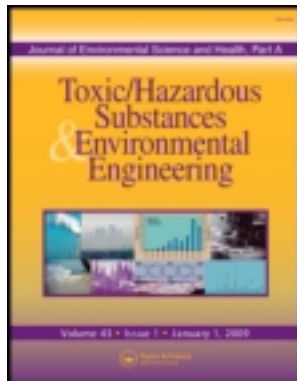


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# Sono-alkalization pretreatment of sewage sludge containing phthalate acid esters

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This work experimentally elucidates the efficiencies of sono-alkalization treatment on municipal sewage sludge. The total solids (TS) concentration of the sewage sludge was pre-adjusted at 29.7 g/L. Two parameters such as sodium hydroxide (NaOH) dosage and sonication time were considered by the central composite design (CCD) program to investigate the effect on the degradation of phthalate acid esters (PAEs) and solubilization of soluble chemical oxygen demand (SCOD). The mean concentrations of dibutyl phthalate (DBP), di-(2-ethylhexyl) phthalate (DEHP) and butyl benzyl phthalate (BBP) in the sewage sludge were 718, 41 and 8 mg/kg dry weight sludge, respectively. Sono-alkalization process was effective on the degradation of DBP but worthless for DEHP and BBP. Overall degradation of DBP in sewage sludge was estimated to be 100% at the NaOH dosage of 68 mM and sonication time of 2.2 min. Sono-alkalization was responsible for 6,000 mg/L increase of SCOD based on the decrease of volatile solids in sewage sludge.

**Keywords:** Central composite design, phthalate acid esters, sewage sludge, soluble chemical oxygen demand, sono-alkalization.

## Introduction

Widespread occurrence of phthalate acid esters (PAEs) in the environment raises concerns about their toxicological effects on living organisms. USEPA listed six PAEs including dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), butyl benzyl 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.<sup>[1]</sup> DEHP was included in class B2 (probable human carcinogen) while butyl-benzyl phthalate (BBP) was in class C (possible human carcinogen). Other commercial phthalates (DBP, DEP and DMP) were included in class D (have not been classified as human carcinogens). Those PAEs were proven as toxic compounds to human beings and animals and accumulated in the bio-organisms to affect the food chains in ecosystems. Once PAEs enter in the environment they partition between air, water, soil and sediments.<sup>[2–9]</sup> However, they would preferentially be

sorbed to the organic fraction of soil or sediments, as well as to the organic matter suspended in water based on the low solubility and highly hydrophobic nature of these compounds.<sup>[8–10]</sup> Hence efficient removal of phthalate esters in wastewater treatment plants (WWTP) is becoming an increasing priority in many countries.

During wastewater treatment processes, higher molecular weight PAEs including DBP, DEHP and BBP could be easily attached to the surfaces of sewage sludge and transferred to sludge treatment units. When PAEs containing wastewater was introduced into a wastewater treatment plant: (1) part of PAEs was degraded by physical, chemical and biological treatment during wastewater treatments and (2) the other part was strongly adsorbed on the surface of sludge.<sup>[11–13]</sup> Sorbed PAEs that were not degraded during the anaerobic digestion of sewage sludge would accumulate in the sewage sludge solids (bio-solids) at concentrations several orders of magnitude higher than in the influent wastewater. Fauser et al.<sup>[14]</sup> proved the above fact and indicated that PAEs concentration of 2% was found in the treated water in which 70% was biodegraded and 28% was adsorbed in the sludge.

Aerobic and anaerobic biodegradation of PAEs in sludge, soil and sediment were studied in these decades. Saeger and Tucker<sup>[15]</sup> tested the primary and ultimate biodegradability of phthalic acid, monobutyl phthalate, and five structurally diverse PAEs in river water and activated sludge samples. PAEs and intermediate degradation

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products readily underwent ultimate degradation in different mixed microbial systems in aerobic condition. However, it was found that 80% of BBP could be readily biodegraded in the first two weeks and followed by a slow biodegradation. Roslev et al.<sup>[12]</sup> examined the fate of DMP, DBP, BBP and DEHP in a full scale activated sludge WWTP with biological removal of nitrogen and phosphorus. The mean concentrations of DMP, DBP, BBP and DEHP at the WWTP inlet were 1.9, 20.5, 37.9, and 71.9 mg/L, respectively. Less than 0.1%, 42%, 35%, and 96% of DMP, DBP, BBP and DEHP were associated with suspended solids, respectively. The overall microbial degradation of DMP, DBP, BBP and DEHP in the WWTP was estimated to be 93%, 91%, 90%, and 81%, respectively. Seven to nine percent of the incoming PAEs were recovered in the WWTP effluent.

Wang et al.<sup>[16]</sup> investigated the biodegradation by anaerobic sludge of three phthalates such as DMP, DBP and di-nonyl phthalates (DNP). Biodegradation rate and biodegradability of three phthalates under anaerobic conditions appeared to be related to the length of the alkyl-side chains. More than 90% of DMP and DBP with the short alkyl-side chain phthalates were degraded, whereas the DNP degradation appeared to be relatively slow under the same conditions. Gavala et al.<sup>[17]</sup> studied the anaerobic biodegradation of DBP, DEP and DEHP in sludge and calculated their relative degradation rates. The degradation of DEP, DBP and DEHP was adequately described by the first-order kinetics. Batch and continuous experiments showed that DEP and DBP in sludge were rapidly degraded under mesophilic anaerobic conditions while DEHP is degraded at a rate between one to two orders of magnitude lower. Also, accumulation of high levels of DEHP (more than 60 mg/L) in the anaerobic digester had a negative effect on DBP and DEHP removal rates as well as on the biogas production.

Staple et al.<sup>[2]</sup> proposed a photolysis in UV light wave length of 290–400 nm to remove PAEs. Shorter wavelengths were attenuated by passage through the atmosphere and water column so that the half-lives of photo-degradation for PAEs removal were as much as shorter than hydrolysis. Chen<sup>[18]</sup> mentioned that the removal of DEHP by the combination of UV light and hydrogen peroxide was better than that by direct UV catalysis. More acid or more alkaline PAEs containing aqueous solution got the better photo-degradation than the neutral aqueous solution.<sup>[19,20]</sup> However, photo-degradation of PAEs was carried out in aqueous phase only because of a shadow effect by suspended particles was taking place to prevent the UV light passing through the sludge particles. Therefore, ultrasonic technology has been considered as a tool to degrade the PAEs containing in soil or sludge.

Chang et al.<sup>[21]</sup> applied the ultrasonic and various treatments before aerobic degradation of DEP, BBP, DBP and DEHP in sludge. The effect on PAEs degradation of treating sludge with a 20 min sonication period at a power level

of 0.1 W mL<sup>-1</sup> was evaluated, and the degradation rates of the four PAEs were DBP > BBP > DEP > DEHP. The optimal pH for PAEs degradation in sludge was 7.0 at 30°C. Ultrasonic pretreatment combined with biodegradation was proven that it could effectively remove PAEs from sludge. Gonze et al.<sup>[22]</sup> tried to use a low-frequency (20 kHz) and high intensity ultrasonic treatment of sewage plant sludge disrupts the flocs and lyses the bacterial cells. Experimental results showed that ultrasound treatment caused the disruption of most particle sizes and led in an efficient release of free and interstitial water containing organic matters and proteins and therefore a reduction in the particle volume.

Dewil<sup>[9]</sup> investigated the application of ultrasonic treatment of waste activated sludge (WAS) and found that the ultrasonic treatment could reduce WAS quantities, achieve a better dewaterability, provoke a release of soluble chemical oxygen demand (SCOD) from the bio-solids and destroy the filamentous microorganisms responsible for sludge bulking. Not only the ultrasonic treatment but also the Fenton method was investigated to oxidize the DEHP in wastewater sludge (WWS). Pham et al.<sup>[23]</sup> used the ultrasound and Fenton oxidation individually as the pretreatments to improve the biodegradability of WWS and bioavailability of the target compounds for digestion and fermentation. After 20-day aerobic digestion, DEHP removal was 72%, 89%, and 85%, respectively for raw, ultrasound, and Fenton-oxidized sludge. The results suggested that aerobic stabilization could remove the phthalates, and pretreatment of WWS was also effective in improvement of DEHP biodegradation.

To increase the concentration of SCOD from the treated sludge was also important during the degradation of PAEs. Alkalization was effectively used to increase the SCOD concentration in sludge system, because the hydroxyl ions produced by alkalization could attack the cell walls of microorganisms and release intracellular organics to liquid phase.<sup>[24,25]</sup> In alkalization treatment, more NaOH dosages could get more SCOD increase of sludge, because higher hydroxyl ions enhanced the reaction rate between hydroxyl ions and organics.

Other researchers pretreated sludge by sonication to increase the SCOD. Chiu et al.<sup>[26]</sup> and Wang et al.<sup>[27]</sup> combined alkalization and sonication as a treatment to facilitate the soluble organics increase and remove recalcitrant and toxic organics. The successful treatment by this combination facilitated the applications of sludge cake for land application, composting and landfill. Thiem et al.<sup>[28]</sup> 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.

The sono-alkalization process has been proven as the useful method in the treatment of waste sludge to increase the concentration of SCOD. However, how to obtain the better or optimal reaction condition during the reaction is

still important for the experiments. In this study, the central composite design (CCD) program is used to investigate the effect of reaction conditions on the sludge treatment. Even the CCD has been used in simplifying the number of experiments and obtained the better reaction condition,<sup>[29]</sup> it is seldom to apply the CCD program in experimental parameters design in sono-alkalization system. Therefore, the objectives of this study were to use a combination of sonication and alkalization, namely sono-alkalization, in sewage sludge treatment to and apply the CCD program in examining the effects of NaOH dosage and sonication time on the degradation of three PAEs (DBP, BBP and DEHP) and increase of SCOD concentration.

## Materials and methods

### Materials

The sewage sludge (composing primary and biological sludge) was collected from the Di-Hua wastewater treatment plant located in Taipei, Taiwan. The pH of the sludge was 6.70. Prior to 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 was settled by gravity to the total solids (TS) concentration was about 29.7 g/L. The pre-adjusted sludge was refrigerated at 4°C. The volatile solids (VS) concentration of this concentrated sludge was 20.8 g/L where the ratio of VS/TS was almost 0.7. The average total COD (TCOD) and SCOD of sludge samples were 26,500 mg/l and 140 mg/l, respectively. Concentrations of DBP, DEHP and BBP in the sludge were 718, 41 and 8 mg/kg dry weight (kg-dw), respectively.

### Experimental design

A glass reactor with the working volume of 1 L equipped with a mechanic mixer was used in this study. In sole alkalization pretreatment, NaOH (1 M) was added into the reactor and mixed well for 24 hours at the mixing speed of 400 rpm then the samples were collected for further analysis. In sonication pretreatment, a K-Sonic sonicator (Industrial Technology Research Institute, Taiwan) was used to conduct with the sewage sludge and the frequency, power output and surface diameter of horn of this sonicator were 20 kHz, 1 kW and 48 mm, respectively, where the power density and power intensity were 1 W/mL and 55 W/cm.<sup>2</sup> During sonication, the distance between the surface of sludge and the rim of beaker was kept as higher as possible to avoid the splashing of sludge around the horn. In sono-alkalization, the alkalization pretreatment was carried out first then followed by sonication.

Two experimental parameters, NaOH dosage (0–80 mM) and sonication time (0–15 min) were investigated in CCD program and the operation conditions for eleven runs were

shown in Table 1. In this table, it was observed that Runs 3, 7 and 8 were carried out in same condition, which could be considered as the triplicate tests. After sono-alkalization treatment, sludge sample was collected for analytic measurements such as TS, VS, PAEs concentration (DBP, DEHP and BBP), COD, SCOD and pH changes. To understand the treatment efficiency of high strength DEHP sludge, the DEHP was spiked to the collected sewage sludge with the level of 200 mg/kg-dw; after spiking, the detected DEHP concentration was 215 mg/kg-dw.

## Analytical methods

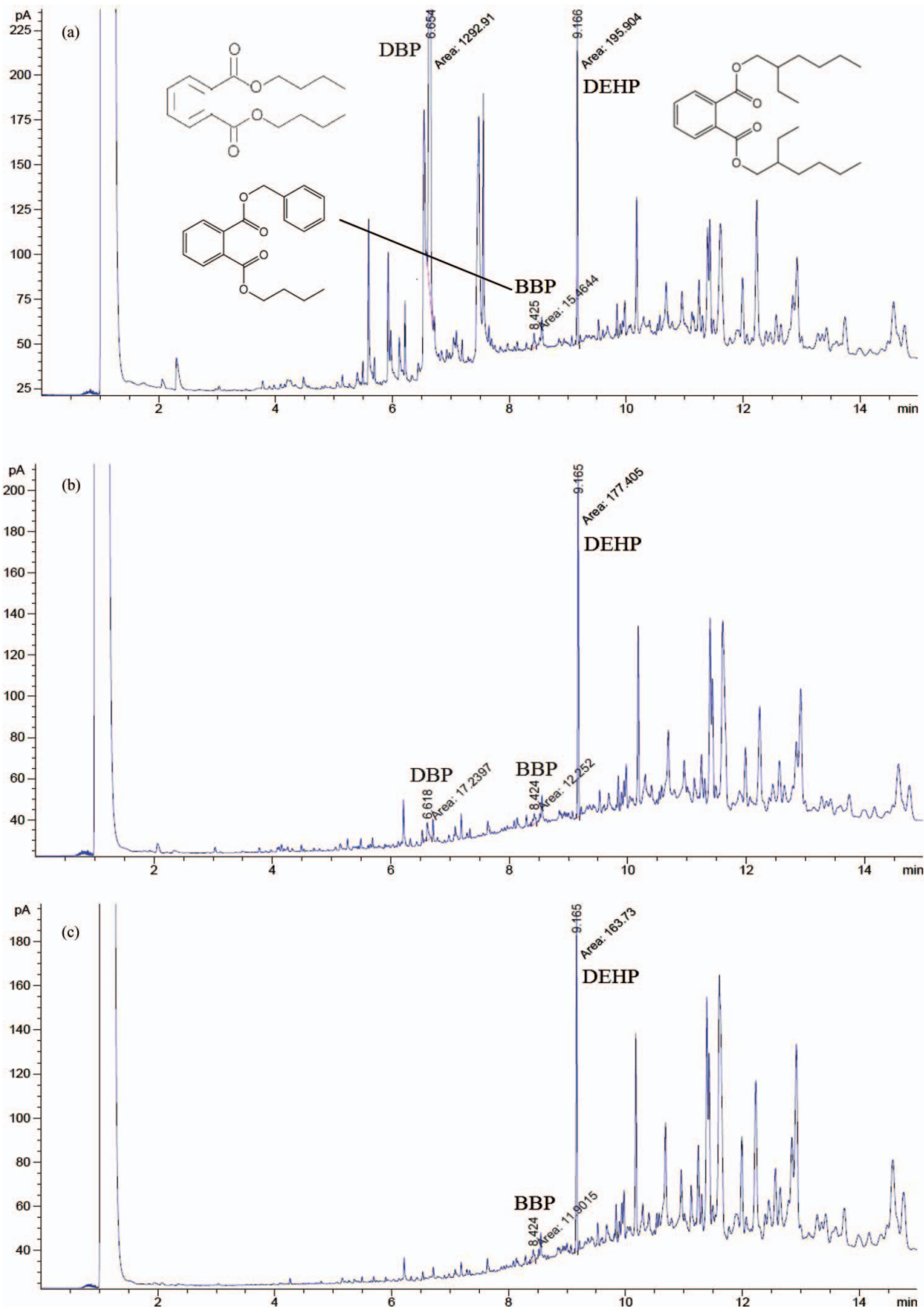
Analysis of PAEs followed the steps reported by Heise and Litz.<sup>[30]</sup> Sludge was dried at 105°C for 16 h prior to extraction, and then the dried sludge was ground by a grinder. After grinding, 2 g dried sludge was added to Teflon centrifugal tube, followed by the addition of 10 mL solvent (n-hexane and dichloromethane at a volume ratio of 1:1). The sample was shaken for 24 hours at ambient temperature then the extracted sample was centrifuged by the Harmonic Series centrifuge machine for 10 min at 3,500 rpm. The supernatant of extracted solvent was collected to analyze PAEs concentration by the GC-FID.

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 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 (Fig. 1); their method detective limits (MDLs) were 0.43, 0.27 and 0.98 mg/l, respectively. The recovery of spiked DEHP was 85.4%. Analyses of TS, VS, pH, SCOD and TCOD were according to the standard methods.

## Results and discussion

### Changes in sludge qualities after pretreatments

The pH values of sewage sludge before and after treatments in Table 1 show that NaOH alkalization response for the increase of the pH values from 6.70 (initial) to 7.88–11.50. In Run 9, the pH value with 80 mM NaOH alkalization was 11.50, which was higher than other 10 tests; in Runs 2, 3, 6, 7, and 8, the pH value was 8.15 with 40 mM NaOH dosage. Table 1 also shows the pH change of the sludge sample after sonication. The pH changed from its initial value (after alkalization) of 6.70–11.50 to 6.55–11.36 at the end of runs. It was found that the pH values were limited decreased by sonication, where the difference before and after sonication was as high as in order of 0.27 unit. This



**Fig. 1.** GC-FID spectrum of DBP, BBP and DEHP (a) before pretreatment (b) alkalinization in 68 mM NaOH and (c) alkalinization in 68 mM NaOH and sonication for 12.8 min (color figure available online).

**Table 1.** Experimental design of NaOH dosage and sonication time in sono-alkalization process and the changes of pH, TS and VS values before and after alkalization and sonication pretreatments.

Run	NaOH (mM)	Sonication (min)	pH After alkalization	TS and VS (g/L)					
				Initial		After alkalization		After sonication	
				TS	VS	TS	VS	TS	VS
1	68	12.8	10.48	29.7	20.8	28.5	18.9	28.4	18.7
2	40	0.0	8.15			29.4	19.4	29.4	19.4
3*	40	7.5	8.15			29.5	19.4	29.4	19.2
4	0	7.5	**					29.7	20.6
5	68	2.2	10.48			28.9	18.9	28.9	18.9
6	40	15.0	8.15	29.7	20.8	29.4	19.4	29.4	19.0
7*	40	7.5	8.15			29.5	19.4	29.5	19.2
8*	40	7.5	8.15			29.4	19.4	29.3	19.2
9	80	7.5	11.50			28.3	18.7	28.3	18.5
10	12	2.2	7.88			29.7	20.2	29.7	20.1
11	12	12.8	7.88			29.6	20.1	29.6	19.8

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

\*\*Without NaOH addition.

slight pH decrease might be explained by the production of soluble organic compounds containing acidic functional groups from the sewage sludge.<sup>[23]</sup>

During pretreatments, the solids mass (including TS and VS) were found to be changed by NaOH dosage and sonication. As the NaOH was added into the system, the sludge was hydrolyzed by NaOH and the TS was reduced at the end of runs. Li et al.<sup>[31]</sup> investigated the acidification and alkalization of textile chemical sludge to study the reduction of sludge volume and solid concentration. Experimental results indicated that reduction of total suspended solids (TSS) increased with increasing pH levels or alkaline dosages. When the pH level was increased from 6.5 (original) to 9 and 11, 3.5% and 37.6% of TSS reduction were observed, respectively. In this study, the original TS concentration was 29.7 g/L. When the NaOH dosage of 12–80 mM were added into the reactor for 24 h alkalization, TS concentrations were reduced to 29.6 g/L–28.3 g/L.

Table 1 also shows the changes of VS by alkalization. It was clear that increased NaOH dosages caused the higher decrease of VS concentrations. When the NaOH was raised from 12–80 mM, the residual VS concentration decreased from 20.2 g/L to 18.7 g/L, where the degradation of VS increased from 2.9% to 10.1%. Many studies proposed that the VS contained in WAS would be hydrolyzed by NaOH and the SCOD concentration increased with increasing alkaline dosages.<sup>[24,25]</sup>

Even the above description indicates that addition of NaOH is available to the SCOD increase in sludge treatment, the effect of mono-valent cation (for example, Na<sup>+</sup> and K<sup>+</sup>) addition of the dewatering property of sludge should be also noted.<sup>[32–34]</sup> Higgins and Novak<sup>[32]</sup> investigated the effect of cations on the settling and dewatering of activated sludge using laboratory scale activated sludge reactors. Addition of the sodium to the feed resulted in a

deterioration in settling and dewatering properties when the mono-valent to divalent cation ratio exceeded approximately 2 to 1, expressed on an equivalent basis.

Novak et al.<sup>[33]</sup> further checked the influence to the settling and dewatering properties of activated sludge, especially for industrial wastewaters in which very high concentrations of mono-valent cations. It was found that when Na<sup>+</sup> and K<sup>+</sup> concentrations in the raw wastewater decreased significantly to less than 10 and 0.1 milliequivalents (meq), respectively, settling and dewatering properties improved substantially. In this study, degradation of PAEs and increase of SCOD from sludge was the priority in the sono-alkalization system, therefore, dosages of NaOH added in sludge was much higher than above studies.

Bougrier et al.<sup>[35]</sup> studied the solubilisation of WAS by sonication, which indicated that sonication did not change the total matter quantity and the TS were constant. The results shown in Table 1 indicated that the TS concentrations were almost constant and the VS concentrations were all lower than the results before sonication. The degradation of VS was found to be linearly dependent on the sonication time. Tiehm et al.<sup>[28]</sup> treated the WAS by sonication to improve the anaerobic sludge stabilization. Longer sonication brought about the break-up of cell walls, the sludge solids were disintegrated and dissolved organic compounds were released. When the sonication time was raised from 7.5 to 150 min, degradation of VS increased from 21.5% to 33.7%.

#### PAEs degradation by sono-alkalization

Figure 1 shows the GC-FID spectrum of DBP, BBP and DEHP before treatment, with a sole alkalization and with a sono-alkalization (NaOH in 68 mM and sonication for 12.8 min) in sludge. It was found that the peak area of DBP

**Table 2.** Contribution percentages for DBP removal between two pretreatments.

Run	NaOH concentration (mM)	Sonication time (min)	Removal of DBP ( $C_0-C/C_0$ ) $\times 100$	Contribution (%)	
				Alkalization	Sonication
1	68	12.8	100.0	98.7	1.3
2	40	0.0	58.6	100.0	0.0
3	40	7.5	64.1	91.4	8.6
4	0	7.5	4.2	0.0	100.0
5	68	2.2	100.0	98.7	1.3
6	40	15.0	80.5	72.7	27.3
7	40	7.5	62.9	93.2	6.8
8	40	7.5	64.0	91.6	8.4
9	80	7.5	100.0	100.0	0.0
10	12	2.2	0.8	NA*	NA
11	12	12.8	0.0	NA	NA

\*Not available.

significantly decreased by alkalization. For BBP and DEHP, the peak areas were comparable before and after alkalization, which could be explained by the molecular structures of DEHP and BBP. The phthalate functional group was presented in DBP, BBP and DEHP. However, longer alkyl chains with branch structure and benzyl functional group were observed in DEHP and BBP, respectively. This longer and complex structure led to the difficulty for the degradation of organics by alkalization. In followed sonication, almost none DBP was observed in the spectrum (Fig. 1(c)), which indicated that the residual DBP was effectively degraded by the sonication.

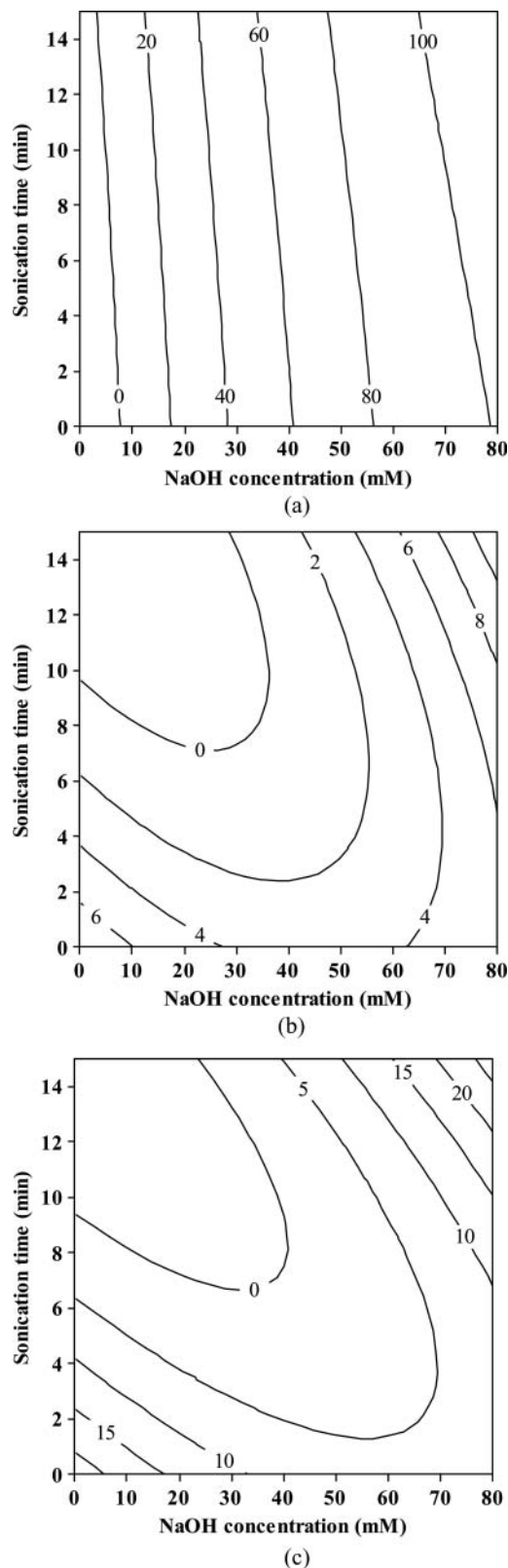
In Run 4, the sole sonication (without alkalization) marginally degraded the DBP from 718 to 687.8 mg/kg-dw and the DEHP and BBP were almost same before and after sonication (data were not shown). Yim et al.<sup>[28]</sup> discussed the change in the concentration of PAEs (DMP, DEP and DBP) during the sonication and the pseudo first-order of degradation of PAEs with irradiation time. The degradation of DEP and DBP were almost completed with 60 min of sonication, which indicated that the shorter branch contained in the molecules was effective on the organic compounds degradation. Chang et al.<sup>[25]</sup> proposed that the PAEs degradation rates were higher with a sonication than without a sonication in sterile sludge. It appeared that the more hydrophobic DBP, BBP and DEHP were readily susceptible to sonochemical degradation and the less hydrophobic DEP was more recalcitrant. However, it was found that the degradation rate constant of DBP was much higher than BBP and DEHP at same ultrasonic power and reaction time. This was comparable to the results shown in this study.

Table 2 shows the results of DBP removal in sewage sludge by the sono-alkalization process for 11 runs. Its complete elimination could be obtained by in Runs 1, 5 and 9, where the NaOH dosage was higher than 68 mM, notably upon the application of sono-alkalization. In Runs 3, 7 and 8, they were carried out in same reaction condition, which

could be considered as the triplicate experiments. The average removal percentage of DBP in the triplicate experiments was  $63.63 \pm 0.64\%$ . Also, as high as 92% of DBP was degraded by alkalization and only 8% of DBP was degraded by 7.5 min sonication. In Run 6, the NaOH dosage was same to Run 3 but the sonication time was extended to 15 min. It was observed that longer sonication provided better degradation efficiency (from 64.1% to 80.5%) in DBP removal, which was comparable to the results shown in Yim et al.<sup>[36]</sup>. The contribution of sonication in DBP removal increased from 8.6% to 27.3%. In Runs 10 and 11, the removal of DBP was very low by the sono-alkalization, based upon insufficient NaOH dosage (12 mM) in sludge.

Therefore, the removal percentages of DBP in these two runs were less than 1%. In Run 4, 4.2% of DBP was removed by a sole sonication, which was higher than Runs 10 and 11. In Table 1, it was found that the pH values before sonication in Run 4 and in Runs 10 and 11 were 6.7 and 7.88, respectively. It is well-known that the sonication can provide more OH radicals in acidic solution. Therefore, in Run 4, the removal of DBP was slightly higher than those of Runs 10 and 11. This result could be explained by the reaction between the 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.<sup>[36]</sup> The more hydroxyl ions lead to more DBP degradation. Since the BBP and DEHP were not decreased with alkalization, it was understood that lower molecular weight PAEs such as DBP could be easily degraded by hydroxyl ions.

Figure 2 shows the contour plots of DBP, BBP and DEHP removal efficiencies in sewage sludge by the sono-alkalization process. The response surface equations of PAEs removal in three contour plots calculated from Minitab 14 are listed in Table 3. In Figure 2(a) to 2(c), it was found that the removal of PAEs significantly related to the dosage of NaOH. However, in Figure 2(b) and 2(c), the maximum removal percentage of BBP and DEHP were



**Fig. 2.** Contour plot of (a) DBP (b) BBP (c) DEHP removal by the sono-alkalization pretreatments.

**Table 3.** Response surface equations of PAEs removal and SCOD concentration.

Item	Response surface equation	$R^2$
TDBP	$z = -16.739 + 2.313x + 0.506y - 0.011x^2 + 0.010y^2 + 0.001xy$	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
SCOD	$z = -288.165 + 125.622x + 599.105y - 0.847x^2 - 24.978y^2 - 1.567xy$	0.965

$x$  = NaOH concentration (mM).

$y$  = Sonication time (min).

$z$  = PAEs removal (%) or SCOD concentration (mg/L).

less than 10 and 20%, respectively, resulting in the low R-square values of both contour plots simulation (lower than 0.75). For DBP removal, the R-square value was as high as 0.94, which indicated that this simulation could be used to assume the removal of DBP in designed alkaline dosage and sonication time.

#### SCOD change by sono-alkalization

Chu et al.<sup>[37]</sup> investigated the change in ultrasonically treated WAS and found that in all the experiments a progressive increase of SCOD/TCOD was appreciated with sonication time. The SCOD/TCOD ratio increased from 0 (original) to higher than 0.2 (sonication time of 100 min). Table 4 shows the result of SCOD concentration, SCOD/TCOD ratio and contribution of SCOD increase by alkalization and sonication of sewage sludge, respectively. It was found that the higher NaOH dosages and longer sonication time showed the higher solubilisation of VS to SCOD and SCOD/TCOD ratio. The original SCOD was 140 mg/L. After the sono-alkalization, the total TCOD concentration were almost same to the original value, but the SCOD concentration increased to more than 3,000 mg/L, based on the hydrolysis phenomenon by alkalization and sonication. Comparison of the results in Runs 1 and 5 proposed that longer sonication (from 2.2 to 12.8 min) gave better ultrasonic degradation and SCOD increase in sludge treatments.

Bougrier et al.<sup>[32]</sup> tried to solubilize the WAS by a sonication. For each experiment, while the energy input increased, TCOD was constant but the soluble/particulate COD repartition varied: SCOD increased strongly for specific supplied energy. Grönroos et al.<sup>[38]</sup> applied a sonication assisted method to increase SCOD of sewage sludge for digestion and found that larger SCOD increase was obtained with same energy consumption when using high ultrasonic power together with short treatment time as when using low ultrasound power with long treatment time. In this study, after the sono-alkalization, the SCOD/TCOD increased from 0.5% to more than 19% in Runs 1 and 5, which



**Table 4.** Results of SCOD change during the sono-alkalization pretreatments.

Run	NaOH (mM)	Sonication (min)	SCOD (mg/L)	SCOD/COD (%)	Contribution (%)	
					Alkalinization	Sonication
1	68	12.8	6,400	23.9	73.6	26.4
2	40	0.0	3,750	14.0	100.0	0.0
3	40	7.5	6,050	22.6	61.2	38.8
4	0	7.5	3,350	12.5	0.0	100.0
5	68	2.2	5,100	19.0	92.9	7.1
6	40	15.0	6,100	22.8	60.5	39.5
7	40	7.5	6,050	22.6	61.1	38.9
8	40	7.5	5,900	22.0	62.7	37.3
9	80	7.5	6,600	24.6	87.6	12.4
10	12	2.2	1,710	6.4	14.6	85.4
11	12	12.8	3,950	14.7	6.0	94.0

indicated that the dosage of NaOH got a better solubilization of sewage sludge and saved the reaction time for sonication.

Higher dosages of NaOH also played an important role in the increase of SCOD. In Runs 3, 4 and 9, the SCOD concentration after the sono-alkalization increased to 3,350 mg/L (with sole sonication) and 6,600 mg/L (with NaOH of 80 mM and sonication for 7.5 min), where the SCOD/TCOD increased to 12.5% and 24.6%, respectively. Contribution of SCOD concentration increased by alkalization and sonication also gave us important information. Generally, contribution of SCOD increase was greater than 60% by alkalization. However, in Runs 10 and 11, as the NaOH dosage was 12 mM only, the contribution of SCOD increase by a sonication was greater than 85%. This result indicated that sonication could use in the increase of

SCOD when the lower NaOH dosage was carried out in sludge treatments.

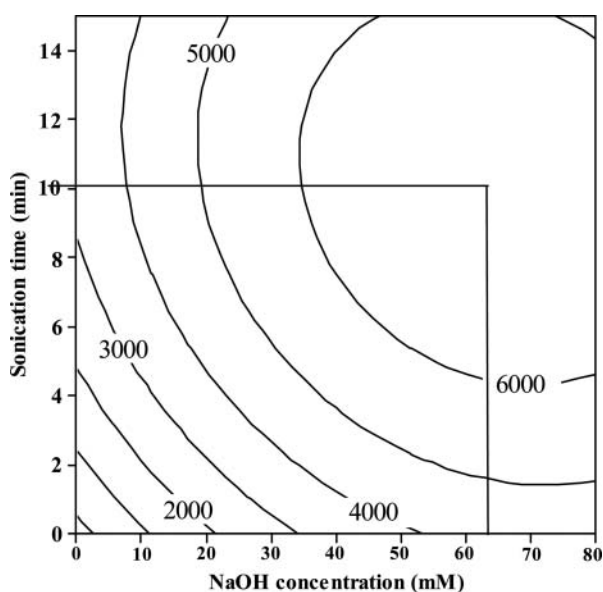
As illustrated in Figure 3, the contour plot of SCOD at different NaOH dosages and sonication time showed that the SCOD concentration increased with an increase of NaOH dosage and sonication time; the response surface equation with a high R-square value ( $>0.96$ ) was obtained and shown in Table 3. Based on this equation, a better treatment operation condition was obtained as the NaOH dosage of 68 mM and sonication time of 10 min.

## Conclusion

Concluding, DBP, BBP and DEHP were observed in the sewage sludge collected from the Di-Hua wastewater treatment plant, in an order of DBP > DEHP > BBP. A complete degradation of DBP was carried out by a Sono-alkalization at NaOH dosage of 68 mM and sonication time of 2.2 min. Batch experiments showed that the SCOD solubilisation increased with an increase of NaOH dosage and sonication time. The final SCOD was as high as 6,000 mg/L when the sono-alkalization was carried out at NaOH 68 mM and sonication time 10 min obtained from the CCD experimental tests.

## References

- [1] Cecil, L.H.; Zenz, D.R.; Kuchenrither, R. *Municipal Sewage Sludge Management: Processing, Utilization, & Disposal*, Technomic Publishing Company, Philadelphia, PA, USA, 1992.
- [2] Staples, C.A.; Peterson, D.R.; Parkerton, T.F.; Adams, W.J. The environmental fate of phthalate esters: A literature review. *Chemosphere* **1997**, *35*(4), 667–749.
- [3] Guidotti, M.V.; Cremisini, G.M. Phthalate esters in freshwaters as markers of contamination source: A site study in Italy. *Environ. Int.* **1997**, *23*(3), 337–347.
- [4] Staples, C.A.; Parkerton, T.F.; Peterson, D.R. A risk assessment of selected phthalate esters in North American and Western European surface waters. *Chemosphere* **2000**, *40*(8), 885–891.



**Fig. 3.** Contour plot of SCOD by the sono-alkalization pretreatments.

- [5] Vikelsoe, J.; Thomsen, M.; Carlsen, L.; Phthalates and nonylphenols in profiles of differently dressed soils. *Sci. Total Environ.* **2002**, *296*(1–3), 105–116.
- [6] Yuan, S.Y.; Liu, C.; Liao, C.S.; Chang, B.V. Occurrence and microbial degradation of phthalate esters in Taiwan river sediments. *Chemosphere* **2002**, *49*(10), 1295–1299.
- [7] Wang, J.; Zhao, X.; Wu, W. Biodegradation of phthalic acid esters (PAEs) in soil bioaugmented with acclimated activated sludge. *Proc. Biochem.* **2004**, *39*(12), 1837–1841.
- [8] Amir, S.; Hafidi, M.; Merlina, G.; Hamdi, M.; Jouraiphy, A.; Gharousc, M.; Revel, J.C. Fate of phthalic acid esters during composting of both lagooning and activated sludges. *Proc. Biochem.* **2005**, *40*(6), 2183–2190.
- [9] Dewil, R.; Baeyens, J.; Goutvrind, R. Ultrasonic treatment of waste activated sludge. *Environ. Prog.* **2006**, *25*(2), 121–128.
- [10] Alatrisme-Mondragon, F.; Iranpour, R.; Ahring, B.K. Toxicity of di-(2-ethylhexyl) phthalate on the anaerobic digestion of wastewater sludge. *Water Res.* **2003**, *37*(6), 1260–1269.
- [11] Marttinen, S.K.; Kettunen, R.H.; Sormunen, K.M.; Rintala, J.A. Removal of bis (2-ethylhexyl) phthalate at a sewage treatment plant. *Water Res.* **2003**, *37*(6), 1385–1393.
- [12] Roslev, P.; Vorkamp, K.; Aarup, J.; Frederiksen, K.; Nielsen, P.H. Degradation of phthalate esters in an activated sludge wastewater treatment plant. *Water Res.* **2007**, *41*(5), 969–976.
- [13] Dargnat, C.; Teil, M.J.; Chevreuil, M.; Blanchard, M. Phthalate removal throughout wastewater treatment plant: Case study of Marne Aval station (France). *Sci. Total Environ.* **2009**, *407*(4), 1235–1244.
- [14] Fauser, P.; Vikelsoe, J.; Sorensen, P.B.; Carlsen, L. Phthalates, nonylphenols and LAS in an alternately operated wastewater treatment plant-fate modelling based on measured concentrations in wastewater and sludge. *Water Res.* **2003**, *37*(6), 1288–1295.
- [15] Saeger, V.W.; Tucker, E.S. Biodegradation of phthalic acid esters in river water and activated sludge. *Appl. Environ. Microbiol.* **1976**, *31*(1), 29–34.
- [16] Wang J.; Chen, L.; Shi, H.; Qian, Y. Microbial degradation of phthalic acid esters under anaerobic digestion of sludge. *Chemosphere* **2000**, *41*(8), 1245–1248.
- [17] Gavala, H.N.; Alatrisme-Mondragon, F.; Iranpour, R.; Ahring, B.K. Biodegradation of phthalate esters during the mesophilic anaerobic digestion of sludge. *Chemosphere* **2003**, *52*(4), 673–682.
- [18] Chen, C.Y. The oxidation of di-(2-ethylhexyl) phthalate (DEHP) in aqueous solution by UV/H<sub>2</sub>O<sub>2</sub> photolysis. *Water Air Soil Pollut.* **2010**, *209*(1–4), 411–417.
- [19] Kaneco, S.; Katsumata, H.; Suzuki, T.; Ohta, K. Titanium dioxide mediated photocatalytic degradation of dibutyl phthalate in aqueous solution-kinetics, mineralization and reaction mechanism. *Chem. Eng. J.* **2006**, *125*(1), 59–66.
- [20] Lertsirisopon, R.; Soda, S.; Sei, K.; Ike, M. Abiotic degradation of four phthalic acid esters in aqueous phase under natural sunlight irradiation. *J. Environ. Sci. (China)* **2009**, *21*(3), 285–290.
- [21] Chang, B.V.; Wang, T.H.; Yuan, S.Y. Biodegradation of four phthalate esters in sludge. *Chemosphere* **2007**, *69*(7), 1116–1123.
- [22] Gonze, E.; Pillot, S.; Valette, E.; Gonthier, Y.; Bernis, A. Ultrasonic treatment of an aerobic activated sludge in a batch reactor. *Chem. Eng. Proc.* **2003**, *42*(12), 965–975.
- [23] Pham, T.T.H.; Tyagi, R.D.; Brar, S.K.; Surampalli, R.Y. Effect of ultrasonication and Fenton oxidation on biodegradation of bis(2-ethylhexyl) phthalate (DEHP) in wastewater sludge. *Chemosphere* **2011**, *82*(6), 923–928.
- [24] Lin, J.G.; Ma, Y.S.; Huang, C.C. Alkaline hydrolysis of the sludge generated from a high-strength, nitrogenous-wastewater biological-treatment process. *Bioresour. Technol.* **1998**, *65*(1–2), 35–42.
- [25] Chang, C.N.; Ma, Y.S.; Lo, C.W. Application of oxidation-reduction potential as a controlling parameter in waste activated sludge hydrolysis. *Chem. Eng. J.* **2002**, *90*(3), 273–281.
- [26] Chiu, Y.C.; Chang, C.N.; Lin, J.G.; Huang, S.J. Alkaline and ultrasonic pretreatment of sludge before anaerobic digestion. *Water Sci. Technol.* **1997**, *36*(11), 155–162.
- [27] Wang, F.; Wang, Y.; Ji, M. Mechanisms and kinetics models for ultrasonic waste activated sludge disintegration. *J. Hazard. Mater.* **2005**, *123*(1–3), 145–150.
- [28] Tiehm, A.; Nickel, K.; Zellhorn, M.M.; Neis, U. Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization. *Water Res.* **2001**, *35*(8), 2003–2009.
- [29] Ma, Y.S.; Kumar, M.; Lin, J.G. Degradation of carbofuran-contaminated water by Fenton process. *J. Environ. Sci. Health Pt. A* **2009**, *44*(9), 914–920.
- [30] Heise, S.; Litz, N. *Phthalates German Federal Environmental Agency*, Berlin, Germany, 2004.
- [31] Li, H.; Jin, Y.; Mahar, R.B.; Wang, Z.; Nei, Y. Effects and model of alkaline waste activated sludge treatment. *Bioresour. Technol.* **2008**, *99*(11), 5140–5144.
- [32] Higgins, M.J.; Novak, J.T. The effect of cations on the settling and dewatering of activated sludges: Laboratory results. *Water Environ. Res.* **1997**, *69*(2), 215–224.
- [33] Novak, J.T.; Love, N.G.; Smith, M.L.; Wheeler, E.R. The effect of cationic salt addition on the settling and dewatering properties of an industrial activated sludge. *Water Environ. Res.* **1997**, *70*(5), 984–996.
- [34] Murthy, S.N.; Novak, J.T. Effects of potassium ion on sludge settling, dewatering and effluent properties. *Water Sci. Technol.* **1998**, *37*(4–5), 317–324.
- [35] Bougrier, C.; Carrère, H.; Delgenès, J.P. Solubilisation of waste-activated sludge by ultrasonic treatment. *Chem. Eng. J.* **2005**, *106*(2), 163–169.
- [36] Yim, B.; Nagata, Y.; Maeda, Y. Sonolytic degradation of phthalate acid esters in aqueous solutions. Acceleration of hydrolysis by sonichemical action. *J. Phys. Chem. A* **2002**, *106*(1), 104–107.
- [37] Chu, C.P.; Chang, B.V.; Liao, G.S.; Jean, D.S.; Lee, D.J. Observations on changes in ultrasonically treated waste-activated sludge. *Water Res.* **2001**, *35*(4), 1038–1046.
- [38] Grönroos, A.; Kyllönen, H.; Korpijärvi, K.; Pirkonen, P.; Paavola, T.; Jokela, J.; Rintala, J. Ultrasound assisted method to increase soluble chemical oxygen demand (SCOD) of sewage sludge for digestion. *Ultrason. Sonochem.* **2005**, *12*(1–2), 115–120.