

國立交通大學

環境工程研究所

碩士論文

結合鹼化與超音波法降解污泥中鄰苯二甲酸酯類(PAE)之研究

PAE removal from sewage sludge by alkalization and ultrasonic degradation



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中華民國九十九年四月

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摘要

鄰苯二甲酸酯類 (phthalate acid esters, PAEs) 被廣泛地運用於工業用途中，由於使用含 PAEs 產品可導致 PAEs 流至污水處理廠內，而實行污水處理過程中，高分子量 PAEs 如鄰苯二甲酸二正丁酯 (dibutyl phthalate, DBP)、鄰苯二甲酸二-(2-乙基己基) 酯 [di-(2-ethylhexyl) phthalate, DEHP] 與鄰苯二甲酸丁基苯甲酯 (butylbenzyl phthalate, BBP) 等容易附著於污泥顆粒表面上，隨之傳入污泥處理單元而不易處理，因此，利用污泥前處理程序去除污泥中所含之 PAEs 實有其必要性。本研究係結合鹼化與超音波程序做為前處理法降解污泥中之 PAEs，期能有效減少污泥中 PAEs 之含量，以利後續生物處理之進行。

污泥中 DBP、DEHP 與 BBP 之初始濃度分別為 718、215 與 8 毫克/公斤-乾重，污泥前處理實驗係添加不同濃度之氫氧化鈉於污泥中，均勻攪拌 24 小時後進行超音波反應。超音波之頻率為 20 仟赫茲，超音波密度為 1 瓦特/毫升，強度為 55 瓦特/平方公分，污泥總固體濃度則為 3%。中央合成設計 (central composite design, CCD) 設定鹼化與超音波前處理之變異參數分別為氫氧化鈉濃度 (0 - 8 毫莫爾) 與超音波反應時間 (0 - 15 分鐘)。

污泥經氫氧化鈉鹼化後，僅對 DBP 具明顯去除效果，DEHP 與 BBP 則無顯著去除，同時，每加入 1 毫莫爾氫氧化鈉即可增加 8.37 毫克/公升之溶解性化學需氧量 (soluble chemical oxygen demand, SCOD)。結合鹼化與超音波前處理後，鹼化前處理對 DBP 去除之貢獻程度高於 90%，且對 SCOD 上升之貢獻程度高於 60%。由 CCD 與反應曲面法對 SCOD 上升之分析結果得知，最佳氫氧化鈉濃度與超音波反應時間分別為 68 毫莫爾與 10 分鐘。

關鍵字：鄰苯二甲酸酯類 (PAE)、污泥、鹼化、超音波程序、中央合成設計 (CCD)



PAE removal from sewage sludge by alkalization and ultrasonic degradation

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Abstract

Phthalate acid esters (PAEs) are widely used in various industries where the usage of PAEs containing products leads to the entrance of PAEs into wastewater treatment plant. During wastewater treatment processes, higher molecular weight PAEs including dibutyl phthalate (DBP), di-(2-ethylhexyl) phthalate (DEHP) and butylbenzyl phthalate (BBP) could be easily attached to the surfaces of sewage sludge and transferred to sludge treatment units. Therefore, sludge pretreatment to remove PAEs before sludge treatment and disposal is necessary. In this study, alkalization combined with ultrasound was adopted for removing the PAEs from sewage sludge.

The initial DBP, DEHP and BBP concentrations in sewage sludge were 718, 215 and 8 mg/kg-dw, respectively. Pretreatments were carried out by adding sodium hydroxide (NaOH) individually for designed concentrations to sewage sludge and mixing gently for 24 hours followed by sonication. The frequency of ultrasound was 20 kHz with the ultrasound power density and power intensity of 1 W/mL and 55 W/cm². The total solids (TS) concentration of the sewage sludge was 3%. The central composite design (CCD) was used

in this study to find out the better operation condition which the designed parameters were NaOH concentration (0 - 80 mM) and sonication time (0 - 15 min).

NaOH alkalization of sewage sludge led to DBP removal only; removals of DEHP and BBP were almost zero. Increase of the soluble chemical oxygen demand (SCOD) in pretreated sewage sludge was 8.37 mg/L per 1 mM NaOH addition. Alkalization was responsible for more than 90% of DBP removal and more than 60% in SCOD increase in the alkalization-sonication pretreatment. The optimal NaOH concentration and sonication time were estimated as 68 mM and 10 min based on the CCD and response surface plots, respectively.

Keywords: Phthalate acid ester (PAE), Sewage sludge, Alkalization, Sonication, Central composite design (CCD)



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時光飛逝，研究所生涯即將於此刻告一段落。非常榮幸在此時此刻能夠完成碩士論文，也順利通過論文口試，代表這兩年來的腦汁與血汗，值得換取寶貴的收穫。在此研究所生活中，參雜無數的苦衷、歡樂、熱血與悲傷，以至於研究室不僅是做研究的環境，也是培養感情的好所在。辛苦代價已過去，但此回憶仍浮現於腦海裡。

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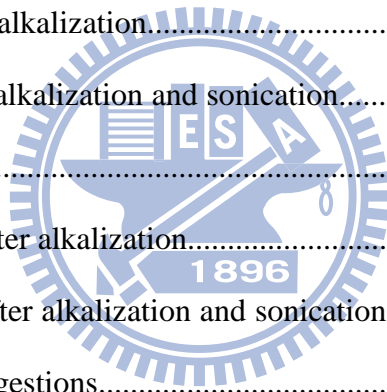
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Chapter 1 Introduction

1-1 Research background

Plasticizers containing several phthalate acid esters (PAEs) are widely used in industries because of its stability, fluidity and low volatility (Woodward, 1988). The usage of PAEs containing products lead to the release of PAEs to the environment, especially in wastewater, natural water, surface water, sediment, soil and sludge, respectively (Staple et al., 1997; Vatali, 1997; Staples et al., 2000; Vikelsee et al., 2002; Yuan et al., 2002). PAEs are well-known endocrine-disrupting compounds, which have been proven as toxic compounds to human beings and animals. Moreover, PAEs are accumulated in the bio-organisms to affect the food chains in ecosystems. USEPA listed six PAEs including dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), butylbenzyl phthalate (BBP), di-n-octyl phthalate (DOP) and di-(2-ethylhexyl) phthalate (DEHP) as the priority pollutants, indicating that the above six PAEs should be effectively removed from the contaminated sources (Cecil et al., 1992).

Since 1920, PAEs were applied as the plasticizers and continued to be the largest class of plasticizers in the 21st century. PAEs were hydrophobic, odorless and colorless liquids, but they could be easily dissolved by organic solvents. DBP has gained a dominant position among plasticizers, which is widely used in cosmetics, nail polish, printing inks, specialized adhesive formulations, and other personal care products (Gomez-Hens and Aguilar-Caballos, 2003). DEHP is the most widely used plasticizer since the 1930s, which is used in flooring, wall covering, car undercoating, cables, foot wear, clothes, gloves, medical devices, toys, car interior, tarpaulins, furniture, paints, printing ink and adhesives

(Rank, 2005). BBP was extensively used in vinyl flooring, synthetic leather, inks, adhesives, and as a component of materials used in contact with food products (Gomez-Hens and Aguilar-Caballos, 2003). In addition, DEHP and BBP have wide applications as plasticizers in the polymer industry to improve flexibility, workability and general handling properties, which occupied 80% in all of PAEs (Gomez-Hens and Aguilar-Caballos, 2003). Therefore, if the PAEs are contained in the sludge, they should be removed by suitable pretreatment methods to get great social and economical benefits.

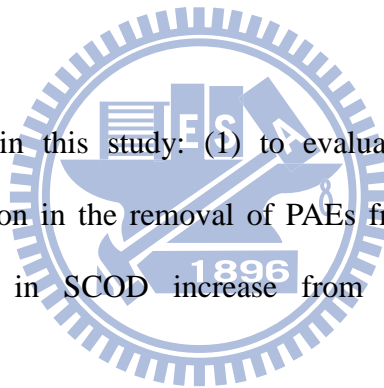
When the PAEs containing wastewater is introduced into a wastewater treatment plant, the higher molecular weight PAEs, i.e. DBP, DEHP and BBP, could not be easily removed by physical, chemical and biological methods during wastewater treatments. They could be easily attached to the surface of sludge and then transferred into sludge treatment units. Therefore, PAEs in the sewage sludge must be removed during sludge treatments. Recently, ultrasound pretreatment is considered as the novel sludge pretreatment technology, which could be used in ultrasound wave to react with sewage sludge. Chiu et al. (1997) and Wang et al. (2005) combined alkalization and sonication as a pretreatment to facilitate the soluble organics increase and remove recalcitrant and toxic organics. The successful pretreatment by this combination could facilitate the applications of sludge cake for land application, composting and landfill (Spinosa, 2001).

1-2 Research scopes

The feasibility of alkalization, sonication and their combination for the removal of PAEs from sewage sludge was investigated in this study. In pretreatment experiments, different NaOH additions and sonication time were carried out. The experiments were designed by the central composite design (CCD) and the PAEs removal and increase in soluble chemical oxygen demand (SCOD) were used to evaluate the treatment feasibility by different methods.

1-3 Research goals

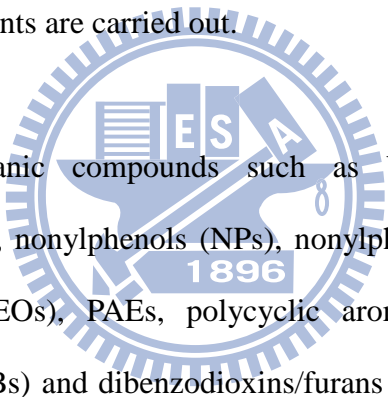
There were two goals in this study: (1) to evaluate the effect of alkalization, sonication and their combination in the removal of PAEs from sewage sludge and (2) to investigate the improvement in SCOD increase from sewage sludge by different pretreatments.



Chapter 2 Literature review

2-1 Hazardous pollutants in sewage sludge

Sewage sludge is a complex mixture containing organic compounds, heavy metals, microorganisms and nutrients, respectively. Organic compounds such as biodegradable organics, recalcitrant organics, toxic organics and microorganisms (composed of beneficial microorganisms for final disposal and harmful pathogens) are generally found in sewage sludge. In order to remove the toxic pollutants from sewage sludge, many physical, chemical and biological treatments are carried out.

The logo of the Water Engineering and Science (WES) department is a circular emblem. It features a gear-like outer border. Inside the circle, there is a stylized building with the letters 'W', 'E', and 'S' on its facade. Below the building, the year '1896' is inscribed. The logo is semi-transparent and overlaid on the text.

Several hazardous organic compounds such as bisphenol A (BPA), linear alkylbenzene sulfonates (LAS), nonylphenols (NPs), nonylphenol diethoxylates (NPDEs), nonylphenol ethoxylates (NPEOs), PAEs, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and dibenzodioxins/furans (PCDD/Fs) were observed in sewage sludge (Angelidaki et al., 2000; Fauser et al., 2003; Barnabe et al., 2007). Moreover, plasticizers, pharmaceuticals, personal care products, pesticide residues and flame retardants were also observed in sewage sludge. The gasoline additives had potential carcinogenic, teratogenic and endocrine disrupting properties (Barnabe et al., 2007). The release of recalcitrant and endocrine disrupting chemicals into the environment could cause a serious threat to the ecosystem (Barnabe et al., 2007). The releases of these toxic pollutants are due to the human activities, atmospheric deposition on the soil, urban runoff and industrial emissions. During wastewater treatment, the toxic pollutants could be accumulated in sewage sludge due to their non polar and hydrophobic nature that favored adsorption onto suspended solids. To decrease the harmfulness, toxic organic compounds must be controlled.

In Denmark, the municipal sewage sludge were produced approximately 170,000 ton/dry-matter in 1994 and 140,000 ton/dry-matter in 2002. In the last decade, approximately 65% of sewage sludge was used for agriculture purpose (Jensen and Jepsen, 2005). European Union (EU) concerned about the available purpose for sewage sludge and reported the Directive 86/278 on environmental protection for agriculture. Therefore, EU and Denmark Environmental Protection Agency set the limit value of hazardous organics as shown in Table 2-1. Sewage sludge treatment with toxic organic compounds removal could protect the ecosystem, avoid public reluctances over beneficial use and favor commercialization of the final product.

Table 2-1 Limit value of hazardous compounds in sewage sludge (Spinosa, 2001; Jensen and Jepsen, 2005)

Compound	Limit value (mg/kg-dw)	
	EU	Denmark
DEHP	100	50
LAS	2,600	1,300
NPs and NPEOs	50	10
PAHs	6	3
PCBs	0.8*	-
PCDD/Fs	100	-

*ng-TE/kg-dry matter

2-2 Physical and chemical properties of PAEs

The structures and characteristics of DBP, DEHP and BBP are listed in Figure 2-1 and Table 2-2, respectively. In general, PAEs are liquids at room temperature. All of these PAEs have melting points below -25°C and boiling points at about 350°C . The high boiling point of these PAEs could prevent thermal decomposition in the ambient temperature. The low melting point and high boiling point of these PAEs contribute to their usefulness as plasticizers, heat transfer fluids and carriers. Water solubility is an extremely important property that influences the biodegradation, bioaccumulation potential and aquatic toxicity. Water solubility is also a determining factor controlling the environmental distribution of chemicals. The more hydrophilic compounds with the shorter alkyl side-chains such as DBP are more soluble in water than those with the large alkyl-chains such as DEHP and BBP. The equilibrium distribution of an organic chemical between water and octanol (K_{ow}) is an important physical constant for predicting the tendency of a chemical to partition to water, sediment, sludge and soil. With increasing alkyl chain length, the $\log K_{ow}$ increases indicating greater hydrophobicity. Most of the dialkyl phthalates are soluble in common organic solvents such as benzene, toluene, xylene, diethyl ether, chloroform and petroleum ether. Vapor pressure plays an important role in the fate of fugitive emissions and other releases of PAEs to the atmosphere. The vapor pressures of PAEs are declined with increasing alkyl chain length. Ideal plasticizers are highly compatible with polymers, stable in both high and low temperature environments, sufficiently lubricative over a wide temperature range, intensive to solar ultraviolet radiation, resistant for leaching and migration and inexpensive (Rahman and Brazel, 2004).

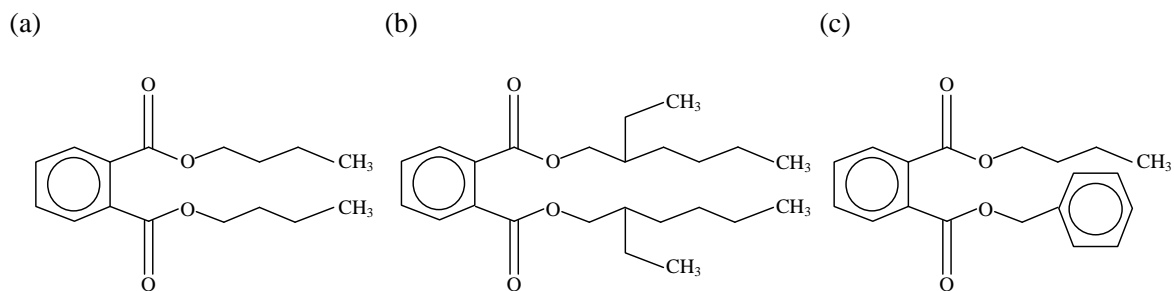


Figure 2-1 PAEs structures (a) DBP, (b) DEHP and (c) BBP

Table 2-2 Physical and chemical properties of PAEs (Woodward, 1988; Staples et al., 1997)

Characteristics	DBP	DEHP	BBP
CAS no. ^a	84-74-2	117-81-7	85-68-7
Formula	C ₁₆ H ₂₂ O ₄	C ₂₄ H ₃₈ O ₄	C ₁₉ H ₂₀ O ₄
Alkyl chain length	4	8	4, 6 ^e
Specific gravity	1.047	0.986	1.116
Molecular weight	278	390	312
Melting point (°C)	-35	-50	-35
Boiling point (°C) ^b	340	370	370
Flash point (°C)	189	225	390
Water solubility (mg/L)	11.2	0.003	2.7
Log K _{ow} ^c	4.45	7.50	4.59
Vapor pressure (mmHg) ^d	2.7×10 ⁻⁵	1.0×10 ⁻⁷	5.0×10 ⁻⁶

^aChemical abstracts service number

^bAt atmosphere

^cEquilibrium distribution of octanol/water partitioning

^dAt 25°C

^eAromatic ring

2-3 Origins of PAEs into sewage sludge and its effect on sewage sludge treatment

PAEs enter the environment during production, manufacture, leaching, migration and volatilization by the usage and disposal of the products (Heise and Litz, 2004). Also, PAEs are released to wastewater and then transferred into wastewater treatment plant. When PAEs containing wastewater is introduced into a wastewater treatment plant: (1) one part of PAEs is degraded by physical, chemical and biological treatment during wastewater treatments and (2) the other part is strongly adsorbed on the surface of sludge (Marttinen et al., 2003; Roslev et al., 2007; Dargnat et al., 2009). PAEs concentration of 2% was found in the treated water in which 70% was biodegraded and 28% was adsorbed in the sludge (Fauser et al., 2003). PAEs could be removed by chemical and biological methods; however, almost one-third of PAEs were still contained in the sewage sludge (Table 2-3).

Roslev et al. (2007) and Dargnat et al. (2009) proposed that the residual DEHP concentration was greater than DBP and BBP owing to its difficulty in biodegradation during sludge digestion. In addition, Cheng et al. (2000) analyzed the concentration of DEHP in three different wastewater treatment plants located in northern Taiwan and found that the concentration of DEHP in wastewater (including influent and effluent) and influent of sludge were lower than detection limits. However, after sludge treatment, the concentrations of DEHP were increased from 105.16 to 153.15 mg/kg-dw. These results indicate that the adsorbed DEHP in sludge would release in solution phase after sludge treatment.

Table 2-3 Average PAEs concentration in wastewater treatment plant

Site	Compounds	Wastewater treatment (µg/L)		Sludge treatment (mg/kg-dw)		Reference
		Influent ^a	Effluent	Influent ^b	Dewatered	
Min-Shen (Taiwan)	DEHP	ND ^c	ND	ND	142.86 ^d	Cheng et al. (2000)
Ba-Li (Taiwan)	DEHP	ND	ND	ND	105.16 ^e	
Di-Hua (Taiwan)	DEHP	ND	ND	ND	153.15 ^e	
Espoo (Finland)	DEHP	209.00	6.00	180.00	163.00 ^e	Marttinen et al. (2003)
Aalborg (Denmark)	DBP	20.48	2.38	ND	1.19 ^e	Roslev et al. (2007)
	BBP	37.87	3.13	ND	3.41 ^e	
	DEHP	71.89	4.92	ND	67.18 ^e	
Marne (France)	DBP	1.10	0.15	ND	0.09 ^f	Dargnat et al. (2009)
	BBP	1.12	0.30	ND	0.37 ^f	
	DEHP	22.46	5.02	ND	72.10 ^f	

^aWater containing municipal and industrial wastewater and returned sludge

^bSludge containing primary and biological sludge before sludge treatment

^cNot detected

^dDewatered sludge after aerobic digestion

^eDewatered sludge after anaerobic digestion

^fDewatered sludge without pretreatment, digestion and adjusting

2-4 Methods available for PAEs removal from sewage sludge

Many physical, chemical and biological methods are used for PAEs removal from sewage sludge in recent years. In physical and chemical catalogs, four methods such as hydrolysis, photodegradation, enzyme reaction and thermal reaction have been carried out to remove PAEs. PAEs could undergo two hydrolytic steps, producing first the mono-ester and one free alcohol moiety and a second hydrolytic step creating phthalic acid and a second alcohol (Staple et al, 1997). But the degradation rate was very slow, especially in DEHP. The aqueous hydrolysis half-life of DEHP was 2,000 years while the aqueous hydrolysis half-lives of DBP and BBP were 22 and 0.3 years (Gledhill et al., 1980; Wolfe et al., 1980). Staple et al. (1997) also proposed that on aqueous photolysis occurred through absorption of UV light from sunlight in the region of 290-400 nm could be used to remove PAEs. Shorter wavelengths were attenuated by passage through the atmosphere and water column, so that the half-lives of photodegradation for PAEs removal were as much as shorter than hydrolysis (Lertsirisopon et al., 2009). Chen (2009) mentioned that the DEHP removal by the combination with UV light and hydrogen peroxide was better than that by direct UV catalysis. More acid or more alkaline PAEs containing aqueous solution could get better photodegradation than the neutral aqueous solution (Kaneco et al., 2006; Lertsirisopon et al., 2009). Enzymatic treatment could effectively remove PAEs of sludge. Gavala et al. (2004) contrasted the PAEs removal between 100 and 1,000 enzymic units/L of enzyme concentration, in which the PAEs degradation rates of 1,000 enzymic units/L of enzyme reaction was faster than of 100 enzymic units/L. For 1,000 enzymic units/L of enzyme reaction, PAEs could be degraded more than 50% after a week at 28°C. Although thermal treatment could remove PAEs but the degradation rate was very slow. Gavala et al. (2004) demonstrated that PAEs were degraded less than 20% by thermal pretreatment at

70°C for one week.

Since the PAEs were removed from sludge by biological treatments, several operation conditions affected the degradation rates. Shelton et al. (1984) and Wang et al. (1996) demonstrated that the lower molecular weight PAEs were easily biodegraded than the higher ones. In anaerobic digestion, removal of DBP was higher than DEHP owing to the long side-chains in DEHP (Alatrisme-Mondragon et al., 2003). PAEs could be biodegraded in both aerobic and anaerobic conditions, but degradation rates were higher in aerobic than that in anaerobic condition (Angelidaki et al., 2000). Banat et al. (1999) proposed that the higher oxygen aeration rate was effective on the increase of DEHP removal; it was estimated that the DEHP could contact with more dissolved oxygen at the short time. Alatrisme-Mondragon et al. (2003) and Gavala et al. (2003) showed that DEHP accumulation in sludge coincided with a decrease in both gas production and in the efficiency of DBP removal. Chang et al. (2007) tested the single PAE aerobic biodegradation at different initial concentration. According to the first order kinetics of DBP biodegradation, the degradation rate constant (k) and half-lives ($t_{1/2}$) of 100 mg/kg-dw DBP of sludge were 0.794 day^{-1} and 0.9 day, while the values of k and $t_{1/2}$ of 1,000 mg/kg-dw DBP of sludge were 0.198 day^{-1} and 3.5 day, respectively. The results indicated that the higher initial concentration of DEHP led to the lower biodegradation rate. Chang et al. (2005) proposed that enough alkalinity could facilitate PAEs biodegradation even though alkalinity was increasing during biological reaction. Sludge might contain mesophilic bacteria and thermophilic bacteria. Mesophilic bacteria could live at 35°C environment while thermophilic bacteria could adapt at 55°C environment. Chang et al. (2005) and Roslev et al. (2007) conducted PAEs biological removal at different temperature in the range of 30 and 50°C, in which the best temperature of PAEs removal was 50°C. In other words, thermophilic bacteria could degrade PAEs faster than mesophilic bacteria.

2-5 Pretreatment for PAEs removal from sewage sludge

Many researchers pointed out that the goals of sludge pretreatment were to break the cell wall to facilitate the release of intracellular matter in the aqueous phase and break down many toxic and recalcitrant organic pollutants (Neis, 2002; Bien et al., 2004; Chang et al., 2007). Thus, sludge pretreatments were helpful for biological sludge digestion to get the better quality of sludge (Chiu et al., 1997; Lin et al., 1999; Kim et al., 2002; Gonze et al., 2003; Gronroos et al., 2005; Ding et al., 2006; Kim et al., 2009).

2-5-1 Alkalization pretreatment

The hydroxyl ions produced by alkalization could attack the cell walls of microorganisms and then release intracellular organics to liquid phase. Therefore, the types of alkaline reagents used in alkalization affected the efficiency of sludge pretreatment. Li et al. (2008) used sodium hydroxide (NaOH) and calcium hydroxide [$\text{Ca}(\text{OH})_2$] to demonstrate the efficiency of SCOD increase in pretreatment and the results indicated that NaOH was more applicable for sludge pretreatment than $\text{Ca}(\text{OH})_2$. Kim et al. (2003) used NaOH, potassium hydroxide (KOH), magnesium hydroxide [$\text{Mg}(\text{OH})_2$] and $\text{Ca}(\text{OH})_2$ as alkalization reagents in sludge alkalization pretreatment. When adding the same concentration of these reagents to sludge individually, the order of high efficiency of SCOD increase was: $\text{NaOH} > \text{KOH} > \text{Ca}(\text{OH})_2 > \text{Mg}(\text{OH})_2$. In $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ pretreatment, the disintegrated floc fragments and soluble organic polymers could be re-flocculated with the help of calcium and magnesium cations, so $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ were not applicable to conduct the sludge pretreatment.

In alkalization pretreatment, more NaOH concentration could get more SCOD increase

of sludge because higher hydroxyl ions enhanced the reaction rate between hydroxyl ions and organics. In addition to hydroxyl ion concentration, total solids (TS) contents of sludge also affected the alkalization efficiency. Higher sludge TS concentration could provide higher organics in sludge alkalization. Hence, the more TS of sludge increased more SCOD after alkalization (Lin et al., 1998; Kim et al., 2009).

Table 2-4 SCOD increase in different alkalization method

Authors	NaOH concentration (mM)	Reaction time (min)	TS (%)	SCOD increase (mg/L)
		200		3,100
Chiu et al. (1997)	40	350	1	4,000
		1,440		5,000
Lin et al. (1998)	30	1,440	0.5	844
			1	2,506
			2	3,016
Lin et al. (1999)	20	1,440	1	760
	40			1,120
Kim et al. (2009) ^a	7.78	ND ^b	0.4	830
			1.4	1,020

^aCombined with 20 kGy gamma-ray irradiation

^bNot detected

2-5-2 Ultrasound pretreatment

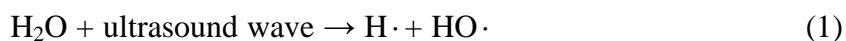
1. Physical mechanisms in sonication

During sonication, energy transportation is facilitated as electrical energy, acoustic energy, and chemical energy (Adewayi, 2001). When the ultrasound wave is propagated in the sludge, it generates a repeating pattern of compressions and rarefactions in sludge. As a result of reduced pressure, micro-bubbles are formed in the rarefaction regions. These micro-bubbles are known as cavitation bubbles containing vaporized liquid and gas that could be previously dissolved in the liquid phase. When the wave propagated, micro-bubbles oscillated under the influence of positive pressure and rapidly collapsed. Cavitation was the phenomenon where micro-bubbles were formed in the aqueous phase and expand to unstable size, then rapidly collapsed. The collapsing of the bubbles resulted in localized temperature up to 5,000 K and pressures up to 180 MPa. The sudden and violent collapse of huge numbers of micro-bubbles generated powerful hydro-mechanical shear forces in the bulk liquid surrounding the bubbles. The collapsing bubbles disrupted adjacent microorganisms by extreme shear forces, rupturing the cell wall and membranes. Hence, SCOD in sludge could increase during ultrasound reaction (Adewayi, 2001; Khanal et al., 2007).

2. Chemical mechanisms in sonication

Chemical mechanisms in sonication are listed below. When the ultrasound wave is propagated in the sludge, the heat could decompose H_2O into hydrogen radicals ($H\cdot$) and hydroxyl radicals ($HO\cdot$). During quick cooling, $H\cdot$ and $HO\cdot$ could recombine to hydrogen peroxide (H_2O_2) and H_2 . At the same time, $H\cdot$ could react with dissolved oxygen to form

$\text{HO}_2\cdot$ and it could transform to H_2O_2 . Hence, $\text{H}\cdot$, $\text{HO}\cdot$, $\text{HO}_2\cdot$ and H_2O_2 could react with recalcitrant organics during sonication (Riesz et al., 1985; Suslick, 1989).



In sonication, the more power input and sonication time could facilitate more SCOD increase (Bougrier et al., 2005; Dewill et al., 2006). Many researchers pretreated sludge by different sonication methods and discussed the effect of experimental condition on the increase of SCOD (Table 2-5). Thiem et al. (2001) demonstrated the effects of degree of disintegration for SCOD at different ultrasound frequency, where the lower ultrasound frequency got better degree of disintegration. In other words, lower ultrasound frequency increased more soluble organics of sludge. Chu et al. (2001) and Zhang et al. (2007) have investigated the ultrasound reaction at different power densities, which showed that the more ultrasound density the more SCOD increase. In addition, Chiu et al. (1997) combined alkalization and sonication pretreatments and demonstrated that the more NaOH concentration to sludge or the more sludge pH, the more SCOD increase. It was explained that the hydroxyl ions addition could attack and weaken the bacterial cell-wall then facilitate better destruction by following ultrasound reaction (Wang et al., 2005). On the other hand, Wang et al. (2005) showed that sodium bicarbonate (NaHCO_3) addition could mask the oxidizing effect of $\text{OH}\cdot$ to disturb ultrasound reaction. In brief, addition of hydroxyl ion instead of HCO_3^- could facilitate SCOD increase in pretreatments. Under higher TS contents, the violent collapsing of micro-bubbles could accelerate the particles in vicinity of the bubbles, which could bombard the adjacent particles. Particles at a higher TS

contents could facilitate the sludge disruption due to particle-to-particle collision. Wang et al. (2005), Dewil et al. (2006) and Show et al. (2007) reported higher SCOD increase under higher TS of sludge.

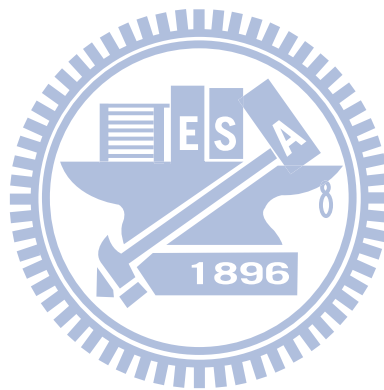


Table 2-5 SCOD changes after sonication

Authors	Frequency (kHz)	Density (W/mL)	pH	TS (%)	Reaction time (min)	SCOD increase (mg/L)	SCOD/COD (%)	DD _{COD} (%) ^a
Chu et al. (2001)	20	0.11 0.33	7.0	0.82	120	ND ^b	2.3 21.5	ND
Thiem et al. (2001) ^c	41							13.9
	207	ND	ND	2.59	60	ND	ND	3.6
	360							3.1
	1,068							1.0
Bougrier et al. (2005) ^c	20	0.45	ND	1.85	0.45	ND	10.5	ND
					1.85		22.3	
					9.97		41.6	
Wang et al. (2005) ^d	20	ND	8	ND	30	750	ND	ND
			9					
			10					
			11					
			12					
Wang et al. (2005)	20	1.44	ND	0.50	30	3,966	ND	ND
				1.00		9,019		
Dewill et al. (2006)	20	0.43	ND	0.85	2.4	400	ND	ND
					8.1	1,250		
					11.1	2,900		

Table 2-5 SCOD changes after sonication (Continue)

Authors	Frequency (kHz)	Density (W/mL)	pH	TS (%)	Reaction time (min)	SCOD increase (mg/L)	SCOD/COD (%)	DD _{COD} (%) ^a
Dewil et al. (2006)	20	0.43	ND	0.85	4.8	2,900	ND	ND
				1.40		3,600		
Show et al. (2007)	20	0.52	ND	1.00	15	2,200	ND	ND
				1.70		2,800		
				2.90		3,700		
				0.20		1,040		
Zhang et al. (2007)	25	0.50	6.9	1.00	30	2,790	ND	ND
		1.50		4,690				

^aDegree of disintegration = $(\text{SCOD}_{\text{US}} - \text{SCOD}_0) \times 100 / (\text{SCOD}_{\text{NaOH}} - \text{SCOD}_0)$, which SCOD_{US} was SCOD after sonication, $\text{SCOD}_{\text{NaOH}}$ was SCOD after 1M NaOH treated for 24 hours before sonication, and SCOD_0 was original SCOD

^bNot detected

^c1M NaOH treated before sonication

^dCombination with NaOH alkalization and sonication

Chapter 3 Materials and methods

3-1 Sludge source

The sewage sludge (composing primary and biological sludge) was collected from Di-Hua wastewater treatment plant in Taipei, Taiwan. The pH of the sludge was 6.70. Prior the experiments, the sludge was sieved through a mesh (no.16 with the pore size of 1.5 mm) to remove impurities and floating matters, then settled by gravity until the TS was about 3%. Finally, the pre-adjusted sludge was refrigerated at 4°C. The characteristics of this concentrated sludge were shown in Table 3-1.

The ratio of volatile solids contents (VS) and TS was 70% while the total COD and soluble COD were 26,500 mg/L and 140 mg/L, respectively. Cheng et al. (2000) measured the DEHP concentration in sewage sludge collected from Di-Hua wastewater treatment plant, where the result of 153.15 mg/kg-dw sludge was higher than the EU limit value (Table 2-3). Also, the sewage sludge contained large amount of other PAEs, especially DBP. Therefore, the sewage sludge collected from Di-Hua wastewater treatment plant was used as the sludge source to demonstrate the PAEs changes during alkalization and sonication pretreatment.

Table 3-1 Characteristics of sewage sludge in Di-Hua wastewater treatment plant

Characteristics	Data
TS	2.97%
VS	2.08%
COD	26,500 mg/L
SCOD	140 mg/L
pH	6.70
DBP	718 mg/kg-dw
DEHP	41 mg/kg-dw
BBP	8 mg/kg-dw

Sampling date: Aug. 20th, 2009

3-2 Chemicals and reagents

The chemicals used in the present study are listed in Table 3-2. Two organic solvents, n-hexane and dichloromethane, were used in GC-FID analysis for PAEs determination. Three PAEs such as DBP, DEHP and BBP with the purist grade (purity > 98%) were used in this study as the target compounds. Other chemicals with the reagent grade were used in this study without further purification.

Table 3-2 Experimental chemicals in this study

Chemical	Purpose
Sodium hydroxide (NaOH): 98%, Panreac (EU)	Alkalization
DBP (C ₁₆ H ₂₂ O ₄): 99%, Panreac (EU)	
DEHP (C ₂₄ H ₃₈ O ₄): 99%, Riedel-deHaen (Germany)	
BBP (C ₁₉ H ₂₀ O ₄): 98%, Aldrich (USA)	PAEs analysis
n-hexane (C ₆ H ₁₄): 96%, Scharlau (EU)	
Dichloromethane (CH ₂ Cl ₂): 99.9%, Mallinckrodt (USA)	
Potassium dichromate (K ₂ Cr ₂ O ₇): 99.5%, Panreac (EU)	
Mercuric sulfate (HgSO ₄): 99%, Riedel-deHaen (Germany)	
Sulfuric acid (H ₂ SO ₄): 98%, Panreac (EU)	
Boiling stone: Hanawa (Japan)	
Silver sulfate sulfuric acid (AgSO ₄): 10 g/L, Fluka (Germany)	COD analysis
1, 10 phenanthroline monohydrate (C ₁₂ H ₈ N ₂ ·H ₂ O): 99.5%, Riedel-deHaen (Germany)	
Iron (II) sulfate 7-hydrate (FeSO ₄ ·7H ₂ O): 99.5%, Ferak (Germany)	
Ferrous ammonium sulfate 6-hydrate, fine crystal (Fe(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O) (USA)	

3-3 Experimental procedures and designs

Figure 3-1 shows the experimental design of this study. Experiments of alkalization and ultrasound pretreatment followed the steps as reported by Chiu et al. (1997). DEHP was the most quantitative PAEs in municipal sewage sludges for many cities around the world (Table 2-3). In order to understand the treatment efficiency of high strength DEHP sludge, DEHP was spiked to the collected sewage sludge with the level of 200 mg/kg-dw, which was higher than the limit value designed by the EU. Two experimental parameters, i.e. NaOH concentration and sonication time were investigated to understand the effect on PAEs removal and SCOD increase (Table 3-3 and Table 3-4). The procedures of pretreatment experiment were as follows: (1) alkalization reaction for 24 hours by adding 1 M NaOH and (2) ultrasound reaction for designed sonication time. After a combined alkalization-sonication pretreatment experiments, sludge sample was collected to obtain the results of TS, VS, DBP, DEHP, BBP, COD, SCOD and pH changes.

The CCD was used to simplify the number of experiments and create response surface (Montgomery, 2006). CCD was operated by Minitab 14 because it not only calculated the natural variables in the range of different parameters but also randomized the experimental order of different variables. Besides, the software created the response surfaces and calculated the equation of response surface and R^2 value. In this study, the changeable parameters were NaOH concentration (ranged between 0 and 80 mM) and sonication time (ranged between 0 and 15 min) listed in Table 3-3 and Table 3-4.

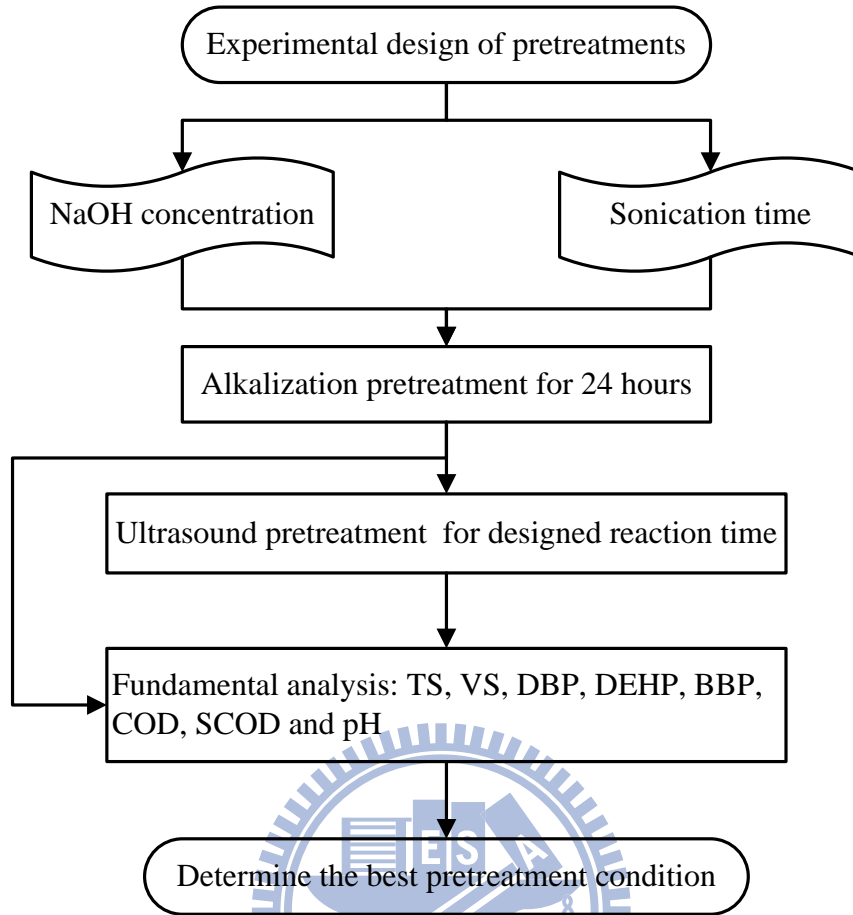


Figure 3-1 Experimental processes in this study

Table 3-3 Ranges and levels of designed factors for CCD

Factors	Levels				
	-1.414	-1	0	1	1.414
A: NaOH concentration (mM)	0	12	40	68	80
U: Sonication time (min)	0.0	2.2	7.5	12.8	15

Table 3-4 Sequence of runs for CCD

Run order	NaOH concentration (mM)	Sonication time (min)
1	68	12.8
2	40	0.0
3*	40	7.5
4	0	7.5
5	68	2.2
6	40	15.0
7*	40	7.5
8*	40	7.5
9	80	7.5
10	12	2.2
11	12	12.8

*Runs 3, 7 and 8 could be considered as the triplicate tests

3-4 Experimental apparatus

3-4-1 Alkalization experiment

The alkalization pretreatment was conducted in a glass reactor equipped with a mechanic mixer (Figure 3-2). The sewage sludge was added to glass reactor and agitated by the mechanic mixer. During agitation, 1 M NaOH was added into the reactor and mixed well for 24 hours at the mixing speed of 400 rpm. Adding 12, 40, 68 and 80 mM NaOH to sewage sludge was equal to adding 12.0, 41.5, 72.9 and 87.2 mL of 1 M NaOH to 1 L sewage sludge, individually. After alkalization reaction, the alkalized sludge was taken for

further ultrasound pretreatment.

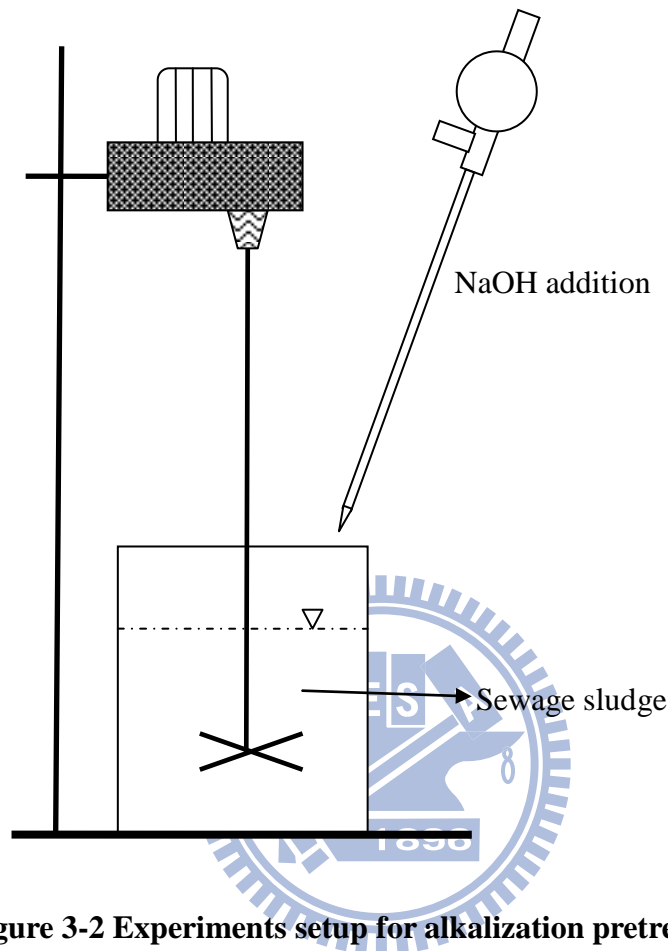


Figure 3-2 Experiments setup for alkalization pretreatment

3-4-2 Ultrasound experiment

In this study, K-Sonic sonicator was used to conduct the ultrasound pretreatment of sewage sludge. Frequency, power output and surface diameter of horn of this sonicator were 20 kHz, 1 kW and 48 mm, respectively. The schematic diagram of the sonicator is shown in Figure 3-3 and the operation parameters in sonication are given in Table 3-5. The converter was used to convert the electrical energy into ultrasound energy. The booster was a mechanical amplifier that helped to increase the amplitude (vibration) to the horn. The horn was used to deliver the ultrasonic energy to the sludge. During sonication, the distance

between the surface of sludge and the rim of beaker was kept as high as possible to avoid the splashing of sludge around the horn.

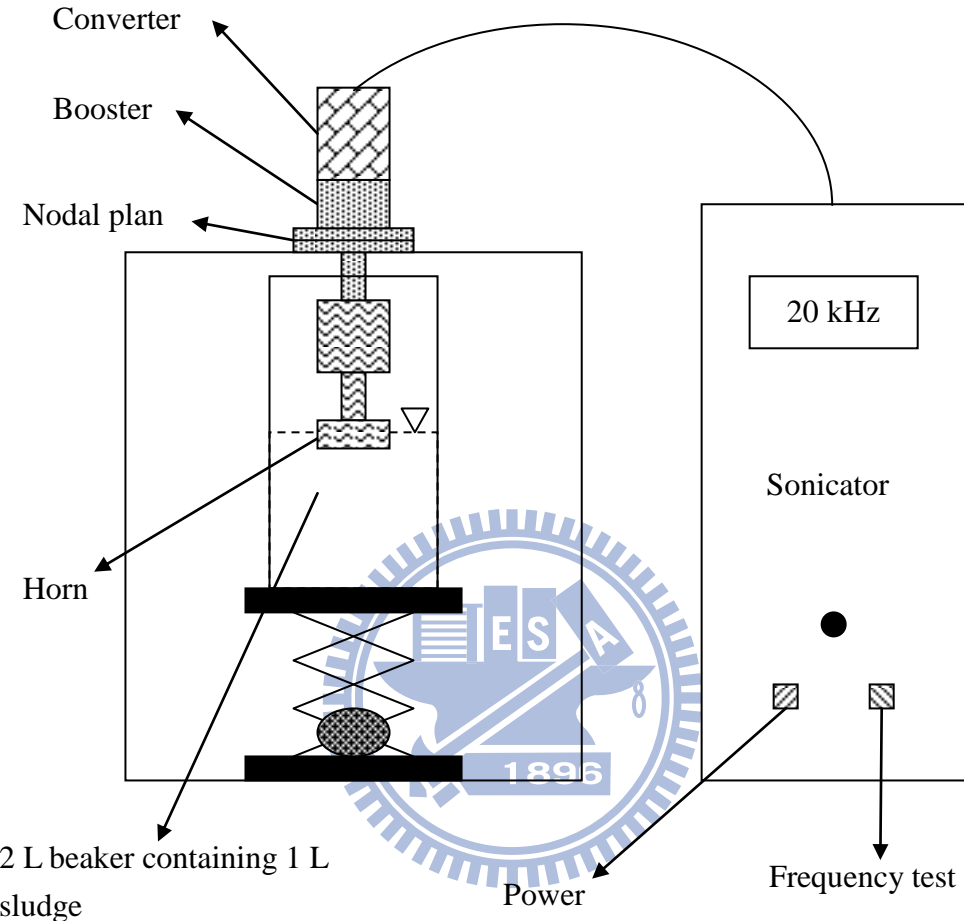


Figure 3-3 Diagram of K-sonic sonicator

Table 3-5 Fixing parameters during sonication

Parameters	Data
Frequency	20 kHz
Power density	1 W/mL
Power intensity	55 W/cm ²
TS of sludge	3%

3-5 Analytical methods

3-5-1 Analysis of PAEs

1. Extraction steps

Analysis of PAEs followed the steps reported by Heise and Litz (2004). Sludge was dried at 105°C for 16 hours prior to extraction, then the dried sludge was ground by a grinder. Because of the high boiling point of PAEs, the characteristics of them are very stable during sludge drying. After grinding, 2 g dried sludge was added to Teflon centrifugal tube, then added with 10 mL of solvent n-hexane and dichloromethane at a volume ratio of 1:1. The sample was shaken by a shaker for 24 hours at ambient temperature. After shaking, the extracted sample was centrifuged by Harmonic Series centrifuge machine for 10 minutes at 3,500 rpm. After centrifugation, the supernatant of extracted solvent was collected to analyze PAEs concentration by GC-FID. The recovery of spiked DEHP was 85.4%.

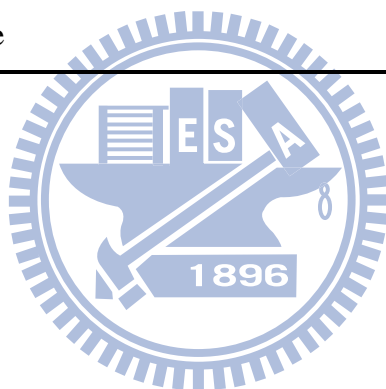
2. GC-FID analysis

A GC-FID (Agilent Technology 7890A) equipped with a HP-5 capillary column (Agilent 19091J-413, 30 m long, 0.32 mm inner diameter, 0.25 µm film thickness) was used in this study for PAEs determination. The operating conditions of GC-FID are listed in Table 3-6. The temperature of oven was programmed as followed: initial temperature of 120°C and hold for 1 min, then raise to 300°C with a rate of 20°C/min and hold for 5 min. During GC-FID analysis, the retention times of DBP, BBP and DEHP were 6.66, 8.42 and

9.17 min, respectively (Figure 3-4).

Table 3-6 Fixing parameters of GC-FID conditions

Parameters	Data
Front inlet temperature	280°C
Front detector temperature	280°C
Makeup gas flow rate (He)	3 mL/min
N ₂ flow rate	22 mL/min
H ₂ flow rate	40 mL/min
Air flow rate	450 mL/min
Injection volume	1 µL



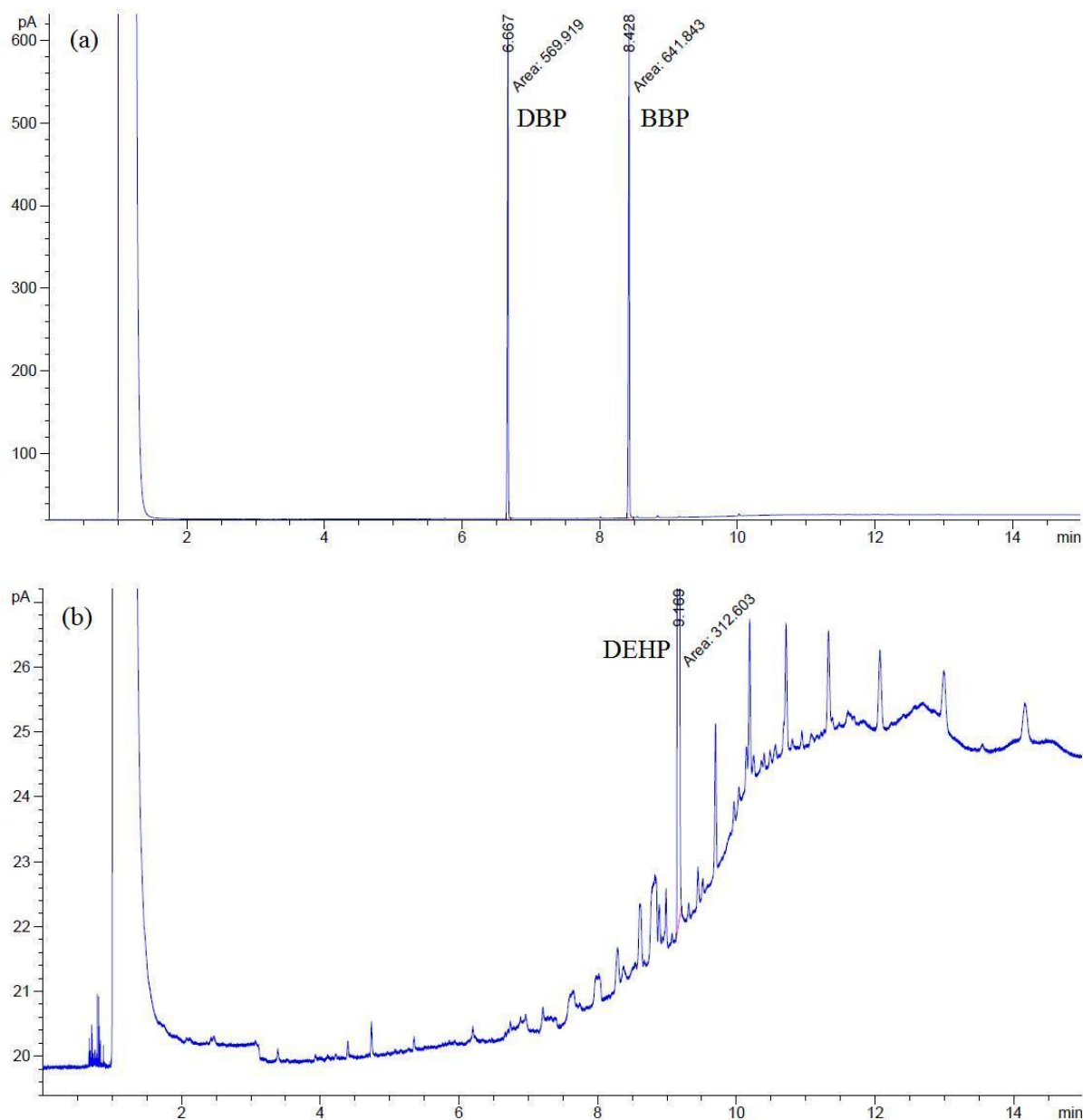


Figure 3-4 Peak locations of standards: (a) DBP and BBP and (b) DEHP

3. Calibration curves

Five different PAEs standards (5, 10, 25, 50 and 100 mg/L) were prepared to develop the calibration curves (Figure 3-5). In Figure 3-5, R^2 values were all higher than 0.9991. In addition, 1 mg/L PAEs standards was prepared to get the method detective limits (MDL), where the MDLs of DBP, DEHP and BBP were 0.43, 0.27 and 0.98 mg/L, respectively.

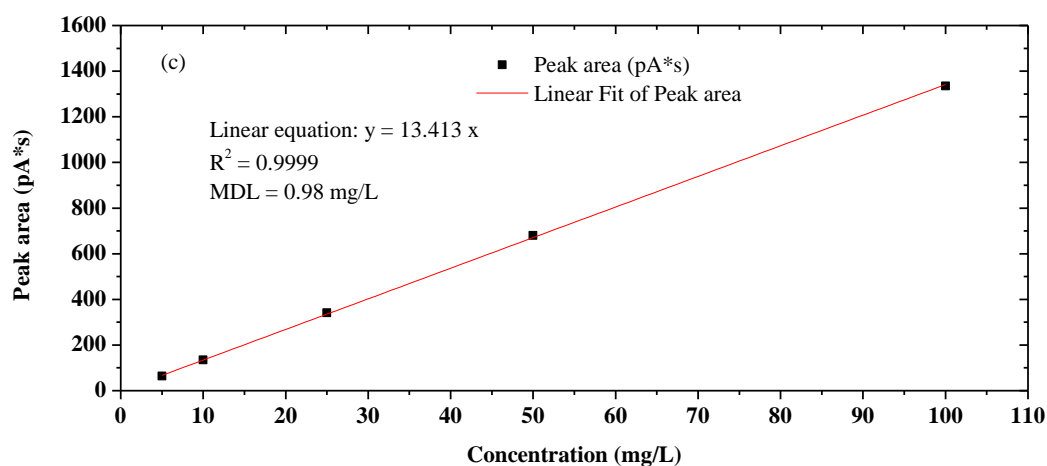
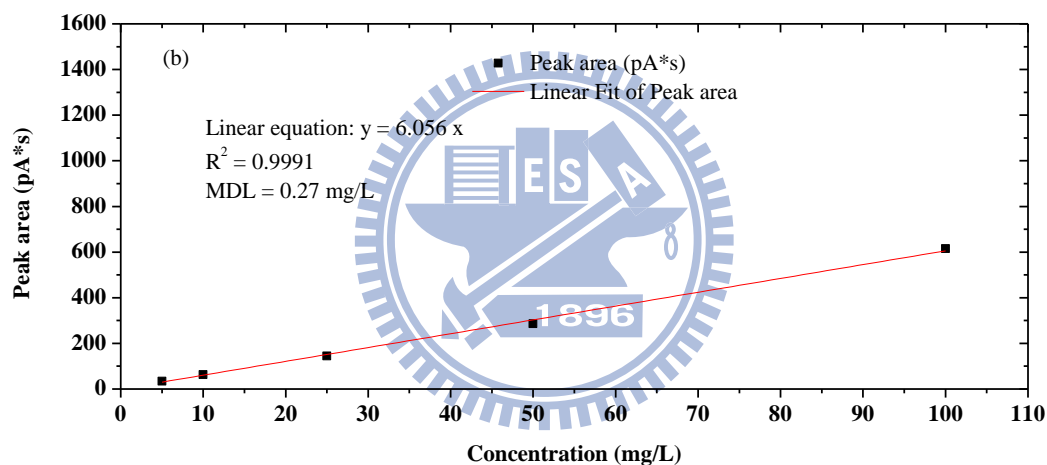
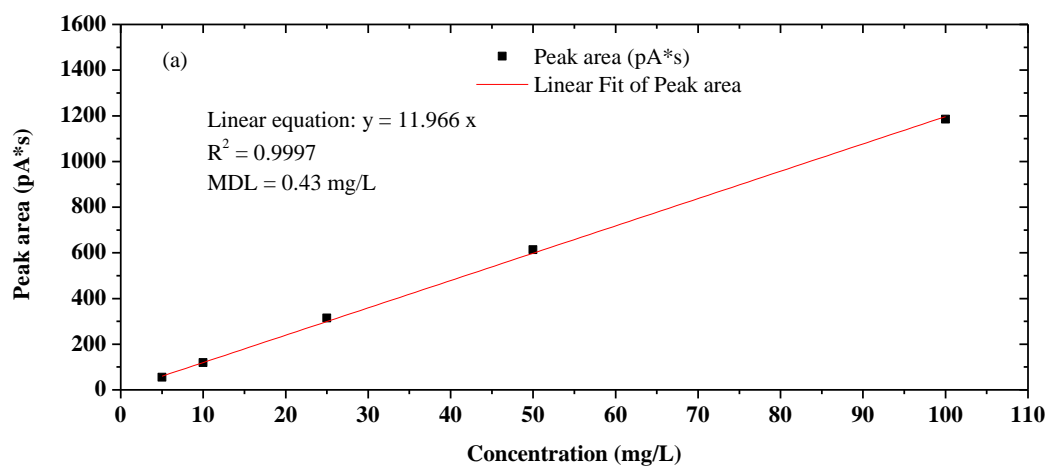


Figure 3-5 Calibration curves of GC-FID analysis: (a) DBP, (b) DEHP and (c) BBP

3-5-2 Analysis of TS, VS, COD and pH

The experimental apparatus used for TS, VS, COD and pH analysis were shown in Table 3-7. TS, VS and COD analyses were according to 2540 B, 2540 E and 5220 B of standard methods, respectively (AWWA, APHA and WEF, 2005). Before analyzing TS and VS, evaporating dishes are prepared. In order to analyze SCOD, sludge sample was centrifuged by Harmonic Series centrifuge machine for 10 min at 3,500 rpm at ambient temperature to separate liquid and solid phase. The liquid phase was filtrated using 0.45 μm Advantec membrane filter. The standard method as reported in AWWA, APHA and WEF, (2005), i.e. open reflux method, was adopted for COD analysis.

Table 3-7 Experimental equipments of fundamental analysis in this study

Equipment	Purpose
Channel 105°C drying oven (DV-602)	TS
Nabertherm 550°C muffle furnace (L9/R)	VS
Sartorius electrical balance (BP221S) (capable of weighing to 0.1 mg)	TS and VS
Den Yng reflux apparatus	COD
Suntex pH meter	pH

Chapter 4 Results and discussions

4-1 PAEs levels in collected sewage sludge

The sewage sludge from Di-Hua wastewater treatment plant was collected on Aug. 20th, 2009 and Jan. 4th, 2010. The order of original PAEs concentrations in the raw sewage sludge was DBP > DEHP > BBP (Table 4-1).

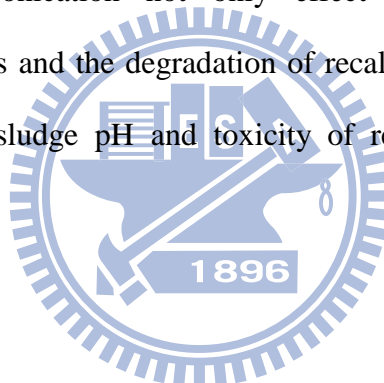
Even part of the PAEs concentration contained in raw sludge are low, the presence of PAEs should be put attention on, especially if the PAEs contained sewage sludge was used in land application, PAEs could transport from sludge to soil then be accumulated in plants/crops (Cecil et al., 1992). In recent years, PAEs had attracted much attention because even at low concentration levels they were suspected of interfering with reproductive and behavioral health in humans and wildlife, through disturbance of the endocrine system (Petrovic et al., 2001). After exposing PAEs by dermal contact, inhalation and ingestion of humans, PAEs could convert to monoesters of which toxicity was more than PAEs in human blood (Woodward, 1988). In order to moderate acute toxic, it is important to control PAEs of their high production volume and their ubiquitous occurrence (Heise and Litz, 2004). In order to decrease the toxicity of PAEs, sludge pretreatment was conducted with alkalization, sonication and a combination of alkalization-sonication in this study.

Table 4-1 PAEs concentration in Di-Hua WWTP sewage sludge

PAEs	Concentration (mg/kg-dw)	
	Aug. 20 th , 2009	Jan. 4 th , 2010
DBP	718	1,971
DEHP	41	74
BBP	8	16

4-2 Influences of sludge qualities after pretreatments

Alkalization and ultrasonication not only effect the transformation between particulate and soluble organics and the degradation of recalcitrant and toxic organics, but also involve in solids mass, sludge pH and toxicity of reagent. The degrees of these effective factors are list in this:



1. Solids mass

During pretreatments, the solids mass could not be changed (Table 4-2). Even though the recalcitrant organics are removed by pretreatments, these recalcitrant organics are transformed to the low molecular weight compounds. Due to this reason, the soluble organics could increase by pretreatments. The values of TS and VS were not changed along with NaOH concentration and sonication time. The values shown in Table 4-2 reveal that pretreatments could maintain the solids mass balance of sewage sludge.

Table 4-2 TS and VS of sludge during pretreatments

Run	NaOH concentration (mM)	Sonication time (min)	Initial		After alkalization		After alkalization-sonication	
			TS (%)	VS (%)	TS (%)	VS (%)	TS (%)	VS (%)
1	68	12.8			2.98	1.99	3.08	2.07
2	40	0.0			2.96	1.94	2.96	1.94
3	40	7.5			2.96	1.94	2.90	1.90
4	0	7.5			2.97	2.08	2.89	1.99
5	68	2.2			2.98	1.99	2.94	1.99
6	40	15.0	2.97	2.08	2.96	1.94	3.03	1.98
7	40	7.5			2.96	1.94	3.04	2.02
8	40	7.5			2.96	1.94	3.05	2.04
9	80	7.5			3.10	1.99	3.05	1.95
10	12	2.2			2.99	2.02	2.88	1.97
11	12	12.8			2.99	2.02	2.99	2.04

2. Sludge pH

In sludge pretreatments, NaOH alkalization not only increased soluble organics to facilitate biodegradation in digestion but also offered the alkalinity of sludge; hydroxides (OH⁻), carbonates (CO₃²⁻) and HCO₃⁻ were the sources of alkalinity (Metcalf and Eddy, 2004). The pH values of sludge before and after pretreatments were listed in Table 4-3. After alkalization, the pH values increased from 6.7 (initial) to 7.8 - 11.5. The role of NaOH played in sludge treatment was not only the pretreatment before digestion but also chemical stabilization after pretreatment (Cecil et al., 1992). Ultrasound pretreatment would not affect the pH value of sludge significantly.

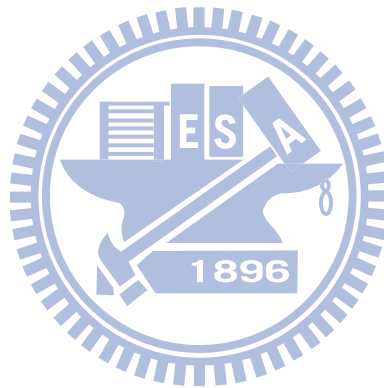


Table 4-3 pH changes during pretreatments

Run	A (mM) ^a	U (min) ^b	pH		
			Initial	After alkalization	After alkalization-sonication
1	68	12.8		10.48	10.34
2	40	0.0		8.15	8.15
3	40	7.5		8.15	8.22
4	0	7.5		6.70	6.15
5	68	2.2		10.48	10.51
6	40	15.0	6.70	8.15	8.31
7	40	7.5		8.15	8.23
8	40	7.5		8.15	8.24
9	80	7.5		11.50	11.36
10	12	2.2		7.88	7.30
11	12	12.8		7.88	7.61

^aNaOH concentration

^bSonication time

3. Toxicity of reagent

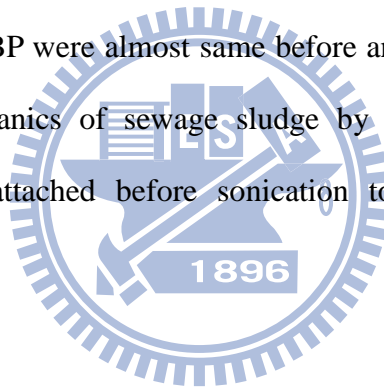
NaOH alkalization could increase the toxicity of sewage sludge which sodium is the toxic light metal. When adding more than 5,000 mg/L of sodium, high concentration of sodium could disturb biological treatment in anaerobic digestion (Cheremisinoff, 1994). In this study, adding 80 mM (or 3,200 mg/L NaOH) to sludge did not affect digestion significantly supposing that the initial sodium concentration of raw sewage sludge was very less. Although enough NaOH concentration could remove recalcitrant organics and harmful

microorganisms, increase SCOD and stable sludge quality, the additional sodium concentration should be controlled during pretreatment or chemical stability.

4-3 PAEs changes

4-3-1 PAEs changes after sonication

According to the plots of peak distribution of sewage sludge in GC-FID analysis (Figure 4-1), the peak areas of each compound between without and with sonication didn't change significantly. In fact, after sonication, only DBP was decreased from 718 to 687.8 mg/kg-dw while DEHP and BBP were almost same before and after sonication. In order to remove some recalcitrant organics of sewage sludge by sonication, other physical or chemical methods must be attached before sonication to facilitate these compounds removal.



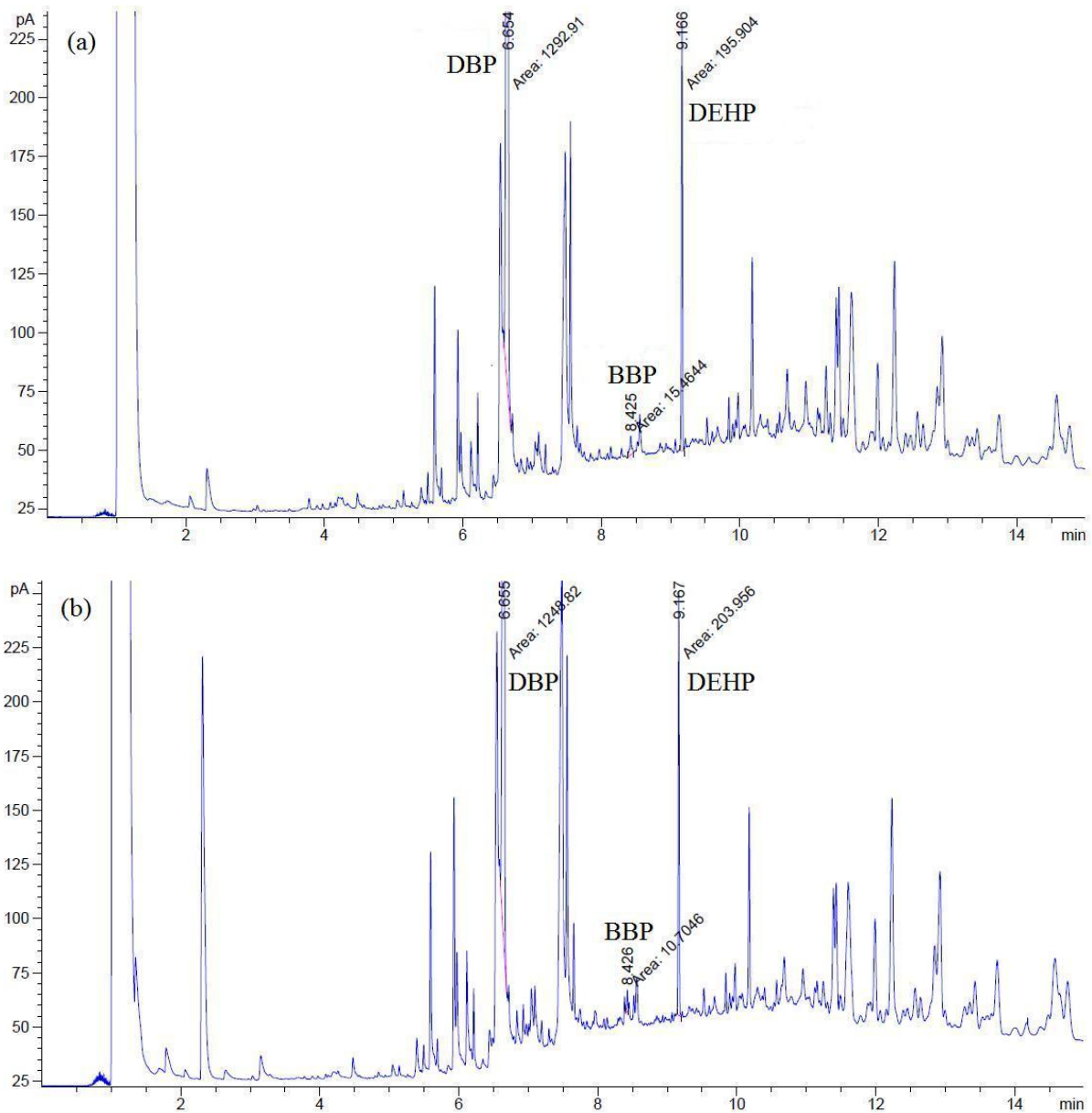


Figure 4-1 Peak distribution of sewage sludge in GC-FID: (a) without sonication and (b) sonication for 7.5 min

4-3-2 PAEs changes after alkalization

PAEs concentrations after the alkalization pretreatment are shown in Table 4-4. In Table 4-4, only 9% of DBP was decreased by alkalization with 12 mM NaOH addition. The concentration of DEHP and BBP were almost constant before and after alkalization.

However, there was an exponential relationship between NaOH concentration and DBP removal (Figure 4-2). If 75 mM of NaOH was added to sludge, removal of DBP achieved nearly to 100%. This result could be explained by the reaction between hydroxyl ions and DBP where the DBP was converted to hydrophilic organics, such as monobutyl phthalate (MBP) so that the DBP was effectively removed by alkalization (Yim et al., 2002). The more hydroxyl ions addition leads to more DBP degradation. Since the BBP and DEHP were not decreased with NaOH addition, it was understood that lower molecular weight PAE such as DBP could be easily degraded by hydroxyl ions.

Table 4-4 PAEs concentration after alkalization

NaOH concentration (mM)	Initial PAE (mg/kg-dw)			PAE after alkalization (mg/kg-dw)		
	DBP	DEHP	BBP	DBP	DEHP	BBP
12	1,971 ^a	215 ^b	8 ^b	1,794	214	8
40				298	212	8
68	718 ^b	215 ^b	8 ^b	9	196	6
80				0	209	8

^aSewage sludge collected on Jan. 4th, 2010

^bSewage sludge collected on Aug. 20th, 2009

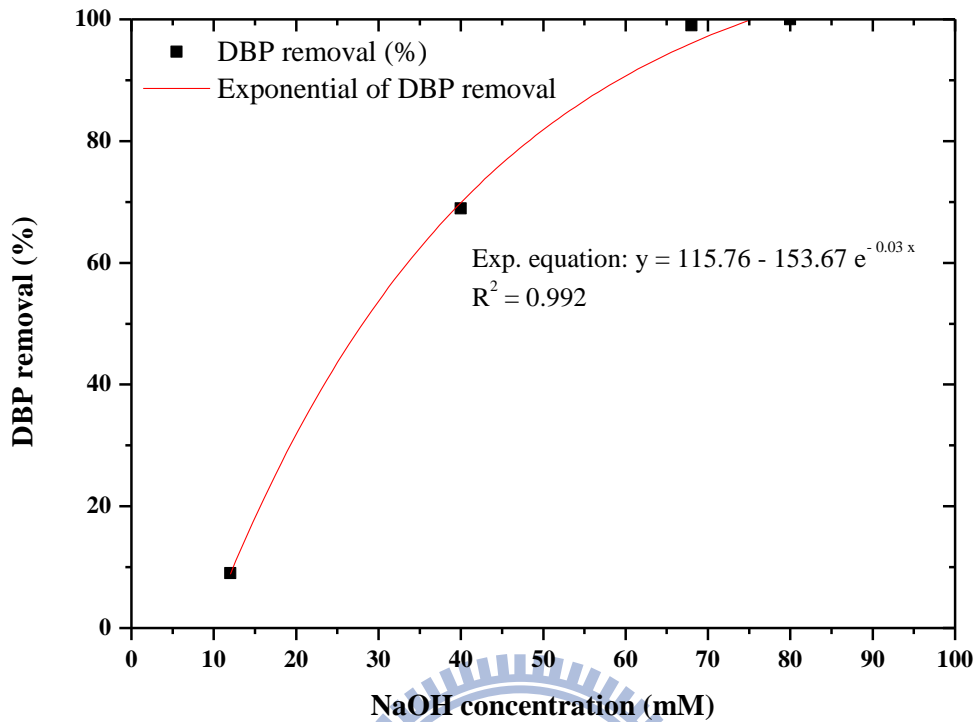


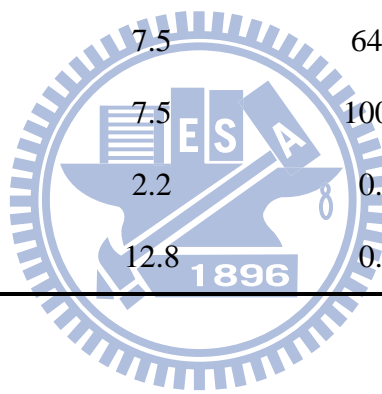
Figure 4-2 DBP removal during alkalization pretreatment

4-3-3 PAEs changes after alkalization and sonication

PAEs removal efficiencies after both alkalization and ultrasound pretreatment are given in Table 4-5, where a response surface contour is plotted by Minitab 14 (Figure 4-3). The response surface equations of three contour plots calculated from Minitab 14 are listed in Table 4-6.

Table 4-5 PAEs removal after pretreatments

Run	NaOH concentration (mM)	Sonication time (min)	Removal (%)		
			DBP	DEHP	BBP
1	68	12.8	100.0	8.3	22.7
2	40	0.0	58.6	1.7	0.0
3	40	7.5	64.1	1.3	0.0
4	0	7.5	4.2	0.0	0.0
5	68	2.2	100.0	6.0	16.0
6	40	15.0	80.5	0.0	0.0
7	40	7.5	62.9	0.0	0.0
8	40	7.5	64.0	0.0	0.0
9	80	7.5	100.0	4.6	0.0
10	12	2.2	0.8	5.0	16.0
11	12	12.8	0.0	0.0	0.0



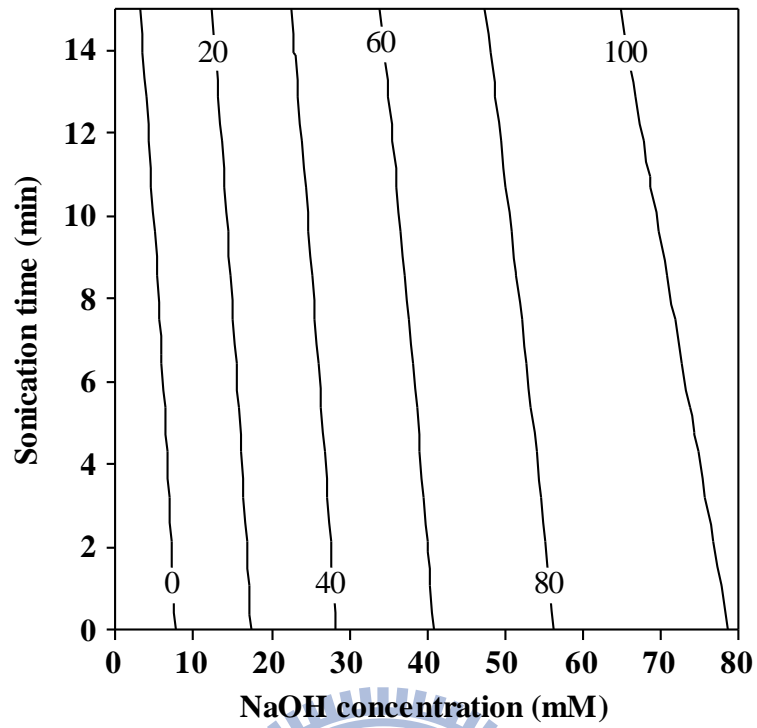


Figure 4-3-1 Contour plot of DBP removal after pretreatments (%)

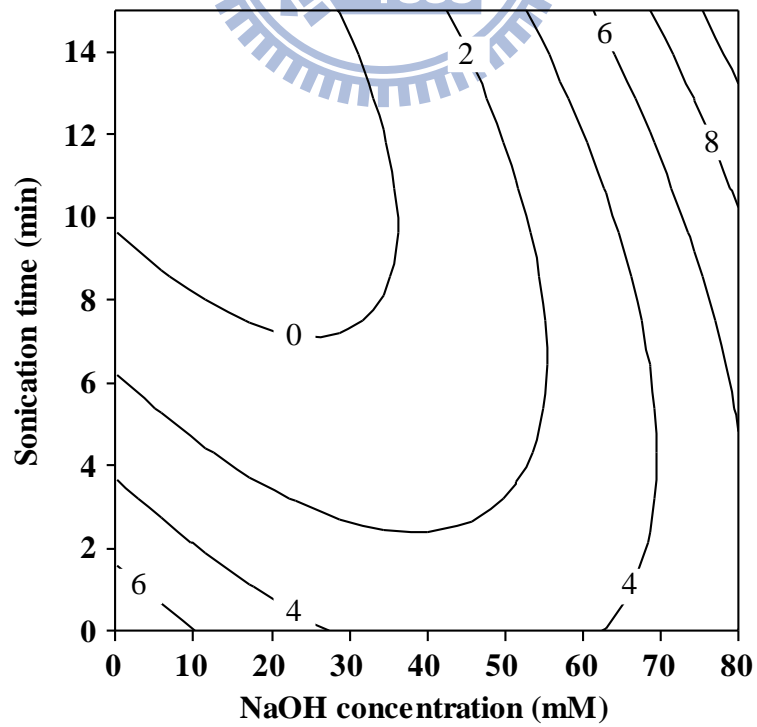


Figure 4-3-2 Contour plot of DEHP removal after pretreatments (%)

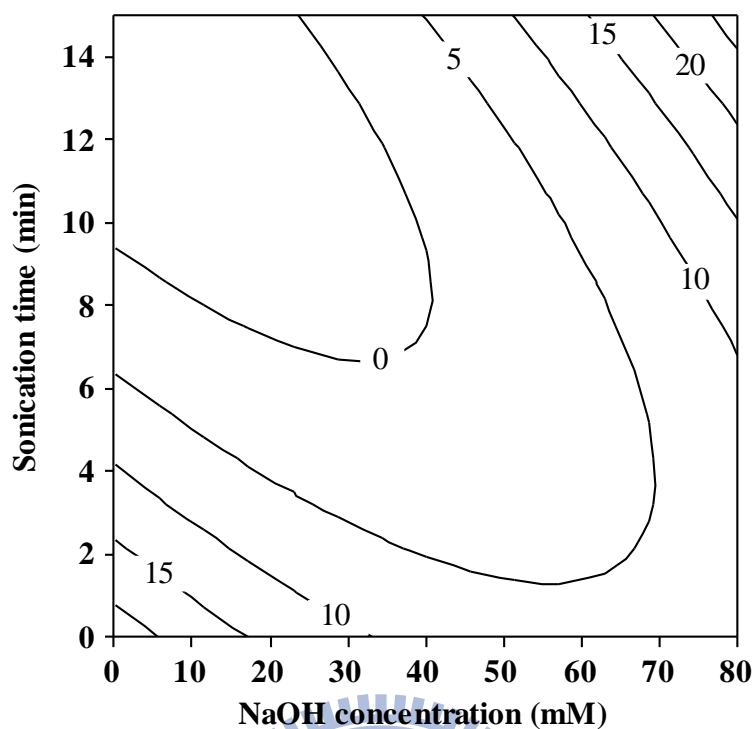


Figure 4-3-3 Contour plot of BBP removal after pretreatments (%)

Table 4-6 Response surface equations of PAEs removal

PAEs	Response surface equation	R ²
DBP	$z = -16.739 + 2.313x + 0.506y - 0.011x^2 + 0.010y^2 + 0.001xy$	0.944
DEHP	$z = 7.725 - 0.196x - 1.151y + 0.002x^2 + 0.036y^2 + 0.012xy$	0.741
BBP	$z = 22.656 - 0.525x - 3.556y + 0.004x^2 + 0.122y^2 + 0.038xy$	0.405

x = NaOH concentration (mM)

y = Sonication time (min)

z = PAEs removal (%)

According to the response surface equations, the equation of DBP removal was applicable for finding the optimal NaOH dosage and sonication time. However, the other equations of DEHP and BBP removal were not used because their R² values were lower

than 0.8. In Figure 4-4, the extracted liquid after alkalization-sonication contained not only DBP, DEHP and BBP but also the other unknown compounds. The compounds with retention times of GC-FID analysis lower than 8 minutes were degraded significantly by pretreatments. The lower molecular weight compounds such as DBP was easily degraded by pretreatments than the higher ones such as DEHP and BBP (Neis, 2002). Combining alkalization and ultrasound pretreatment could facilitate DBP removal of sewage sludge. Even the combination of alkalization and ultrasound pretreatment showed the better result for PAEs removal, the contribution by alkalization and ultrasound individually were different (Table 4-7). In combination pretreatments, alkalization contributed more than 90% for DBP removal in most of runs.



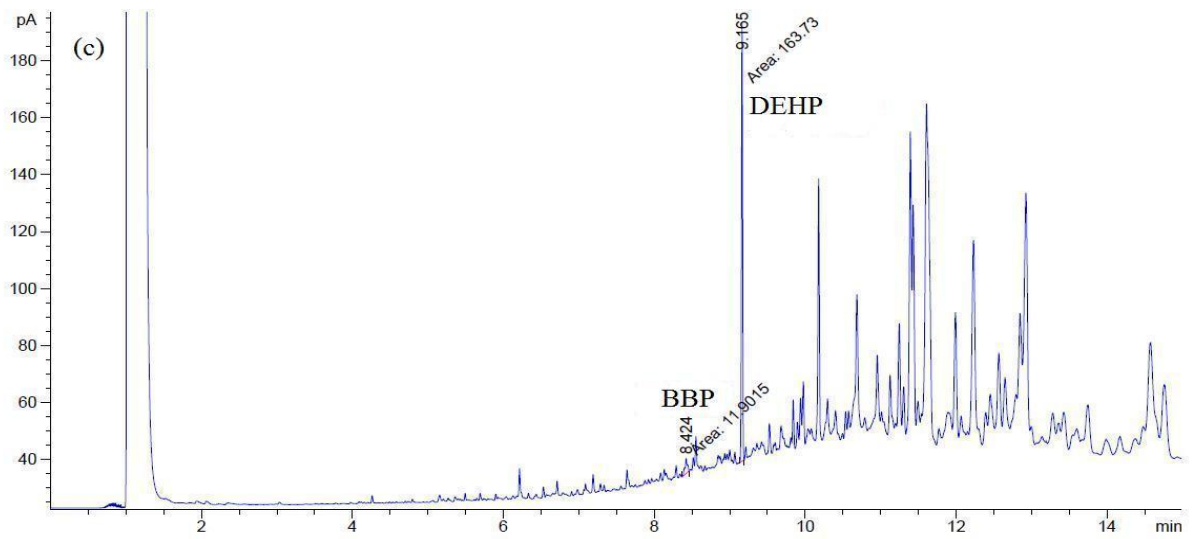
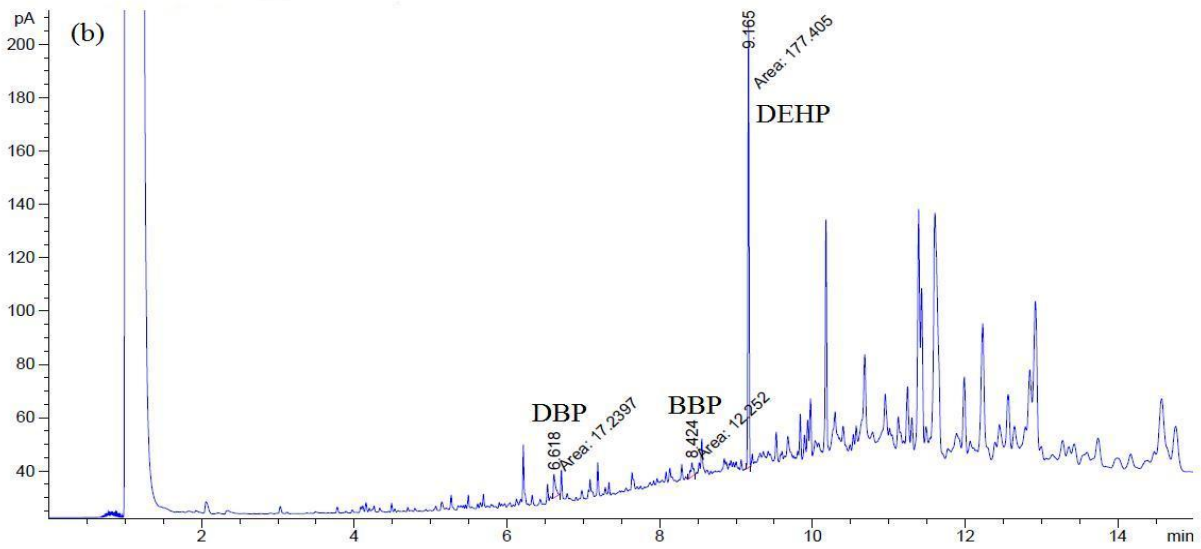
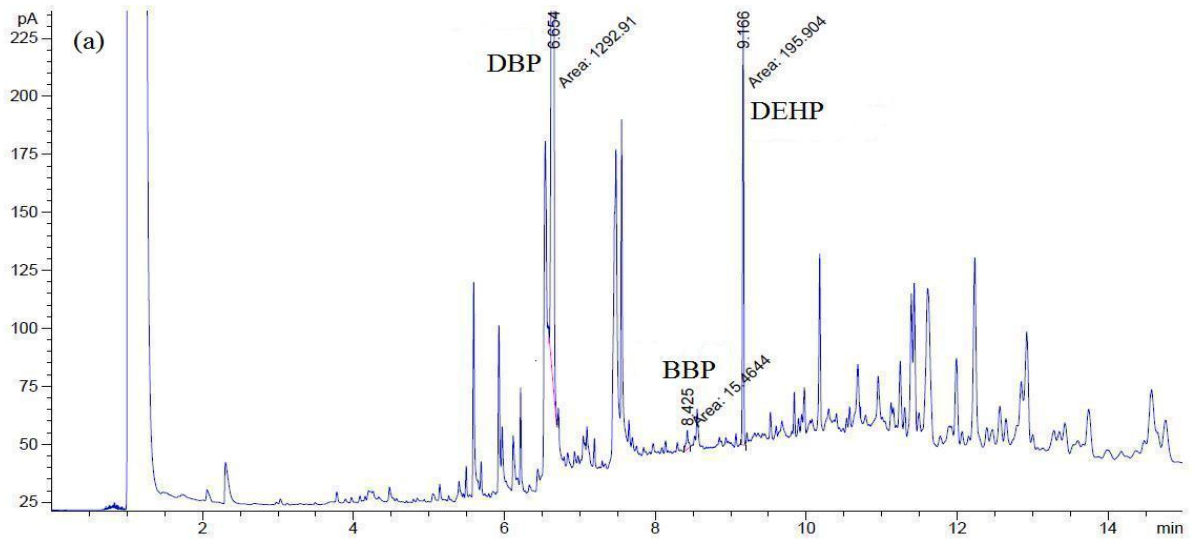


Figure 4-4 Peak distributions: (a) without pretreatment; (b) alkalization for 68 mM NaOH and (c) alkalization for 68 mM NaOH and sonication for 12.8 min

Table 4-7 Contribution percentages for DBP removal between two pretreatments

Run	NaOH concentration (mM)	Sonication time (min)	Contribution (%)	
			Alkalization	Sonication
1	68	12.8	98.7	1.3
2	40	0.0	100.0	0.0
3	40	7.5	91.4	8.6
4	0	7.5	0.0	100.0
5	68	2.2	98.7	1.3
6	40	15.0	72.7	27.3
7	40	7.5	93.2	6.8
8	40	7.5	91.6	8.4
9	80	7.5	100.0	0.0
10	12	2.2	NA*	NA
11	12	12.8	NA	NA

*Not available

4-4 Variation of COD

4-4-1 Variation of COD after alkalization

Figure 4-5-1 shows the relationship between NaOH concentration and SCOD after alkalization. The results indicate that the more hydroxyl increasing the NaOH concentration leads to the better SCOD increase; 8.37 mg/L of SCOD increase was observed as per 1 mM of NaOH addition. In addition, the result of total COD was slightly changed in alkalization, which indicated that the particulate COD could be transferred to SCOD (Figure 4-5-2).

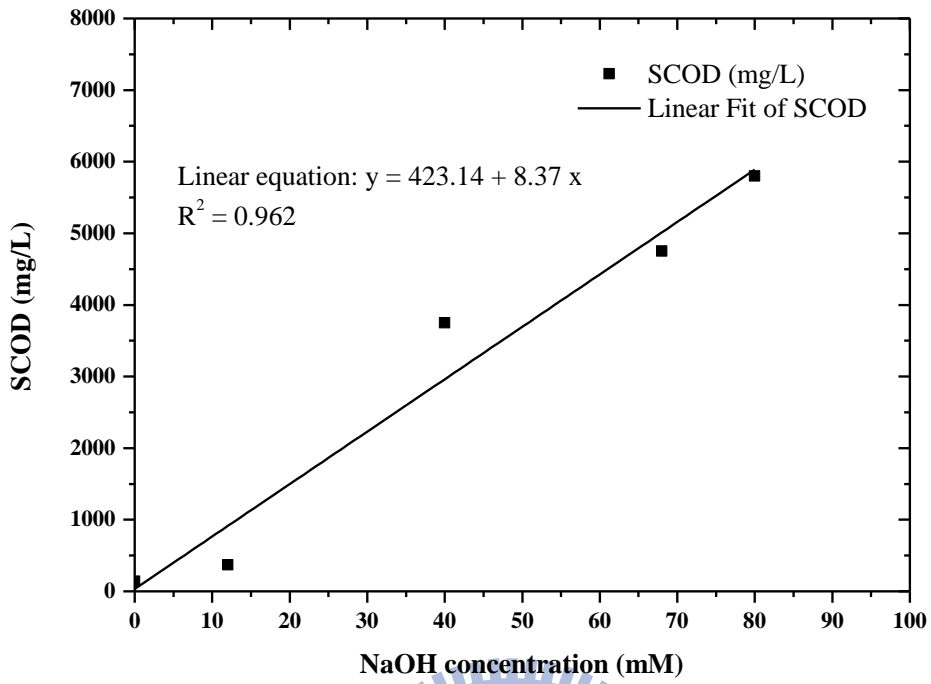


Figure 4-5-1 SCOD after alkalization pretreatment

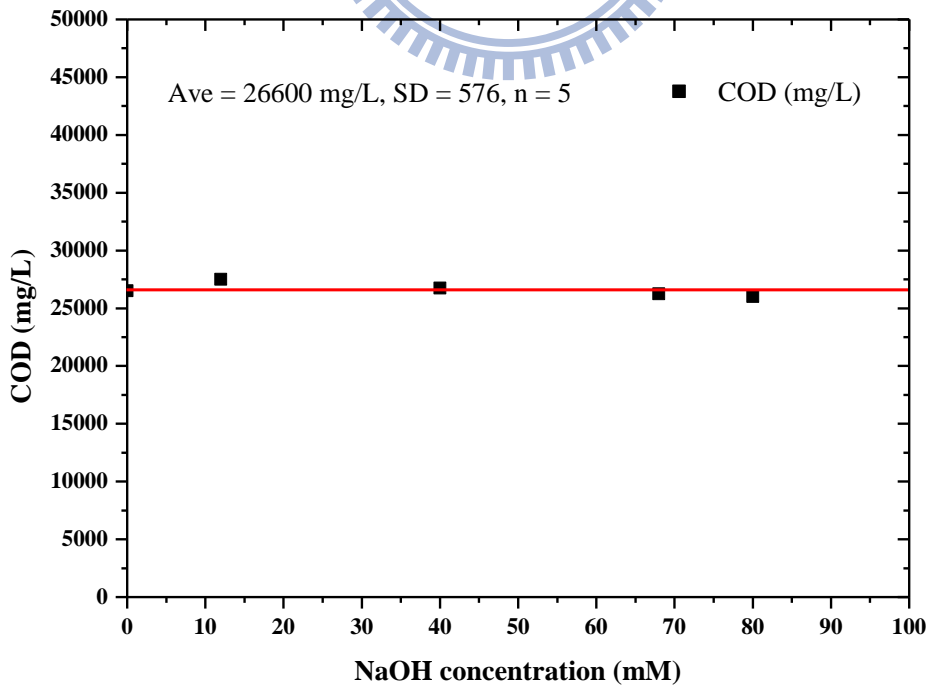


Figure 4-5-2 COD after alkalization pretreatment

4-4-2 Variation of COD after alkalization and sonication

Table 4-8 shows the result of SCOD concentration and SCOD/COD ratio after alkalization-sonication pretreatments. It is found that the higher NaOH concentration addition and longer sonication time get the higher SCOD concentration and SCOD/COD ratio. The contour plot of Figure 4-6 is drawn by Minitab 14 according to the results of Table 4-8 of SCOD concentration and the response surface equation of the contour plot is

$$z = -288.165 + 125.622x + 599.105y - 0.847x^2 - 24.978y^2 - 1.567xy \quad (6)$$

Table 4-8 SCOD and SCOD/COD after alkalization and sonication

Run	NaOH concentration (mM)	Sonication time (min)	SCOD (mg/L)	SCOD/COD (%)
1	68	12.8	6,400	23.9
2	40	0.0	3,750	14.0
3	40	7.5	6,050	22.6
4	0	7.5	3,350	12.5
5	68	2.2	5,100	19.0
6	40	15.0	6,100	22.8
7	40	7.5	6,050	22.6
8	40	7.5	5,900	22.0
9	80	7.5	6,600	24.6
10	12	2.2	1,710	6.4
11	12	12.8	3,950	14.7

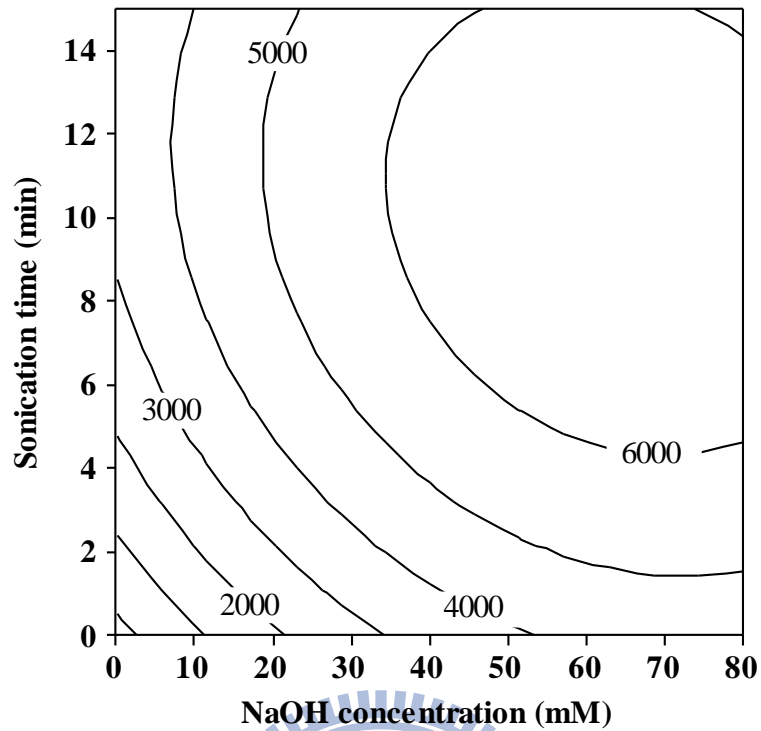


Figure 4-6 Contour plot of SCOD after pretreatments (mg/L)

The optimal point of NaOH concentration and sonication time could be found based on the equation, where the best NaOH concentration and sonication time were 68 mM and 10 min. Even though the NaOH concentration and sonication time increased to 80 mM and 15 min, SCOD increased about 200 mg/L more than that of the optimal pretreatment parameters. In other words, SCOD/COD could increase less than 1% while NaOH concentration and sonication time were 80 mM and 15 min. Total COD could not be changed significantly along with NaOH concentration and sonication time (Table 4-9).

Table 4-9 COD during pretreatments

Run	A (mM) ^a	U (min) ^b	COD (mg/L)		
			Initial	After alkalization	After alkalization-sonication
1	68	12.8		26,250	26,500
2	40	0.0		26,750	26,750
3	40	7.5		26,750	25,750
4	0	7.5		26,500	28,750
5	68	2.2		26,250	26,250
6	40	15.0	26,500	26,750	27,000
7	40	7.5		26,750	26,500
8	40	7.5		26,750	26,500
9	80	7.5		26,000	26,750
10	12	2.2		27,250	27,250
11	12	12.8		27,250	28,000

^aNaOH concentration^bSonication time

If pretreatment combines both alkalization and ultrasound, the contribution percentages were different between the two pretreatments (Table 4-10). If NaOH concentration was 12 mM, ultrasound reaction could contribute more than 80% for SCOD increase. If NaOH concentration was more than 40 mM, ultrasound reaction contributed less than 50% for SCOD increase. Kim et al. (2002) demonstrated the comparison between alkalization and sonication in which soluble organic carbon could increase in alkalization pretreatment (2 M NaOH for 10 min reaction) more than the ultrasound pretreatment (4 W/mL density, 20 kHz for 30 min reaction). In this study, SCOD increase with 40 mM

alkalization was more than with 7.5 min ultrasound reaction (Table 4-11). Combination of two pretreatments could get better result for SCOD increase. The optimal point of response surface plot could be applied for the reaction application.

Table 4-10 Contribution percentages for SCOD increase between two pretreatments

Run	NaOH concentration (mM)	Sonication time (min)	Contribution (%)	
			Alkalization	Sonication
1	68	12.8	73.6	26.4
2	40	0.0	100.0	0.0
3	40	7.5	61.2	38.8
4	0	7.5	0.0	100.0
5	68	2.2	92.9	7.1
6	40	15.0	60.5	39.5
7	40	7.5	61.1	38.9
8	40	7.5	62.7	37.3
9	80	7.5	87.6	12.4
10	12	2.2	14.6	85.4
11	12	12.8	6.0	94.0

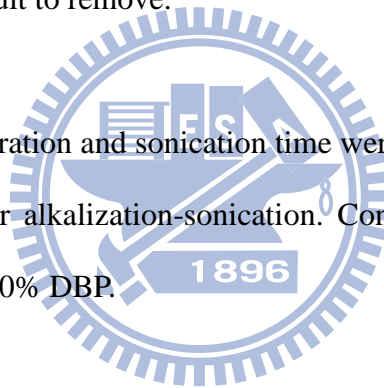
Table 4-11 SCOD increase in single pretreatment

Pretreatment method	SCOD increase (mg/L)
Alkalization in 40 mM NaOH concentration for 24 hours	3,610
Ultrasound reaction for 7.5 minutes for 1 W/mL density	3,210

Chapter 5 Conclusions and suggestions

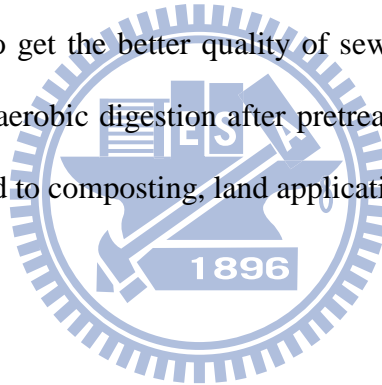
5-1 Conclusions

1. The order of PAEs concentration contained in the sewage sludge collected from the Di-Hua wastewater treatment plant was $DBP > DEHP > BBP$.
2. The combination of alkalization and ultrasound pretreatment significantly removed lower molecular weight PAE such as DBP; higher molecular weight PAEs such as DEHP and BBP were difficult to remove.
3. The optimal NaOH concentration and sonication time were 68 mM and 10 min based on the increase in SCOD after alkalization-sonication. Conducting pretreatment at these conditions could remove 100% DBP.
4. The sole alkalization was a better pretreatment method to remove large PAEs and increase large SCOD of sewage sludge from economical and efficient consideration of engineering design.



5-2 Suggestions

1. If the raw sewage sludge contains less sodium, just conduct alkalization pretreatment to remove large PAEs and increase large SCOD. If the raw sewage sludge contains large sodium and PAEs, combine the alkalization and the ultrasound pretreatment to remove large recalcitrant organics. But the NaOH addition of alkalization pretreatment must be controlled.
2. The product of PAEs removal by pretreatment was probably the hydrophilic products such as mono phthalate acids of which toxicity were more than PAEs. Just conducting pretreatment was enough to get the better quality of sewage sludge. When conducting pretreatment, aerobic or anaerobic digestion after pretreatment is necessary to improve the sludge quality to be used to composting, land application and other uses.



References

- (1) Adewuyi, Y.G. (2001) Sonochemistry: Environmental science and engineering applications. *Industrial & Engineering Chemistry Research* 40, 4681-4715.
- (2) Alatraste-Mondragon, F.; Iranpour, R. and Ahring, B.K. (2003) Toxicity of di-(2-ethylhexyl) phthalate on the anaerobic digestion of wastewater sludge. *Water Research* 37, 1260-1269.
- (3) American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF) (2005) *Standard Method: for the Examination of Water & Wastewater*, 21st edition, American Public Health Association, Washington, USA.
- (4) Angelidaki, I.; Mogensen, A.S. and Ahring, B.K. (2000) Degradation of organic contaminants found in organic waste. *Biodegradation* 11, 377-383.
- (5) Banat, F.A.; Prechtel, S. and Bischof, F. (1999) Experimental assessment of bio-reduction of di-2-ethylhexyl phthalate (DEHP) under aerobic thermophilic conditions. *Chemosphere* 39(12), 2097-2106.
- (6) Barnabe, S.; Yan, S. and Tyagi, R.D. (2007) Fate of toxic organic compounds during bioconversion of wastewater sludge to value added products. IWA specialist conference on biosolids, Moncton, New Brunswick, Canada, 97-102.
- (7) Bien, J.B.; Malina, G.; Bien, J.D. and Wolny, L. (2004) Enhancing anaerobic

fermentation of sewage sludge for increasing biogas generation. *Journal of Environmental Science & Health, Part A: Toxic/Hazardous Substances & Environmental Engineering* 39(4), 939-949.

(8) Bougrier, C.; Carrere, H. and Delgenes, J.P. (2005) Solubilisation of waste-activated sludge by ultrasonic treatment. *Chemical Engineering Journal* 106, 163-169.

(9) Cecil, L.H.; Zenz, D.R. and Kuchenrither, R. (1992) *Municipal Sewage Sludge Management: Processing, Utilization, & Disposal*, Technomic publishing company, Pennsylvania, USA.

(10) Chang, B.V.; Liao, G.S. and Yuan, S.Y. (2005) Anaerobic degradation of di-n-butyl phthalate and di-(2-ethylhexyl) phthalate in sludge. *Environmental Contamination & Toxicology* 75, 775-782.

(11) Chang, B.V.; Wang, T.H. and Yuan, S.Y. (2007) Biodegradation of four phthalate esters in sludge. *Chemosphere* 69, 1116-1123.

(12) Chen, C.Y. (2009) The oxidation of di-(2-ethylhexyl) phthalate (DEHP) in aqueous solution by UV/H₂O₂ photolysis. *Water Air & Soil Pollution*.

(13) Cheng, H.F.; Chen, S.Y. and Lin, J.G. (2000) Biodegradation of di-(2-ethylhexyl) phthalate in sewage sludge. *Water Science Technology* 41(12), 1-6.

(14) Cheremisinoff, P.N. (1994) *Sludge Management & Disposal* PTR Prentice Hall, USA.

- (15)Chiu, Y.C.; Chang, C.N.; Lin, J.G. and Huang, S.J. (1997) Alkaline and ultrasonic pretreatment of sludge before anaerobic digestion. *Water Science Technology* 36(11), 155-162.
- (16)Chu, C.P.; Chang, B.V.; Liao, G.S.; Jean, D.S. and Lee, D.J. (2001) Observations on changes in ultrasonically treated waste-activated sludge. *Water Research* 35(4), 1038-1046.
- (17)Dargnat, C.; Teil, M.J.; Chevreuil, M. and Blanchard, M. (2009) Phthalate removal throughout wastewater treatment plant: Case study of Marne Aval station (France). *Science of the Total Environment* 407, 1235-1244.
- (18)Dewil, R.; Baeyens, J. and Goutvrind, R. (2006) Ultrasonic treatment of waste activated sludge. *Environmental Progress* 25(2), 121-127.
- (19)Ding, W.C.; Li, D.X.; Zeng, X.L. and Long, T.R. (2006) Enhancing excess sludge aerobic digestion with low intensity ultrasound. *Journal of Central South University of Technology* 13(4), 408-411.
- (20)Fauser, P.; Vikelsoe, J.; Sorensen, P.B. and Carlsen, L. (2003) Phthalates, nonylphenols and LAS in an alternately operated wastewater treatment plant: Fate modeling based on measured concentrations in wastewater and sludge. *Water Research* 37, 1288-1295.
- (21)Gavala, H.N.; Alatrisme-Mondragon, F.; Iranpour, R. and Ahring, B.K. (2003) Biodegradation of phthalate esters during the mesophilic anaerobic digestion of sludge. *Chemosphere* 55, 673-682.

- (22) Gavala, H.N.; Yenal, U. and Ahring, B.K. (2004) Thermal and enzymatic pretreatment of sludge containing phthalate esters prior to mesophilic anaerobic digestion. *Biotechnology & Bioengineering* 85(5), 561-567.
- (23) Gledhill, W.F.; Kaley, R.G.; Adams, W.J.; Hicks, O.; Michael, P.R.; Seager, V.W. and Leblanc, G.A. (1980) An environmental safety assessment of butyl benzyl phthalate. *Environmental Science & Technology* 14, 301-305.
- (24) Gomez-Hens, A. and Aguilar-Caballo, M.P. (2003) Social and economic interest in the control of phthalic acid esters. *Trends in Analytical Chemistry* 22(11), 847-857.
- (25) Gonze, E.; Pillot, S.; Valette, E.; Gonthier, Y. and Bernis, A. (2003) Ultrasonic treatment of an aerobic activated sludge in a batch reactor. *Chemical Engineering & Processing* 42, 965-975.
- (26) Gronroos, A.; Kyllonen, H.; Korpijarvi, K.; Pirkonen, P.; Paavola, T.; Jokela, J. and Rintala, J. (2005) Ultrasound assisted method to increase soluble chemical oxygen demand (SCOD) of sewage sludge for digestion. *Ultrasonics Sonochemistry* 12, 115-120.
- (27) Heise, S. and Litz, N. (2004) *Phthalates* German Federal Environmental Agency, Berlin, Germany.
- (28) Jensen, J. and Jepsen, S.E. (2005) The production, use and quality of sewage sludge in Denmark. *Waste Management* 25, 239-247.
- (29) Kaneco, S.; Katsumata, H.; Suzuki, T. and Ohta, K. (2006) Titanium dioxide mediated

photocatalytic degradation of dibutyl phthalate in aqueous solution-kinetics, mineralization and reaction mechanism. *Chemical Engineering Journal* 125, 59-66.

(30)Khanal, S.K.; Grewell, D.; Sung, S. and Leeuwen, J. (2007) Ultrasound applications in wastewater sludge pretreatment: a review. *Critical Reviews in Environmental Science & Technology* 37(4), 277-313.

(31)Kim, J.; Park, C.; Kim, T.H.; Lee, M.; Kim, S.; Kim, S.W. and Lee, J. (2003) Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge. *Journal of Bioscience & Bioengineering* 95(3), 271-275.

(32)Kim, T.H.; Nam, Y.K.; Park, C. and Lee, M. (2009) Carbon source recovery from waste activated sludge by alkaline hydrolysis and gamma-ray irradiation for biological denitrification. *Bioresource Technology* 100, 5694-5699.

(33)Kim, Y.K.; Kwak, M.S.; Lee, S.B.; Lee, W.H. and Choi, J.W. (2002) Effects of pretreatments on thermophilic aerobic digestion. *Journal of Environmental Engineering* 128(8), 755-763.

(34)Lertsirisopon, R.; Soda, S.; Sei, K. and Ike, M. (2009) Abiotic degradation of four phthalic acid esters in aqueous phase under natural sunlight irradiation. *Journal of Environmental Sciences* 21, 285-190.

(35)Li, H.; Jin, Y.; Mahar, R.B.; Wang, Z. and Nei, Y. (2008) Effects and model of alkaline waste activated sludge treatment. *Bioresource Technology* 99, 5140-5144.

- (36)Lin, J.G.; Ma, Y.S.; Chao, A.C. and Huang, C.L. (1999) BMP test on chemically pretreated sludge. *Bioresource Technology* 68, 187-192.
- (37)Lin, J.G.; Ma, Y.S. and Huang, C.C. (1998) Alkaline hydrolysis of the sludge generated from a high-strength, nitrogenous-wastewater biological-treatment process. *Bioresource Technology* 65, 35-42.
- (38)Marttinen, S.K.; Kettunen, R.H.; Sormunen, K.M. and Rintala, J.A. (2003) Removal of bis (2-ethylhexyl) phthalate at a sewage treatment plant. *Water Research* 37, 1385-1393.
- (39)Metcalf and Eddy (2004) *Wastewater Engineering: Treatment & Reuse*, 4th edition, McGraw-Hill, New York, USA.
- (40)Montgomery D.C. (2006) *Design & Analysis of Experiments*, 6th edition, John Wiley & Sons, New York, USA.
- (41)Neis, U. (2002) Intensification of biological and chemical processes by ultrasound. *Ultrasound in Environmental Engineering II* 1-12
- (42)Petrovic, M.; Eljarrat, E.; Lopez, M.J. and Barcelo, D. (2001) Analysis and environmental levels of endocrine-disrupting compounds in freshwater sediments. *Trends in Analytical Chemistry* 20, 637-648.
- (43)Rahman, M. and Brazel, C.S. (2004) The plasticizer market: An assessment of traditional plasticizers and research trends to meet new challenges. *Progress in Polymer Science* 29, 1223-1248.



- (44) Rank, J. (2005) Classification and risk assessment of chemicals: The case of DEHP in the light of research. *The Journal of Transdisciplinary Environmental Studies* 4(3), 1-15.
- (45) Riesz, P.; Berdahl, D. and Christman, C.L. (1985) Free radical generation by ultrasound in aqueous and nonaqueous solutions. *Environmental Health Perspectives* 64, 233-252.
- (46) Roslev, P.; Vorkamp, K.; Aarup, J.; Frederiksen, K. and Nielsen, P.H. (2007) Degradation of phthalate esters in an activated sludge wastewater treatment plant. *Water Research* 41, 969-976.
- (47) Shelton, D.R.; Boyd, S.A. and Tiedje, J.M. (1984) Anaerobic biodegradation of phthalic acid esters in sludge. *Environmental Science & Technology* 18, 93-97.
- (48) Show, K.Y.; Mao, T. and Lee, D.J. (2007) Optimisation of sludge disruption by sonication. *Water Research* 41, 4741-4747.
- (49) Spinosa, L. (2001) Evolution of sewage sludge regulations in Europe. *Water Science & Technology* 44(10), 1-8.
- (50) Staples, C.A.; Parkerton, T.F. and Peterson, D.R. (2000) A risk assessment of selected phthalate esters in North American and Western European surface waters. *Chemosphere* 40, 885-891.
- (51) Staples, C.A.; Peterson, D.R.; Parkerton, T. F. and Adams, W.J. (1997) The environmental fate of phthalate esters: A literature review. *Chemosphere* 35(4), 667-749.
- (52) Suslick, K.S. (1989) The chemical effects of ultrasound. *Science American* 260, 80-86.

- (53)Tiehm, A.; Nickel, K.; Zellhorn, M.M. and Neis, U. (2001) Ultrasound waste activated sludge disintegration for improving anaerobic stabilization. *Water Research* 35(8), 2003-2009.
- (54)Vikelsee, J.; Thomsen, M. and Carlsen, L. (2002) Phthalates and nonylphenols in profiles of differently dressed soils. *The Science of the Total Environment* 296, 105-116.
- (55)Vitali, M. (1997) Phthalate esters in freshwaters as markers of contamination source: A site study in Italy. *Environment International* 23(3), 337-347.
- (56)Wang, F.; Wang, Y. and Ji, M. (2005) Mechanisms and kinetics models for ultrasonic waste activated sludge disintegration. *Journal of Hazardous Materials* 123, 145-150.
- (57)Wang, J.; Liu, P. and Qian, Y. (1996) Biodegradation of phthalic acid esters by acclimated activated sludge. *Environment International* 22(6), 737-741.
- (58)Wolfe, N.L.; Steen, W.C. and Burns L.A. (1980) Phthalate esters hydrolysis: Linear free energy relationships. *Chemosphere* 9, 403-408.
- (59)Woodward, K.N. (1988) *Phthalate Esters: Toxicity & Metabolism* CRC Press, Boca Raton, USA.
- (60)Yim, B.; Nagata, Y. and Maeda, Y. (2002) Sonolytic degradation of phthalate acid esters in aqueous solutions. Acceleration of hydrolysis by sonichemical action. *Journal of Physical Chemistry A* 106, 104-107.

(61) Yuan, S.Y.; Liu, C.; Liao, C.S.; Chang, B.V. (2002) Occurrence and microbial degradation of phthalate esters in Taiwan river sediments. *Chemosphere* 49, 1295-1299.

(62) Zhang, P.; Zhang, G. and Wang, W. (2007) Ultrasonic treatment of biological sludge: floc disintegration, cell lysis and inactivation. *Bioresource Technology* 98, 207-210.

