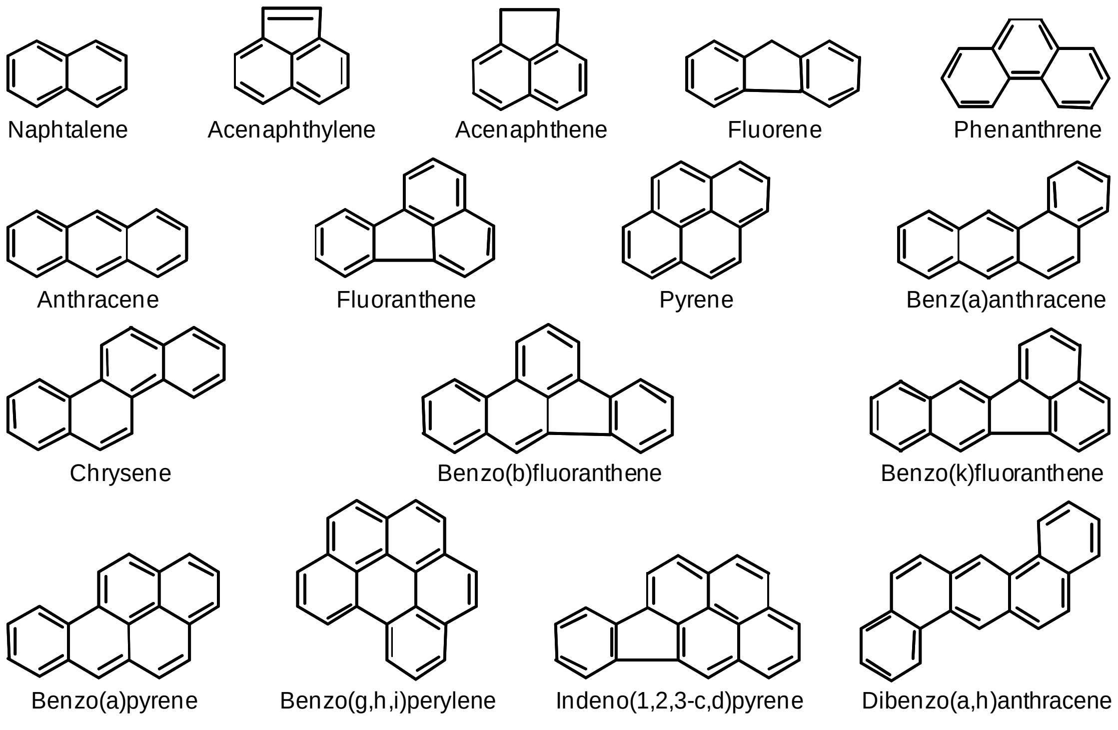


Figure 22: Structures of 16 PAHs on the EPA priority pollutants list

1.2.Physical and chemical properties

PAHs have common characteristics that the solid state at room temperature, the boiling point and melting point is high and vapor pressure is low. Acceptance of PAHs becomes lower when benzene ring increases. PAHs can be filtered by organic solvent and have properties of lipophilic. The physical and chemical characteristics of PAHs differ depending on the number of carbon atoms and the connection pattern of the ring of molecular. The chemical stability increases when the ratio of carbon and hydrogen and the number of concentrated benzene ring increases. Also, the reactivity of PAHs become greater because of the weak double bond by twister on the location of carbon chemically. Thermodynamic stability of PAHs causes incomplete combustion which means incomplete generation of the chemical intermediates. Therefore, PAHs are adsorbed to particulate or organic substances in ecosystems and they should be decomposed by chemical reaction.

Table 8. Physical and chemical properties of PAHs (continuouosed)

Compound	Abbreviation	Molecular formula	Molecular weight	Melting point(˚C)	Boiling point(˚C)	Vapor pressure (kPa, 25˚C)	Log Kow	No. of ring
Naphthalene	Na	$C_{10}H_8$	128.18	80.2	218	1.1×10^{-2}	3.37	2
Acenaphthylene	Acy	$C_{12}H_8$	152.20	92～93	265～280	3.9×10^{-3}	4.07	2
Acenapthene	Ace	$C_{12}H_{10}$	154.20	90～96	279	2.1×10^{-3}	3.98	2
Fluorene	Flu	$C_{13}H_{10}$	166.23	116～118	293～295	8.7×10^{-5}	4.18	2
Phenanthrene	Phe	$C_{14}H_{10}$	178.24	96～101	339～340	2.3×10^{-5}	4.46	3
Anthracene	Ant	$C_{14}H_{10}$	178.24	216～219	340	3.6×10^{-6}	4.50	3
Fluoranthene	FlA	$C_{16}H_{10}$	202.26	107～111	375～393	6.5×10^{-7}	4.90	3
Pyrene	Py	$C_{16}H_{10}$	202.26	150～156	360～404	3.1×10^{-6}	4.88	4

Table 8. Physical and chemical properties of PAHs

Compound	Abbreviation	Molecular formula	Molecular Weight	Melting point(˚C)	Boiling point(˚C)	Vapor pressure (kPa, 25˚C)	Log Kow	No. of ring
Benzo(a)anthracene	BaA	$C_{18}H_{12}$	228.30	157～167	435	1.5×10^{-8}	5.63	4
Chrysene	Chr	$C_{18}H_{12}$	228.30	252～256	441～448	5.7×10^{-10}	5.63	4
Benzo(b)fluoranthene	BbF	$C_{20}H_{12}$	252.32	167～168	481	6.7×10^{-8}	6.04	4
Benzo(k)fluoranthene	BkF	$C_{20}H_{12}$	252.32	198～217	480～481	2.1×10^{-8}	6.21	4
Benzo(a)pyrene	BaP	$C_{20}H_{12}$	252.32	177～179	493～496	7.3×10^{-10}	6.06	5
Indeno(1,2,3-cd)pyrene	IcdP	$C_{22}H_{14}$	276.34	162～163	535	Ca 10^{-11}	6.86	5
Dibenz(a,h)anthracene	DbahA	$C_{22}H_{14}$	278.35	266～270	524	1.3×10^{-11}	6.58	5
Benzo(g,h,i)perylene	BghiP	$C_{22}H_{12}$	276.34	275～278	525	1.3×10^{-11}	6.78	6

1.3.Source of PAHs

The occurrence of PAHs can be divided into natural and anthropogenic activities. The natural emission generated by geochemical activities such as volcanic eruptions and forest fires. The emissions caused by anthropogenic activities can be classified into fuel combustion, incineration and other combustion. PAHs are mainly generated by PVC, plasticizer (naphthalene), pigment (acenaphtene, pyrene), dyes(anthracene, florancene), synthetic intermediates of pesticide, insect repellent, asphalt, and chreosote. In particular, artificial PHAs could have spill at high concentration through a process of direct production in spite of the less range of pollution. Pollutants such as wastewater including dye, lignocellulosic wastewater, other semiconductor, electronic circuits, processing plant wastewater, food (especially sugar factory) are emitted into the wastewater treatment plant which made PAHs.

Table 9. Classification of PAH source

Source	Features
Anthropogenic sources	Oil origin: petroleum products (ex: oil spills, road construction) Combustion origin: the combustion of fossil fuels, forest fires, residues such as coal, bunker C oil at high temperature in the refining process
Natural sources	Generated from terrestrial higher plants Generated by the biological origin of organic matter maturation process of the environment
Stationary sources	Residential heating, industrial production (coke, aluminum, iron, steel production, oil refining, shale oil), asphalt production and use, carbon black (production), power and heat production, incineration and open burning
Mobile sources	The combustion from automobiles (gasoline and diesel) engine Surface water during rainfall or urban runoff in accordance with various types of land uses

1.4.Distribution of PAHs

Vapor pressure is one of the most important physical properties when determining the distribution of compounds within the environment. Adsorption of substances is determined by the characteristics. For example, bicyclic species such as naphthalene compounds exists in the form of gas and compounds that contain several benzene rings is well adsorbed in particulate material. Generally, 100% of the naphthalene presents in the form of gas at 25˚C. The other hand, compounds of PHAs have five to six benzene rings exist as particulate matter significantly. And PAH compounds have three to four benzene rings exist in gaseous and particulate at the same time. PAH compounds which exist in the atmosphere are transported over long distances without change and dilution.

1.5.Toxicity of PAHs

Toxicity for the exposure of sludge can be divided into acute toxicity and chronic toxicity. Acute toxicity become stunted when the plants were exposed to Benzo(a)pyrene at a concentration rate of 0.1% (1000 ppm). LD_{50} (50% lethal dose) was reported in vivo experiments using mice and rats. When Benzo(a)pyrene was administered to the abdominal cavity in mice, mice had a LD_{50} value of 250 mg/kg. And rats had a LD_{50} value of 50 mg/kg when the Benzo(a)pyrene was administered to the subcutaneous of rats.

PAHs affects on human blood when exposed for a long period of time and the impact of PAHs have been identified through biological experiments using animal. However, the symptoms are not always expressed.(consistent?) For example, when experimental mice were treated with 120 mg/kg of Benzo(a)pyrene a day, one of mice died with weight loss and shown the symptom of decreased bone marrow function. The other mice were not observed with any changes or symptoms.

1.6.Carcinogenic of PAHs

Some substance of PAHs has carcinogenic. Benzo(a)pyrene of PAHs is a well-known carcinogen and its carcinogenicity appears in almost all animal species. People who have been exposed for three week suffer from skin cancer. Cancer caused by exposure to Benzo(a)perene such as lung cancer, skin canser or scrotum are now becoming popular because of pollution such as cigarette smoke.

II. Sludge sampling and ultrasonic treatment for analysis of PAHs

2.1.Sludge sampling for analysis of PAHs

The sludge samples were collected from a WWTP, in October 2012. There are a lot of scums in the thickener and the sludge in here began to stink. The color of sludge in settling tank appeared red and brown. The collected sludge samples were transferred to the lab immediately and then stored for shorter than 24 h at 4˚C. We experimented immediately to minimize the impact of corruption and microorganism proliferation in sludge.

Figure 23: Sludge sampling for analysis of PAHs

2.2.Ultrasonic treatment for analysis of PAHs

After inserted to beakers (1,000 mL), 21 individual samples (750 mL) were treated using ultrasound in order to confirm the concentration of PAHs by ultrasonic treatment. The irradiation time was from 5 min to 30 min and intensity was 600 W.

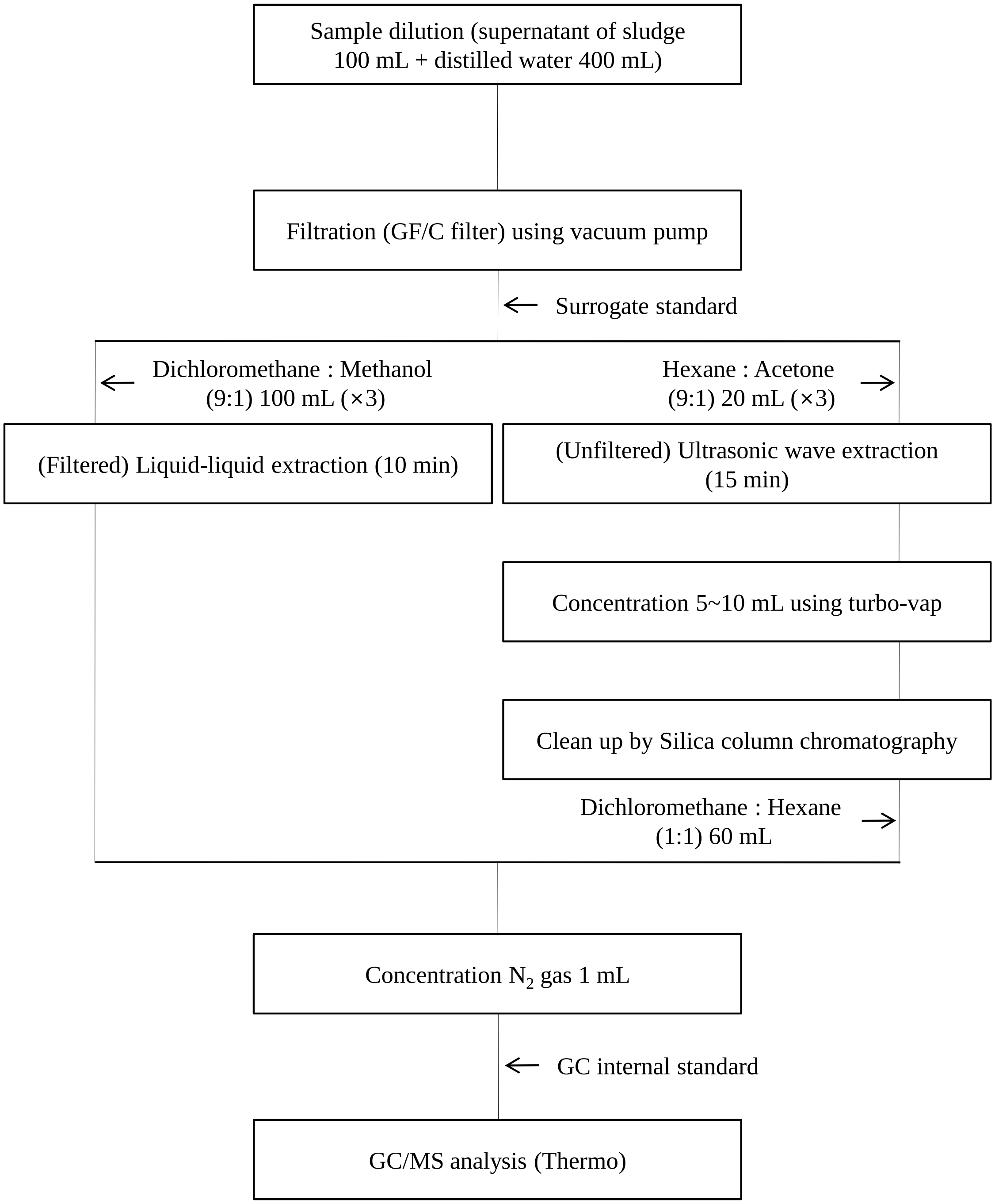
III. Analysis of PAHs

3.1. Analysis of PAHs for supernatant in sludge

In the sludge to analyze the changes in the concentrations of PAHs by ultrasonic treatment, sludge were separated from the supernatant and precipitates by centrifugation. The supernatant was kept after centrifugation at 4 ˚ C immediately.

In other to analysis of PAHs in the supernatant of the sludge, the samples were diluted by mixing the supernatant 100 mL with distilled water and 400 mL. Mixed sample filters using a glass fiber filter paper (GF/C filter). Filtrate were the liquid-liquid extracted for 10 min with a mixture of 9:1 dichloromethane : methanol and surrogate standard (Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrisene-d_{12}, Perylene-d_{12}) 100 ng and this process was repeated three times. After that, the extracts were concentrated using N_2 gas until 1 mL.

GF/C filter were ultrasonically extracted for 15 min with a mixture of 9:1 hexane : acetone and surrogate standard (Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrisene-d_{12}, Perylene-d_{12}) 100 ng. This process was repeated three times. Extract was concentrated until 5 ～10 mL using a turbo-vap. Concentrates were purified through a column consisting 5 g of silica gel and 5 g of sodium sulfate with a mixture of 1:1 dichloromethane : hexane. Purified samples were concentrated using N_2 gas until 1 mL.



Surrogate standards: Naphthalene-d_8, Acenaphthene-d_{10}, Phemamthrene-d_{10}, Chrysene-d_{12}, Perylene-d_{12}

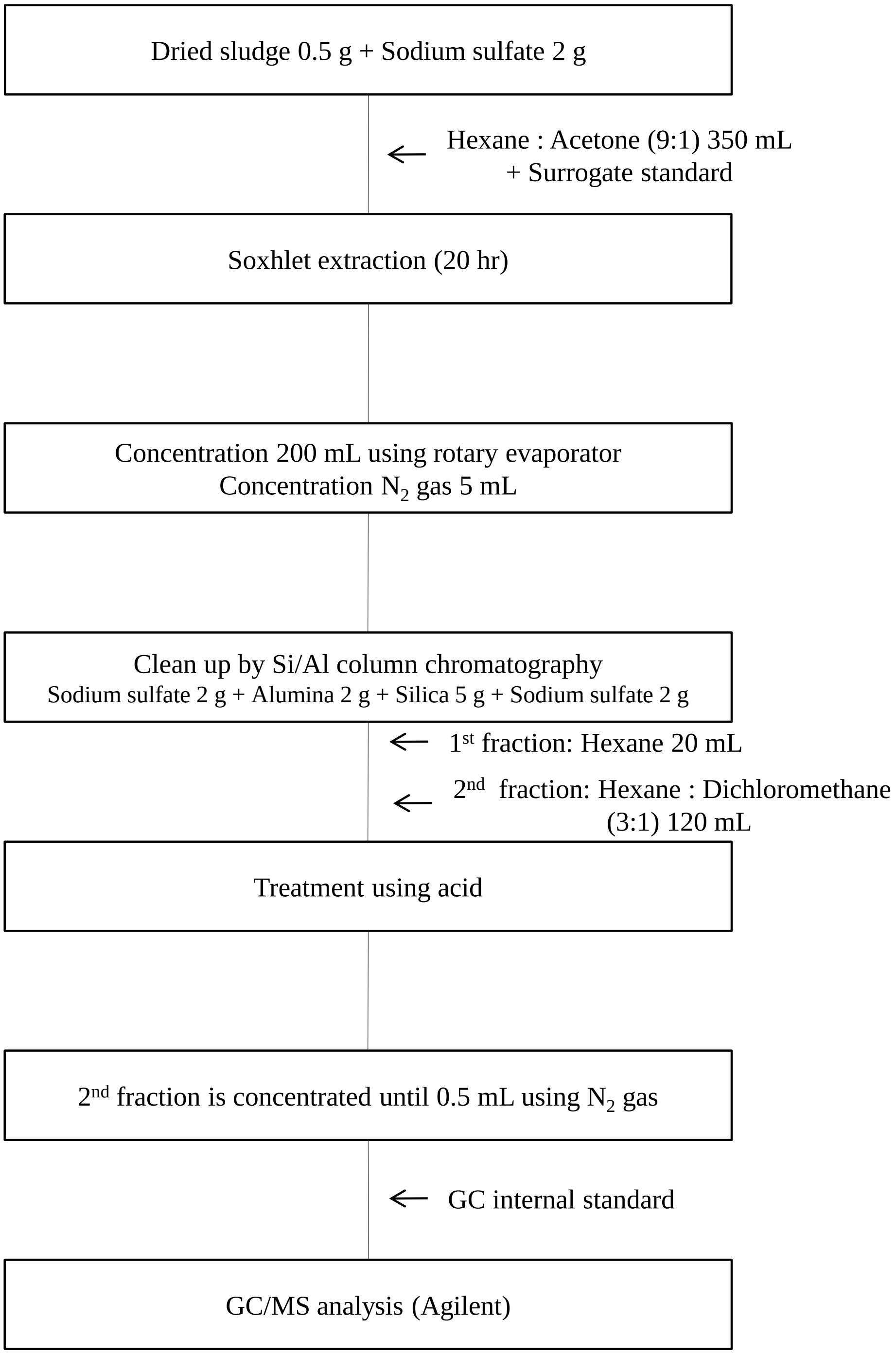
Internal standard: p-Terphenyl-d_{14}

Figure 24: Analytical procedures for PAH concentration of supernatant in sludge

3.2.Analysis of PAHs for sediment in sludge

The precipitate was dried for 24 hours at 120 ˚ C by using electric ovens. In order to analyze the sludge of PAHs in the sediment, 0.5 g of dried sample and 2g of sodium sulfate were extracted in a soxlet apparatus which was filled with a mixture of 9:1 (hexane : 350mL of acetone and 500ng of surrogate standard) (Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrisene-d_{12}, Perylene-d_{12}) for 20 hr.

The extract was concentrated until it came to 200 mL using a rotary evaporator then it was concentrated until it came to 5mL using a N_2 concentrator. Concentrates were purified through a column consisting 2 g of sodium sulfate, 2 g of alumina, 5 g of silica gel, and 2 g of sodium sulfate with a mixture of 1:1 (dichloromethane : hexane). First fraction which was collected with 20 mL of hexane contained interfering substances. The second fraction which was collected with a mixture of 3:1 (hexane : dichloromethane 120 mL). Second fraction samples were concentrated using N_2 gas until they came to 0.5 mL.



Surrogate standards: Naphthalene-d_8, Acenaphthene-d_{10}, Phemamthrene-d_{10}, Chrysene-d_{12}, Perylene-d_{12}

Internal standard: p-Terphenyl-d_{14}

Figure 25: Analytical procedures for PAH concentration of sediments in sludge

3.3.Instrumental analysis of PAHs

In the study, the concentrations of the 16 PAHs included in the US EPA list of priority PAH compounds were analyzed. The target compounds are naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benzo(a)anthracene (BbA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IcdP), divenzo(a,h)anthracene (DahA), benzo(g,h,i)perylene (BghiP).

Finally, all extracts were analyzed for sixteen PAHs with internal standard 100 ng gas chromatographically (Agilent 7890A, U.S.A) equipped with a mass selective detector (Agilent 5975C, U.S.A) and condition is set up as: injection temperature=280℃, injection mode=splitless, carrier gas=helium (1.0 mL/min), column=DB-5MS (30 m × 0.25 mm × 0.25μm), oven condition=50°C (1 min, 10°C /min) → 300°C (5 min), Ionization Voltage=70 eV, mode=EI/SIM. In order to determine the extent of contamination over the procedure of the experiment, laboratory blanks were applied all over the course of the experiment.

To minimize contamination in the experiment, all glasses were washed in acetone (HPLC, GC, PRA grade) and hexane (PRA grade). The recovery of PAHs was resulted as 61~115%. To confirm accuracy, all samples were analyzed for 3 times, and relative standard deviation (RSD) was under 30% for every sample. Limit of quantification (LOQ) was determined as 10 times of standard deviation of values of lab blanks that analyzed for 7 times.

Figure 26: GC/MSD for PAH analysis

IV. Results and discussion of PAHs

4.1. Characteristics of PAHs of sludge

The levels of the total 16 PAHs included in the US EPA list of priority PAH compounds in the supernatant and sediment of wastewater sludge are shown in Figure 27 and 28. We investigated the level of PAH concentration in sludge before ultrasonic treatment. Most of compounds except Nap and Phe have low concentration in supernatant. Nap is present in the air as a large amount[34] thus it is possible to show high concentration level. Terephthalic acid is the main source of sludge in the WWTP and is an isomer of phthalic acid and isophthalic acid. Terephthalic acid is produced by the catalytic oxidation of naphthalene[35] and chemical constitution looks like Figure 29. Therefore, we suggest the reason for high concentration of Nap in sludge was terephthalic acid was the main source of WWTP. Some studies were reported PAHs were disassembled or combined by external energy. [36,37] The disassembled OH radical by ultrasonic was possible to combine other material including sludge thus, grasp of sludge component is very important. In sediment, most of compounds were detected higher than100 ng/g and Acy was show highest level. The concentration of Acy is also high in the other results with different condition. Thus we should study about relations between source of sludge and PAH concentration.

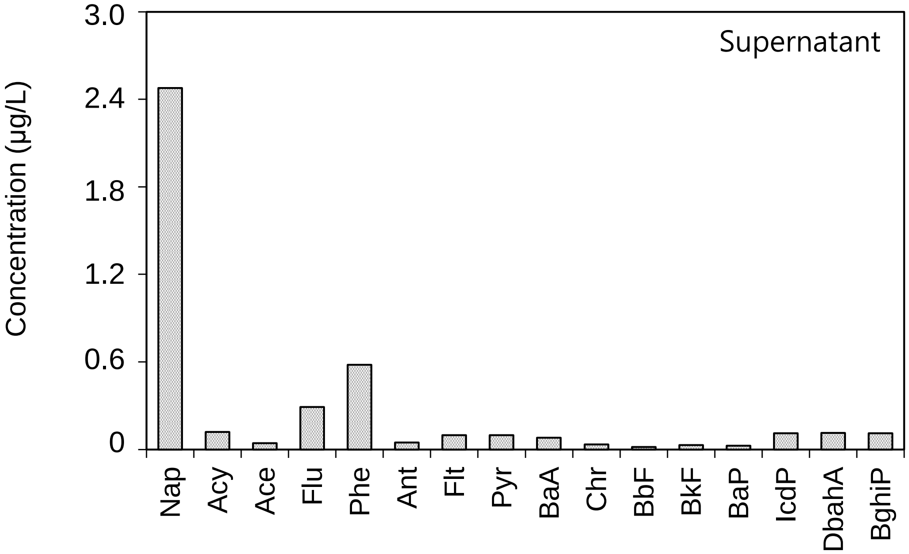


Figure 27: Distribution patterns of PAHs in supernatant before ultrasonic treatment

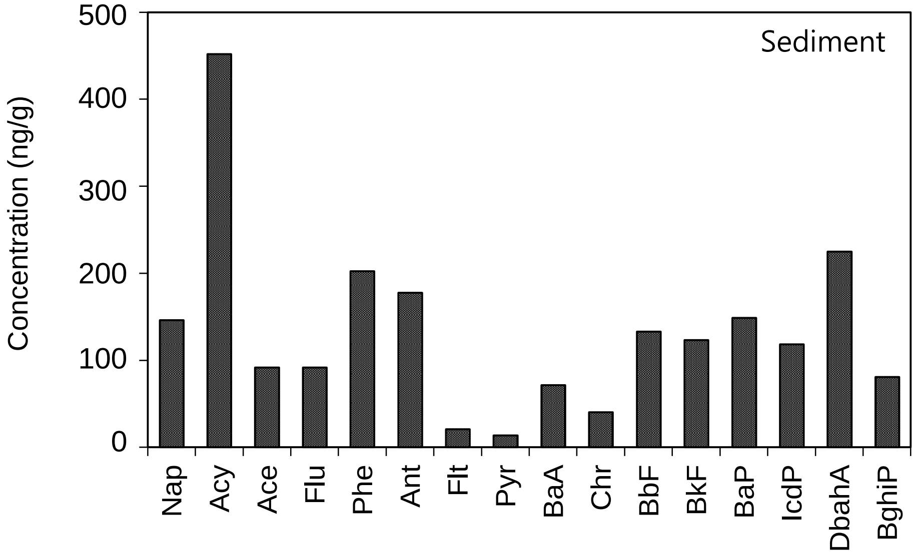


Figure 28: Distribution patterns of PAHs in sediment before ultrasonic treatment

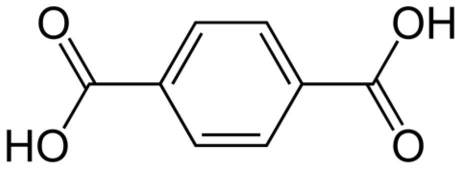


Figure 29: Chemical structure of terephthalic acid

4.2.Changes in PAH levels and patterns by ultrasonic treatment

The concentrations of the 16 PAHs according to the ultrasonic treatment for each supernatant and sediment in the sludge are shown on Table 10. The distribution of concentration of PAHs with different rings in the supernatant is shown on Figure 30. The concentrations of filtered PAHs increased until 15 min and decreased afterward. While the concentration of unfiltered PAHs increased rapidly after 15 min. The reason for the phenomenon is considered to be congested in GF/C filters. When treating sludge using ultrasonic, a lot of cell walls of microorganism in sludge were disintegrated. Thus, the pieces of cell walls were piled up on the filter and did not pass through. Also amount of C, H, O, and N in configuration elements of sludge was approximately 48%. The element was similar to the configuration elements of protein. According to the document reported from the Korea Food and Drug Administration in 2008, PAHs (especially BaP) depends on the existence of protein in tissue. Thus, concentration of PAHs increased due to absorption in protein. Compared with the result of TSS and microscopy with these results (Figure 32), they changed a lot when it comes to the disintegration of sludge at that same time. Thus, we confirmed that the disintegration of microorganism by ultrasonic treatment affects on the concentration of trace-pollutants.

The ratio of unfiltered PAHs with three benzene rings (Acy, Ace, Flu, Ant, and Phe) increased greatly with increased ultrasonic irradiation time. We considered the reason why the concentration of PAHs increased and found out that the main reason was the leaching of supernatant by ultrasonic treatment. We also suggested the reason for this phenomenon was the relationship between source (terephthalic acid) and PAHs such as Nap[35]. Therefore, to identify the reason certainly, we should find the relations between PAH concentrations and constituent of microorganisms in sludge after confirming of constituent closely.

On the other hand, the concentrations of PAHs in the sediment were reduced and the changed ranges in its concentration were not wide (Figure 31). The distributions of the total 16 PAHs with different rings appeared in the order of two rings > five rings > three rings > four rings > six rings. The distinct changes of the distribution depending on each ring were not observed in these results which were different with the results on the supernatant. Since the PAH concentrations in the sediment were much higher than the concentration in the supernatant.

Table 10. Concentration of PAHs due to ultrasonic treatment

PAHs	Supernatant (µg/L)				Sediment (ng/g)	
	Filtered phase		Unfiltered phase			
	0 min	30 min	0 min	30 min	0 min	30 min
Nap	1.17	2.48	2.03	5.08	159.46	155.19
Acy	0.06	0.11	0.01	0.12	428.37	448.35
Ace	0.01	0.60	0.01	0.29	61.24	91.16
Flu	0.14	0.17	0.09	0.63	91.99	89.66
Phe	0.24	0.34	0.30	2.97	201.19	193.24
Ant	0.02	0.04	0.02	1.27	176.59	171.60
Flt	0.03	0.19	0.08	0.39	16.80	14.37
Pyr	0.04	0.74	0.06	0.25	9.57	9.92
BaA	0.02	0.04	0.06	0.08	68.21	58.25
Chr	0.02	0.04	0.02	0.06	38.39	46.07
BbF	0.01	0.02	0.01	0.03	132.52	131.51
BkF	0.02	0.02	0.02	0.04	123.04	122.39
BaP	0.01	0.01	0.01	0.03	150.21	140.23
IcdP	0.02	0.11	0.01	0.14	106.27	77.79
DahA	0.03	0.12	0.01	0.06	224.04	222.07
BghiP	0.02	0.11	0.01	0.12	80.18	75.70
$\sum_{16}$ PAHs	1.84	5.13	2.74	11.54	2068.08	2047.50

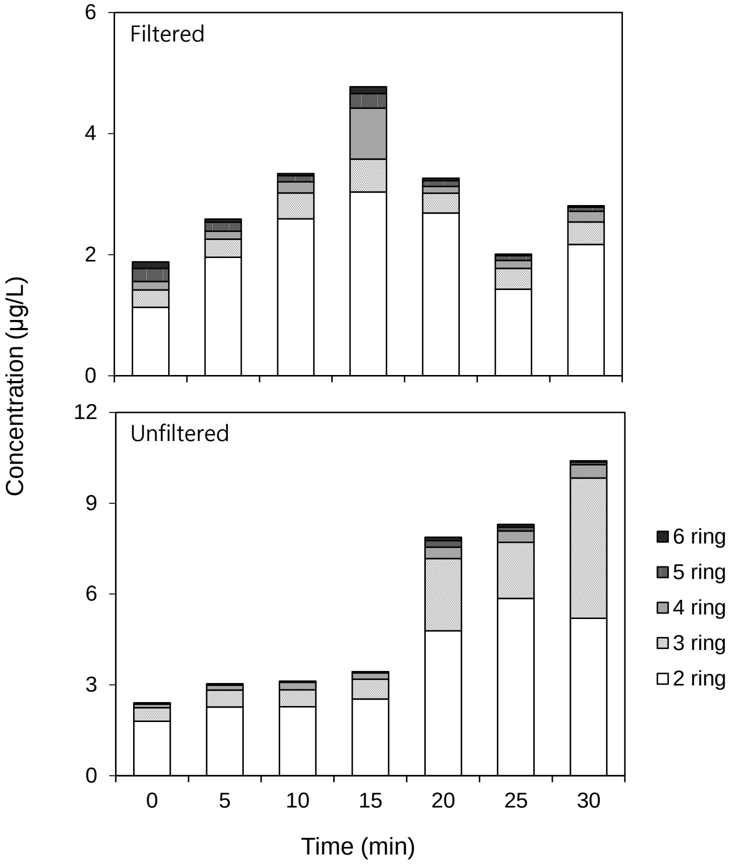


Figure 30: The concentration of PAHs in sludge supernatant after the ultrasonic treatment

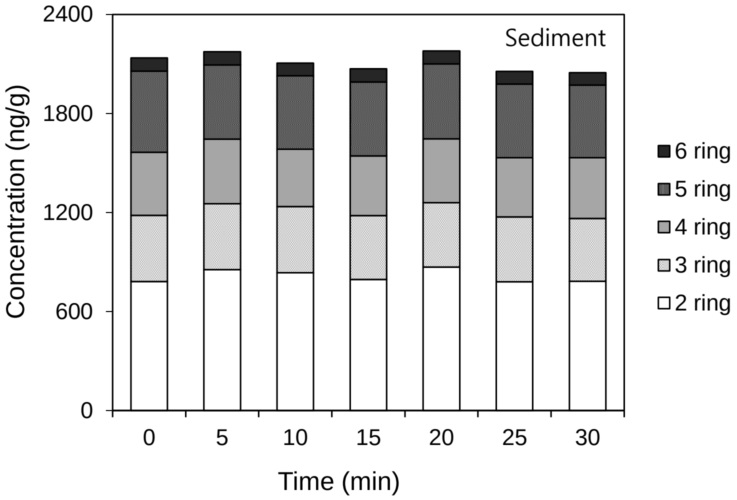


Figure 31: The concentration of PAHs in sludge sediment after the ultrasonic treatment

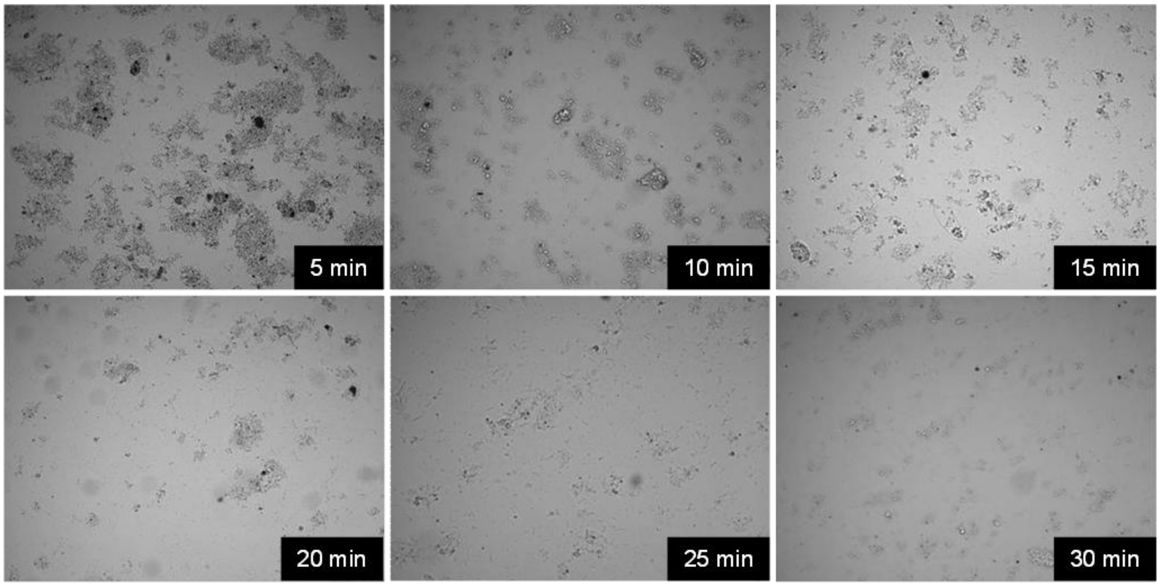


Figure 32: The observation for comparing with the concentration of sludge

4.3.Mass balance of PAHs

According to the result of ultrasonic treatment, the amount of the 16 PAHs for each supernatant and sediment in the sludge are shown in Figure 35. The amount of sludge was calculated by multiplying concentration of sludge by the volume. For example, if there is the concentration of PAHs in sludge per a conical tube (2 ng/mL) and the volume of sludge per a conical tube (40 mL), the amount of PAHs is 80 ng. By increasing irradiation time, the volume and PAH concentration in supernatant increased while these were decreased in sediment. Thus, trend on the fate of PAHs was similar to that of the PAH concentration.

The amount of PAHs respectively increased and decreased in supernatant and sediment. In particular, the amount of unfiltered PAHs in supernatant increased significantly. The amount of filtered PAHs increased 1.5 times (from 4.5% to 6.7%) and the amount of unfiltered PAHs increased 4.3 times (from 5.7% to 24.7%) whereas the amount of PAHs in sediment decreased 1.3 times (from 89.7% to 68.7) by the ultrasonic treatment. According to these results, the fate of unfiltered PAHs was seriously influenced by ultrasonic treatment.

Table 11. Amount of PAHs due to ultrasonic treatment

PAHs	Supernatant (ng)				Sediment (ng)	
	Filtered phase		Unfiltered phase			
	0 min	30 min	0 min	30 min	0 min	30 min
Nap	27.53	60.32	49.31	133.08	86.30	70.11
Acy	2.28	2.64	1.44	3.72	231.02	202.00
Ace	1.10	0.85	0.25	9.25	33.10	41.12
Flu	4.21	5.56	4.83	20.10	49.75	40.50
Phe	7.10	9.37	10.90	94.90	108.02	87.33
Ant	0.59	0.74	0.88	40.70	95.51	77.55
Flt	1.17	1.74	1.88	12.32	9.09	6.49
Pyr	1.67	2.74	1.38	8.02	5.18	4.48
BaA	1.42	1.18	1.10	2.46	36.91	26.30
Chr	0.52	0.65	0.55	1.38	20.70	20.80
BbF	0.27	0.57	0.27	0.96	71.70	59.42
BkF	0.47	0.52	0.47	1.14	66.55	55.20
BaP	0.39	0.46	0.39	0.99	81.20	63.31
IcdP	3.24	0.70	0.19	1.36	57.53	35.10
DahA	3.07	0.97	0.45	0.46	121.00	100.01
BghiP	3.24	0.71	0.19	1.22	43.33	34.22
$\sum_{16}$ PAHs	58.27	89.72	74.48	332.06	1116.89	923.94

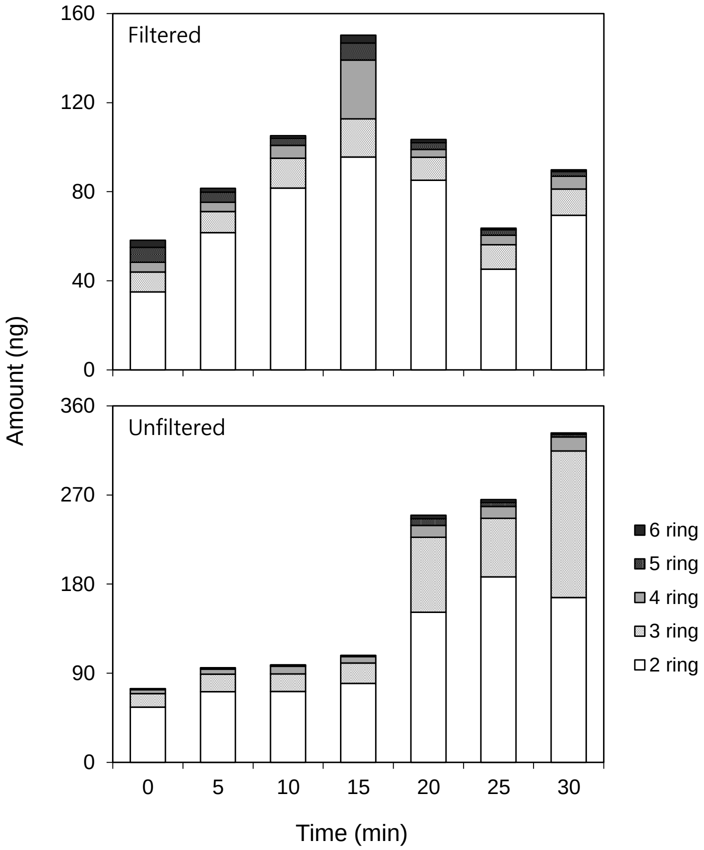


Figure 33: Time trends of PAH amount in sludge supernatants after the ultrasonic treatment

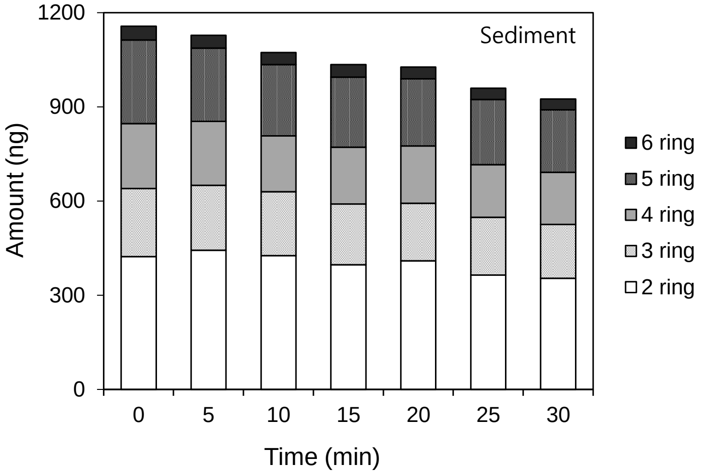


Figure 34: Time trends of PAH amount in sludge sediment after the ultrasonic treatment

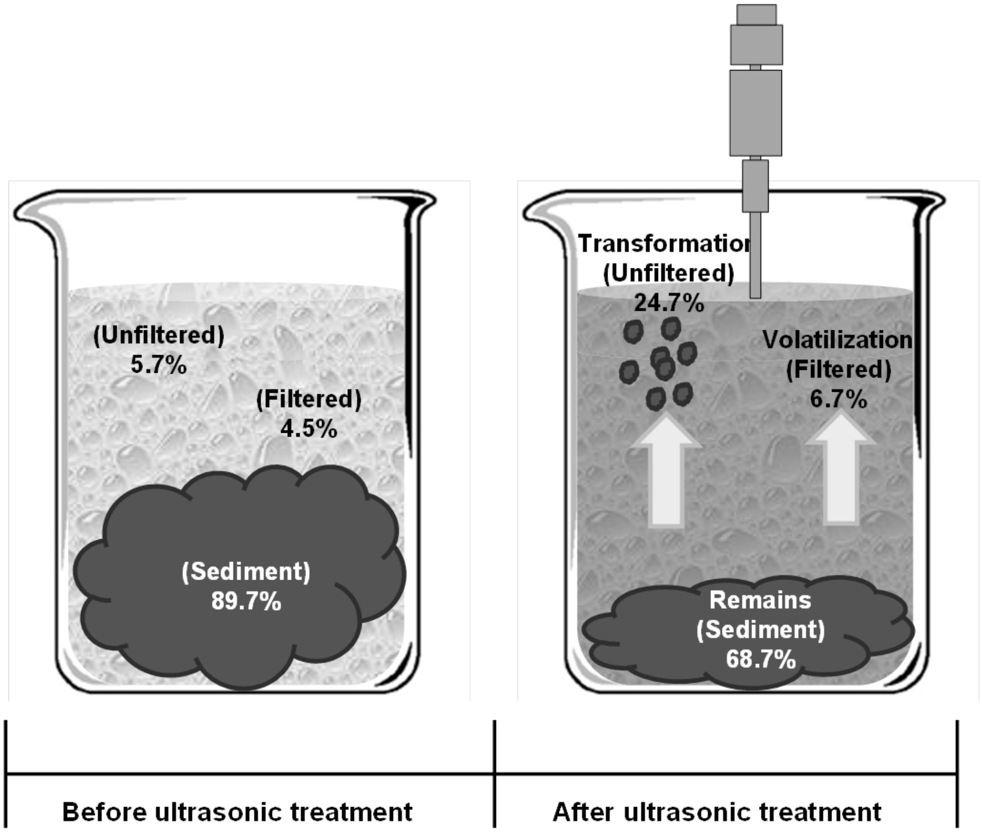


Figure 35: Mass balance of sludge due to ultrasonic treatment

Chapter 5. Conclusions

A lot of studies reporting about ultrasonic treatment have a great effect on reduction of the sludge. Previous studies that tried to clarify the optimal conditions of ultrasonic treatment were performed but studies on the fate of pollutants in sludge using ultrasonic treatment have been rarely reported. In this study, the concentrations of PAHs and heavy metals in each supernatant and sediment were investigated and the fate of trace-pollutants in sludge was confirmed based on these results. The concentrations of PAHs and heavy metals in supernatant increased while they were decreased in sediment by ultrasonic irradiation time because of the elution from sediment to supernatant. As a results of PAH analysis, the concentration of Nap in supernatant of sludge was highest and the concentrations of low molecular weight PAHs were high in sediment of sludge. We suggest the reason for the phenomenon is the source of sludge which is mostly made of terephthalic acid. We also confirmed that the trend of amount (fate) treated by ultrasonic treatment was similar to the trend of concentration treated by it. The concentration ratio and amount ratio of unfiltered PAHs in supernatant increased significantly by leaching trace-pollutants. According to these results, the sources of sludge and ultrasonic treatment have huge impact on concentration and the fate of trace-pollutants. Thus, leached trace-pollutants in supernatants are possible to be the source of sludge treatment in WWTP. On the other hand, the trace-pollutants in sediment decreased stably by extracting them from the sediment of sludge due to ultrasonic treatment which can be used more safely. In order to handle the sludge, the ultrasonic treatment is effective and economical if the technique for treatment of trace-pollutant in supernatant is developed as low expense. Therefore, ultrasonic treatment considering both sludge reduction and safe recycling should be developed by performing continuous monitoring of trace-pollutants in sludge using ultrasonic treatment.

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