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Assessment of di-(2-ethylhexyl)phthalate (DEHP) Removal in a Rotating Biological Contactor and Activated Sludge Process Treating Domestic Wastewater

Hsiao-Fen Cheng, Mathava Kumar, and Jih-Gaw Lin
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Di-(2-ethylhexyl)phthalate (DEHP) is one of the most representative persistent micro-pollutants detected in the sewage sludge. In the present study, the presence of DEHP and its removal in various treatment units of a sewage treatment plant (STP) including an attached growth biological system i.e., a rotating biological contactor (RBC) and a suspended growth biological system i.e., activated sludge process (ASP) were investigated. Representative samples of sewage and sludge were collected at each stage of the STP for 2 years to explore the DEHP flow in the dissolved (DEHP_d) and adsorbed (DEHP_a) phases. The combination of RBC with a final clarifier was responsible for 50.4 and 58.2% of DEHP_d and DEHP_a removals, respectively. Both DEHP_d and DEHP_a removals were greater in RBC compared to ASP, demonstrating that an attached growth biological system is more efficient in the removal of DEHP compared to the suspended growth biological system. A good correlation between DEHP_d and organic matter removal was observed by using Pearson-correlation matrix approach.

Keywords di-(2-ethylhexyl)phthalate; mass balance; persistent micro-pollutants; sewage treatment plant

INTRODUCTION

Sewage sludge is a rich source of organic matter and nutrients, which can be utilized for soil improvement and plant growth. The utilization of sewage sludge for plant growth and converting sludge into renewable resource is often restricted by the presence of hazardous organic matter (HOM). HOM enters the sewer system through various domestic and industrial sources; they are hydrophobic in nature and recalcitrant to microorganisms. HOM have the tendency to accumulate in the sludge during biological wastewater treatment processes and subsequently raise the difficulty of further sludge treatment and/or disposal (1). The application of sewage sludge containing HOM can create a risk to ecosystems. The United States Environmental Protection Agency (USEPA) and the European Union (EU) have enforced a set of disposal standards for the land application of sewage sludge including the level of HOM. Therefore, the determination of HOM and its partitioning behavior between sewage and sludge samples are vital to enhance the degradation efficiency of HOM in a sewage treatment plant (STP).

Di-(2-ethylhexyl)phthalate (DEHP) is the most frequently detected HOM in the municipal sewage sludge samples. It is one of the widely employed industrial chemicals among the phthalate esters (PAEs), and serves as an additive to impart the flexibility in polyvinylchloride (PVC) resins (2). DEHP has been detected in water, sediment, soil, air, and living organisms (2). DEHP leaching from plastic matrices is one of the sources by which it enters the environment (3). Moreover, there has been an increasing focus on likely xeno-estrogenic effects of DEHP and its metabolites (2,4). Based on these findings, DEHP has been categorized under endocrine disrupting chemicals (EDCs). The physicochemical processes are less effective in the removal of DEHP; whereas, the microbial degradation is considered as an effective process for the removal of DEHP in the environment (2,5).

Quantification of DEHP in complex environmental samples is difficult owing to their very low water solubility (6–8). Water solubility is an extremely important property that mainly influences the biodegradation and bioaccumulation of DEHP in various environments. Among the various environments, DEHP was frequently found in waste sludge from STP. However, no detailed information is available about the distribution and degradation of DEHP during sewage or sludge treatment processes in a STP. Several researchers investigated the fate and behavior of surfactants/detergents in a wastewater treatment plant (9–12). The physicochemical properties of DEHP are totally different from surfactants and consequently increase the complexity to the separation of trace amounts of DEHP from aqueous samples. Our preliminary study indicated that DEHP concentration in the sludge samples were higher than the values suggested by EU for land application of sewage sludge (13).
In the present study, the fate and distribution of DEHP (including dissolved-phase, DEHP$_d$ and adsorbed-phase, DEHP$_a$) at various stages of the STP were investigated. In addition, considerable attention was given to explore the DEHP removal/reduction in attached and suspended growth biological treatment systems of the STP.

**MATERIALS AND METHODS**

**Description of the STP**

A sewage treatment plant (STP) located in Northern Taiwan was selected for the present investigation. A simplified layout of the STP and its operating conditions are shown in Fig. 1 and Table 1, respectively. The STP was designed to treat 15500 m$^3$/d (CMD) of raw sewage without any industrial flow. The sewage treatment system in the STP consists of two parallel lines:

1. main line designed to treat a sewage flow of 13500 CMD by conventional activated sludge process (ASP), and
2. the other line designed to treat 2000 CMD of raw sewage by rotating biological contactor (RBC).

The sludge gathered from the clarifiers, i.e., primary clarifier (PS), secondary clarifier (SC), and final clarifier (FC), was stabilized in an aerobic sludge digester unit.

**Sampling**

Five sets of representative samples (both wastewater and sludge) were collected from various stages of the STP (Fig. 1) over a period of 2 years. Immediately after the wastewater sampling, approx. 0.1% (m/m) of NaN$_3$ was added into the sampling bottles to hinder any bacterial activity (14). Before analysis, the wastewater samples were filtered through 0.45 µm membrane filter paper (ADVANTEC MFS, INC.) to separate dissolved and adsorbed phases of DEHP (DEHP$_d$ and DEHP$_a$, respectively). In addition, the sludge samples collected from various stages of STP i.e., primary sludge, secondary sludge, aerobically digested sludge (AD sludge), RBC sludge (collected from FC), concentrated sludge, and sludge cakes, were labeled separately, added with 0.1% (m/m) of NaN$_3$, and filtered through 1.5 µm Whatman (934-AH) filter paper (except the sludge cake). The filtered liquid and filtrate were analyzed for DEHP concentrations i.e., DEHP$_d$ and DEHP$_a$. Before DEHP$_a$ analysis, the filtrate was collected, air-dried, and passed through a 30-mesh sieve (15).

**Extraction of DEHP from Samples and Analysis**

The solid phase extraction (SPE) was applied to extract and purify the DEHP from wastewater samples i.e., DEHP$_d$. The SPE apparatus and commercialized Speedisk were purchased from J. T. Baker. The C$_{18}$ Speedisk, a selective adsorbent to semi-volatile organic matter was used to eliminate the interferences from other types of organic compounds. The Speedisk™ was designed to handle larger volumes and dirty sample separations without any additional purification steps, as compared to the traditional SPE tubes. The extraction and elution procedures of SPE are illustrated in Fig. 2. An optimized supercritical fluid extraction (SFE) method was followed to extract the DEHP from suspended solids and sludge particles (solid-form) (16). The extracts were identified and quantified by

![FIG. 1. Simplified flowchart of the sewage treatment plant (Description: L1: raw sewage; L2: primary effluent; L3: secondary effluent; L4: RBC effluent; L5: final effluent; S1: primary sludge; S2: secondary sludge; S3: RBC sludge; S4: aerobically digested sludge; S5: thickened sludge; S6: sludge cake).](image-url)
GC/MS (HP 1800A) equipped with a HP-1 capillary column (J&W Scientific, Folsom, CA, USA). The mass spectrometer was operated at 70 eV and scanned from 30 to 425 u at 1 scan/s.

Suspended solids (SS), chemical oxygen demand (COD), total solids (TS), and volatile solids (VS) concentrations in the samples were determined as per the procedures reported in the Standard Methods (17). Besides, the dissolved organic carbon (DOC) and total organic carbon (TOC) in the wastewater and sludge samples were determined using a TOC analyzer (OI Analytical 1010).

RESULTS AND DISCUSSION

High purity DEHP extracts were obtained from raw sewage and sludge samples using the combination of SPE and SFE techniques. Subsequently, the high purity DEHP extracts from DEHP_d and DEHP_a were analyzed in a total ion chromatograph (TIC); the typical chromatographs are shown in Fig. 3. The presence of DEHP in raw sewage and dewatered sludge cake is evidenced from the chromatogram with a retention time of 24.09 min.

In the STP, a major portion of wastewater was treated by ASP and a minor portion of primary effluent was treated through RBC. DEHP is more resistant to biodegradation under anaerobic conditions; whereas, it is slowly biodegradable under aerobic condition (13,18). Therefore, the sludge produced in various clarification stages of the STP i.e., PC, SC, and FC, were digested aerobically in the STP (Fig. 1). DEHP concentration in the dissolved and adsorbed phases of each treatment unit is shown in Table 2. A wider variation in DEHP concentration (0.6 to 400 mg/L) was observed owing to the poor solubility of DEHP (Table 2) (2,19). Considerable removals of DEHP_d and DEHP_a can be noticed in each treatment unit; however, DEHP was not completely removed in any of the treatment units. This could be attributed to the poor metabolic activity of the microorganisms performing DEHP biodegradation in the STP.

DEHP Removal in a Rotating Biological Contactor

RBC’s are classified into the attached growth treatment systems, where fixed films of the microorganism in the rotary disks are employed for wastewater treatment.
DEHP concentration in the dissolved phase of raw sewage and primary effluent were in the range of 5.83 to 12.05 μg/L and 4.68 to 8.66 μg/L, respectively. After the wastewater treatment in RBC, DEHP concentration was reduced to 2.51 to 7.15 μg/L. The combination of RBC with FC further reduced the DEHP concentration to a range of 0.86 to 5.86 μg/L. A noticeable reduction of DEHP was also observed in the RBC. Overall, DEHP and DEHP_a removals in the RBC were 23% and 46%, respectively (Table 3).

DEHP Removal in Activated Sludge Process

ASP is the most commonly used conventional biological suspended growth system for sewage treatment. DEHP_d and DEHP_a concentrations in the influent of ASP were 4.68 to 8.66 μg/L and 3.21 to 6.54 mg/kg, respectively. In the secondary effluent (L3), the concentration of DEHP in dissolved and adsorbed phases were from 3.61 to 8.61 μg/L and 1.98 to 5.67 mg/kg, respectively (Table 2). The corresponding removals of DEHP_d and DEHP_a were around 15% and 32.5%, respectively (Table 3). The values of DEHP removals in RBC and ASP demonstrate that DEHP_d removal is greater in the attached growth system than the suspended growth system. Moreover, it was reported that large fractions of resistant organic pollutants were unchanged in conventional activated sludge treatment (20). In the recent decades, RBC’s are not preferred due the practical difficulties in operation and maintenance. Alternatively, the degradability of recalcitrant pollutants including DEHP can be enhanced by the application of acclimated activated sludge (21).

### TABLE 2
Concentrations of DEHP in water samples and sludge samples at the STP during five times of sampling

<table>
<thead>
<tr>
<th>Nature of sample</th>
<th>Sample ID</th>
<th>DEHP_d (µg/L)</th>
<th>DEHP_a (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average^c</td>
<td>Range</td>
</tr>
<tr>
<td>Water samples</td>
<td>L1</td>
<td>8.84</td>
<td>5.83–12.05</td>
</tr>
<tr>
<td></td>
<td>L2</td>
<td>6.25</td>
<td>4.68–8.66</td>
</tr>
<tr>
<td></td>
<td>L3</td>
<td>5.33</td>
<td>3.61–8.61</td>
</tr>
<tr>
<td></td>
<td>L4</td>
<td>4.80</td>
<td>2.51–7.15</td>
</tr>
<tr>
<td></td>
<td>L5</td>
<td>3.10</td>
<td>0.86–5.86</td>
</tr>
<tr>
<td>Sludge samples</td>
<td>S1</td>
<td>5.45</td>
<td>3.44–7.07</td>
</tr>
<tr>
<td></td>
<td>S2</td>
<td>4.28</td>
<td>2.90–5.11</td>
</tr>
<tr>
<td></td>
<td>S3</td>
<td>3.46</td>
<td>0.91–4.37</td>
</tr>
<tr>
<td></td>
<td>S4</td>
<td>2.02</td>
<td>0.79–2.82</td>
</tr>
<tr>
<td></td>
<td>S5</td>
<td>28.77</td>
<td>0.74–95.17</td>
</tr>
<tr>
<td></td>
<td>S6</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

^aDEHP in dissolved phase.

^bDEHP in adsorbed phase.

^c n = 5.
Depletion of DEHP removal from both the dissolved and adsorbed phases is highly essential for the reusability of sludge and the treated wastewater. In Table 2, DEHP concentration in the adsorbed phase (SS) is much greater than in dissolved phase (Table 2). The concentration of DEHP determined in adsorbed phase in raw sewage was varied from 4.57 to 8.81 mg/L. At that particular time, the concentrations of SS in raw sewage was in the range of 46 to 131 mg/L. A considerable portion of DEHP was removed from the adsorbed phase during sewage treatment, which was in good proportion to SS removal. The total removal of DEHP/a is nearly 68%, which is considerably greater than DEHP/d removal owing to the quantitative DEHP adsorbed in suspended solids as well as the high solids removal in the STP (10). The removal efficiency of adsorbed-DEHP was greater in RBC (46%) compared to ASP (32.5%).

### DEHP in Sludge Treatment Processes

The sludge instigated from PC, SC, and FC was pumped into an aerobic digestion tank. The samples of primary sludge, secondary sludge, RBC sludge, AD sludge, concentrated sludge (Fig. 1) and sludge cake were collected and investigated for DEHP concentration. DEHP/a and DEHP/d concentrations in the sludge samples are shown in Table 2. The distribution of DEHP between sludge supernatants (DEHP/a) and sludge particulate matter (DEHP/d) was more pronounced in sludge treatment units compared with wastewater treatment systems. The concentration of DEHP observed in the supernatant is close to the concentration of DEHP determined in filtered raw sewage. Table 2 shows that the average DEHP/a concentration in the concentrated sludge is higher than the DEHP/d concentration in primary, secondary, RBC, and AD sludge.

The presence of dissolved organic matter (DOC) plays an important role as the carrier to assist the interactions between hydrophobic organics such as DEHP with DOC. Moreover, it can further increase the solubility in water (22). Besides, the presence of DOC and salts might alter the solubility behavior of DEHP in the aqueous phase (23). It should be emphasized that water solubility is a key factor affecting the extent of biodegradation for organics in aqueous phase. DEHP removal in the dissolved phase of sludge is around 53% after aerobic digestion (Table 3). The DEHP/a removal percentage in the AD process is close to the DEHP/a removal percentage obtained from wastewater treatment units.

A higher DEHP/a concentration was observed in the sludge samples due to higher DEHP accumulation onto the particulate matter. Turner and Rawling (2000) (23) reported that DEHP partitioning between the aqueous and the solid phases is a function of particle concentration and particulate organic carbon, which is in good accord with the results observed from the adsorbed phase of the wastewater samples. DEHP removal in the sludge particulate matters is around 31%, which is much lower than DEHP/a removal demonstrating that DEHP degradation is mainly occurring in aerobic sludge digestion (Table 3). Madsen et al. (1999) (18) reported that indigenous microorganisms in the sewage sludge were dominant towards DEHP degradation in the sludge treatment process. Eventually, DEHP concentration observed in the sludge cake was below the value suggested by EU for land application of sewage sludge i.e., 100 mg/kg (Table 2).

### DEHP Removal in Aerobic Sludge Digestion Unit Based on Mass Flow

The total inlet solids flow rate through primary (S1), secondary (S2), and final (S3) clarifiers into aerobic digestion unit were 83, 214, and 32 CMD, respectively. A simplified layout of STP and the flow of DEHP through sewage and sludge are shown in Fig. 4. The average influent DEHP concentration from S1, S2, and S3 were 47.5, 41.4, and 35.2 mg/kg, respectively (Table 2). The corresponding DEHP mass flow rates into aerobic digester were 9,120, 17,595, and 1,936 mg/d from PC, SC, and FC, respectively. The total DEHP mass flow into the aerobic digester and sludge thickener units were 28,651 and 19,718 mg/d (S4), respectively. DEHP/a removal in the aerobic digester and sludge thickener units were 31% and 7%, respectively (Table 3).

DEHP/a removal in the aerobic digester unit was much lower than the DEHP/a degradation values reported in the biodegradation studies carried out with adapted/acclimated sludges in lab-scales reactors (20,21). This could be due to the lower bioavailability of DEHP in real

### Table 3

<table>
<thead>
<tr>
<th>Treatment unit</th>
<th>Dissolved phase (%)</th>
<th>Adsorbed phase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC</td>
<td>29.3</td>
<td>23.1</td>
</tr>
<tr>
<td>ASP with SC</td>
<td>14.7</td>
<td>32.5</td>
</tr>
<tr>
<td>RBC</td>
<td>23.2</td>
<td>46.1</td>
</tr>
<tr>
<td>FC</td>
<td>35.4</td>
<td>22.5</td>
</tr>
<tr>
<td>RBC with FC</td>
<td>50.4</td>
<td>58.2</td>
</tr>
<tr>
<td>ASD&lt;sup&gt;a&lt;/sup&gt;</td>
<td>53&lt;sup&gt;b&lt;/sup&gt;</td>
<td>31</td>
</tr>
<tr>
<td>ST&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td>7</td>
</tr>
</tbody>
</table>

<sup>a</sup>Calculations are based on measured DEHP concentrations before and after each wastewater treatment unit.

<sup>b</sup>Calculations are based on mass concentrations of DEHP in sludge treatment unit.

<sup>a</sup>Value reported in [ ] is calculated based on the changes of DEHP concentration in dissolved phase.

<sup>a</sup>DEHP removals

<sup>b</sup>Removals of DEHP in dissolved and adsorbed phases in each treatment unit at the STP

<sup>a</sup>Removals of DEHP in dissolved and adsorbed phases in each treatment unit at the STP.
wastewater treatment systems (24). Fauser et al. (2003) (25) measured DEHP concentrations in a wastewater treatment plant and revealed that about 70% of DEHP was bio-degraded, and 28% of DEHP remained in the sludge. Moreover, Marttinen et al. (2003) (24) reported that 29% of DEHP was removed by the activated sludge process, and 32% of DEHP was removed by anaerobic sludge digestion. These results were consistent with the removals of DEHP addressed in the present study.

Correlation of DEHP with Conventional Parameters

In addition to the determination of DEHP distribution in the STP, the effect of various conventional parameters i.e., COD, TOC, DOC, and SS, in DEHP removal was investigated. The results of COD, TOC\textsubscript{t}, TOC\textsubscript{s}, DOC, SS, DEHP\textsubscript{d}, and DEHP\textsubscript{a} are correlated by using Pearson correlation coefficient matrix approach as shown in Table 4. The presence of DOC and SS has major influence on the partition behavior of DEHP between the dissolved and the adsorbed phases in wastewater and sludge samples. DEHP\textsubscript{a} was in good correlation with DOC and TOC\textsubscript{t} (0.74 and 0.72); whereas DEHP\textsubscript{a} shows a high correlation with COD (0.60), TOC\textsubscript{t} (0.56), and SS (0.43). Sewage and sludge samples often contain high levels of suspended particulate matter, therefore large amounts of particles with highly sorption sites are produced in water. This elevates the partitioning behavior of DEHP with solid matters in the sewage sludge. The experimental outcomes of this investigation clearly indicate that DEHP degradation is more feasible in biological treatment systems compared with the physicochemical treatment processes.

CONCLUSIONS

Biodegradation is the dominant DEHP removal mechanism in the STP. DEHP removals in dissolved and adsorbed phases were higher in RBC compared to ASP. The attached growth system (RBC) is more tolerant to DEHP; thus displaying a higher DEHP removal efficiency compared with the suspended growth system (ASP). The presence of dissolved organic matter has a major influence in the partitioning behavior and the solubility of DEHP\textsubscript{d} in sewage and sludge samples. DEHP tends to adsorb quantitatively onto solid particles and could be removed along with SS. The distribution and transport of DEHP have to be studied in detail to explore the accurate mass balance and the degradation behavior of DEHP during sewage and sludge treatment processes.

ACKNOWLEDGMENTS

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TABLE 4

<table>
<thead>
<tr>
<th></th>
<th>COD</th>
<th>TOC\textsubscript{t}</th>
<th>TOC\textsubscript{s}</th>
<th>DOC</th>
<th>SS</th>
<th>DEHP\textsubscript{d}</th>
<th>DEHP\textsubscript{a}</th>
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<tr>
<td>COD</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>–</td>
<td>–</td>
</tr>
<tr>
<td>TOC\textsubscript{t}</td>
<td>0.72\textsuperscript{a}</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>TOC\textsubscript{s}</td>
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<td>–0.10</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>DOC</td>
<td>0.54</td>
<td>0.94</td>
<td>–0.24</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SS</td>
<td>0.69</td>
<td>0.78</td>
<td>–0.27</td>
<td>0.70</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>DEHP\textsubscript{d}</td>
<td>0.39</td>
<td>0.72</td>
<td>–0.10</td>
<td>0.74</td>
<td>0.42</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>DEHP\textsubscript{a}</td>
<td>0.60</td>
<td>0.56</td>
<td>–0.08</td>
<td>0.50</td>
<td>0.43</td>
<td>0.13</td>
<td>–</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Figures in bold indicates a significant correlation, \( p < 0.05 \).
REFERENCES