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Author(s)	Asakura, Hiroshi; Matsuto, Toshihiko
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Experimental study of behavior of endocrine-disrupting chemicals in leachate treatment process and evaluation of removal efficiency

Hiroshi Asakura*, Toshihiko Matsuto**

* National Institute for Environmental Studies, Onogawa 16-2, Tsukuba, Ibaraki 305-8506, Japan

** Division of Environmental and Resource Engineering, Graduate School of Engineering, Hokkaido University,

Kita 13 Nishi 8, Kita-ku, Sapporo 060-8628, Japan

E-mail: asakura.hiroshi@nies.go.jp

Tel: +81-29-850-2805

Fax: +81-29-850-2694

Abstract

An experimental study of the behavior of endocrine-disrupting chemicals (EDCs) in leachate treatment processes (aeration, coagulation and sedimentation, activated carbon adsorption, and advanced oxidation) was conducted and removal efficiencies were evaluated. Among target EDCs, concentrations of BPA (1800 times), DBP (10 times), BBP (40 times), and DEHP (30 times) in leachate are more than ten times higher than those in surface water. BPA, DBP, and BBP can be treated by aeration and DEHP, by advanced oxidation processes. BPA could not be effectively removed by coagulation and sedimentation because most of BPA partitioned in the supernatant. DEHP could hardly be treated by aeration. The removal ratios of DEHP were approximately 50 to 70% if the generated sediment was removed completely. The removal ratios of DEHP in leachate of 100 m³/d with 100 kg of activated carbon were 50 to 70%, assuming a complete mixing model. The concentration of DEHP was decreased to below one tenth in 120 min by advanced oxidation processes.

Key Words

Endocrine-disrupting chemicals, municipal solid waste landfill site, leachate treatment process, BPA, DEHP

1. Introduction

In Japan and other countries, bisphenol A (BPA) and diethylhexylphthalate (DEHP), which are regarded as endocrine-disrupting chemicals (EDCs), were detected at higher concentrations in leachate from municipal solid waste landfill sites than in surface water (Bauer et al., 1998; Robinson and Gronow, 1998; Yasuhara et al., 1999; Behnisch et al., 2001; Yamamoto et al., 2001; Fromme et al., 2002; Kjeldsen et al., 2002; Jonsson et al., 2003; Asakura et al., 2004). High concentrations of BPA and DEHP may have been flowing out from landfill sites as leachate for many decades (Asakura et al., 2003). Presently, the influence of EDCs on health is not known in detail, and there are few standards for EDCs in environmental water (DEHP is listed only as a substance to be monitored in surface water in Japan). However, as a precautionary approach, it is necessary to decrease the concentrations of EDCs in effluent to as low as those in surface water by leachate treatment for an adequate period.

Because little study has been conducted on the behavior of EDCs in the leachate treatment process (Bauer et al., 1998; Yamada et al., 1999), the details and mechanisms are not known. We have reported that aeration effectively removes BPA (Asakura et al., 2007). However, the mechanisms underlying the decrease of BPA, i.e., whether by volatilization or microbial decomposition, could not be clarified. The required treatment time is also not known. Some alkylphenols (APs) were rarely detected in leachate (Bauer et al., 1998), but there is little information about the behavior in treatment process. In the case of DEHP, none of the existing conventional methods, including aeration, biological treatment, coagulation and sedimentation, and activated carbon adsorption, could decrease its concentration in leachate to less than 10 times that in surface water. Thus, it is necessary to examine other treatment processes.

Several investigations on the behavior of EDCs in the treatment process of wastewater such as sewage have been conducted only about influent and effluent (Fauser et al., 2003; Marttinen et al., 2003; Jiang et al., 2005; Vogelsang et al., 2006; Roslev et al., 2007; Stasinakis et al., 2008; Zhang and Zhou, 2008). Tan et al. (2007) reported a material balance of EDCs around bioreactor and settling tank. However, the initial concentrations of BPA and DEHP were low (0.1 and 0.7 $\mu\text{g/L}$) and the removal efficiencies were below 50%. Therefore, effective treatment processes could not be clarified.

In this study, the removal efficiencies of different types of treatment processes were evaluated through an experimental study of the behavior of EDCs in the leachate treatment process.

2. Materials and methods

2.1. Leachate samples

Two municipal solid waste landfill sites that have leachate treatment facilities in Japan were chosen for leachate sampling. In landfill A, organic matter such as food waste was landfilled. In landfill B, which is a typical landfill site in Japan, incinerated residue and incombustible waste were landfilled.

In leachate treatment facility A, leachate was treated in an indoor equalization tank with aeration, a mixing tank, and a sedimentation tank (only gravitational separation). Then, the treated leachate was discharged into a sewer. In facility B, leachate was treated in an indoor adjustment tank with aeration and rotating biological contactors, and phosphoric acid was added. In the mixing tank, coagulant (FeCl_3 ; maximum dosage is 150 mg/L) and NaOH were added, and after coagulation and sedimentation treatment in the sedimentation tank, the effluent was discharged into a river.

The influent (subscript “I”) and effluent (subscript “E”) of the sedimentation tank at facilities A and B were collected. Leachate samples are called “AW” or “BW” hereafter. In the experiment of aeration and coagulation and sedimentation treatment, influent was used as is. In actual facilities, activated carbon adsorption treatment and advanced oxidation processes are conducted after sand filtration. Therefore, effluent was filtrated through glass fiber filter of 1.0 μm pore size in place of sand filtration. The obtained filtrate was used in the experiment of activated carbon adsorption treatment and advanced oxidation processes. In regard to activated carbon adsorption, purified water (PW, Wako Pure Chemical Industries, hexane-washed) was used as control. The quality of the leachate samples employed in the experiment of leachate treatment is shown in Table 1.

2.2. Analytical procedure

Three groups of substances, i.e., APs, BPA, and phthalic acid esters (PAEs), were chosen as the target EDCs in this study. Among the groups, 4-t-octylphenol (4tOP), 4-n-octylphenol (4nOP), and nonylphenol (NP) as representative APs, and

diethylphthalate (DEP), dibutylphthalate (DBP), butylbenzylphthalate (BBP), and DEHP as representative PAEs were chosen. Leachate samples were extracted with dichloromethane for APs and BPA, and with hexane for PAEs, and the extracts were subjected to GC/MS (HITACHI M7200 GC/3DQMS). In this study, the procedures in “The Interim Manual for Endocrine Disrupting Chemicals Examination” (WMS, 1998) were adopted. The procedures have been described by Asakura et al. (2004) in more detail. In regard to coagulation and sedimentation treatment, EDCs in sediment obtained by filtration through glass fiber filter of 1.0 μm pore size were also determined according to the manual.

Temperature, pH, oxidation-reduction potential (ORP (H)), suspended solids (SS) (glass fiber filter of 1.0 μm pore size), kaolin turbidity (measured as absorbance), and total organic carbon (TOC) in filtrate were determined for the leachate samples as parameters other than EDC concentration.

2.3. Experimental methods

The high concentrations of BPA and DEHP were frequently detected at above 100 and 50 $\mu\text{g/L}$ throughout leachate treatment process (Asakura et al., 2007), respectively. Therefore, standards of BPA and DEHP were added to the leachate samples at above concentrations. In regard to APs, DEP, DBP and BBP, since these substances were detected at low concentrations in leachate treatment process and could not be determined the effective process, standard substances were added to the leachate samples at above 50 $\mu\text{g/L}$.

2.3.1. Aeration treatment

First, overall oxygen transfer coefficient (k_{La}), which indicates the oxygen supply capability by the objective apparatus for aeration, was determined by the sodium sulfite method (SBJ, 1992).

Second, an experiment was conducted with leachate sample to which EDCs were added. BW_1 was used as the leachate sample. Three L each of two types \times two sets of leachate samples (two of BW_1 as is (unsterilized) and two of BW_1 sterilized by passing through glass fiber filter of 0.1 μm pore size) were poured into four glass bottles. EDC standards (Acetonic solution; $<100 \mu\text{L}$) were added to the leachate samples at concentrations of 100 $\mu\text{g/L}$ for APs and BPA, and 50 $\mu\text{g/L}$ for PAEs. Air was

introduced into one set of unsterilized and sterilized bottles, and N₂ gas was introduced into the other set at 1.0 L/min flow rate and 1.0 kg/cm² pressure with stirring. Therefore, the experimental runs were composed of Air/unsterilized, N₂/unsterilized, Air/sterilized, and N₂/sterilized. This is a semi-batch operation (liquid is in batch operation and gas is in continuous operation) (Fig. 1). A small volume of leachate sample was collected at certain elapsed times and ORP, TOC, and EDC concentrations were measured. AW₁ was not used as leachate sample because much foam formed during aeration.

2.3.2. Coagulation and sedimentation treatment

First, a preliminary experiment was conducted to determine the required amount of coagulant and agitation conditions to obtain a pure supernatant. AW₁ and BW₁ were used as leachate samples. The amount of coagulant, the rate and time of slow agitation, and the standing time were varied. One L of leachate sample was poured into a beaker of 1 L capacity, a certain amount of ferric chloride was added (100 to 300 mg/L) as coagulant, and pH was adjusted to 5, 7 or 9 with 1 mol/L HCl or NaOH after addition of ferric chloride. Rapid agitation at 120 rpm for 5 min and slow agitation at 10 to 60 rpm for 5 to 20 min with a jar tester were conducted. After standing for 1 to 3 h, the supernatant was collected by decantation, and SS and turbidity were measured.

Second, an experiment was conducted with leachate samples to which EDCs were added. EDC standards (Acetonic solution; <100 µL) were added to leachate samples at concentrations of 100 µg/L for APs and BPA, and 50 µg/L for PAEs. Coagulant addition, pH adjustment, agitation, and standing time were the same as those for the preliminary experiment. The supernatant was collected by decantation and the sediment was obtained by filtration through glass fiber filter of 1.0 µm pore size. SS, turbidity, and EDC concentrations in supernatant and sediment were measured. A control experiment that involved only agitation and standing without coagulant addition and pH adjustment was also conducted.

2.3.3. Activated carbon adsorption treatment

A preliminary experiment was conducted to determine the required contact time for equilibrium residual concentration of EDCs with activated carbon. The specifications of activated carbon are shown in Table 2. Filtrates of AW_E and BW_E, and PW were used as leachate samples. Five hundred mL of leachate sample was poured into an Erlenmeyer flask of 1 L capacity and

EDC standards (Acetonic solution; <100 µL) were added at concentrations of 100 µg/L for APs and BPA, and 50 µg/L for PAEs. One hundred mg of ascorbic acid (Wako Pure Chemical Industries) as antioxidant and a certain amount of activated carbon (1000 mg for AW_E, 500 mg for BW_E, and 500 mg for PW) were added. The flask was shaken at 180 rpm, 20 °C in a constant temperature box for 30 min to 20 h. A control experiment (no addition of activated carbon) was also conducted. After shaking, the supernatant was collected by decantation and EDC concentrations were measured.

Second, an experiment to determine adsorption isotherms was conducted using leachate samples to which EDCs were added. EDC standards were added to leachate samples and the treated supernatant was collected in the same manner as that for the preliminary experiment, and EDC concentrations were measured. However, the amount of activated carbon was changed in five steps. The maximum amounts added were 1300 mg for AW_E, 1000 mg for BW_E, and 500 mg for PW. A control experiment (no addition of activated carbon) was also conducted.

2.3.4. *Advanced oxidation processes*

Advanced oxidation process consists of the combination of O₃ gas, hydrogen peroxide (H₂O₂) and ultraviolet rays. An experiment on advanced oxidation processes was conducted using O₃ gas and H₂O₂ solution for reason of simplicity of apparatus. OZSD-3000A (Ebara Jitsugyo) as O₃ generator and dried air as raw gas for O₃ were used. Three L of leachate sample was poured into a glass gallon bottle, and air containing O₃ (called “O₃ gas” hereafter) was introduced at 1.0 L/min flow rate and 1.0 kg/cm² pressure with stirring. This is a semi-batch operation and is the same as that in the experiment of aeration treatment (Fig. 1).

O₃ generation capacity and decomposition of organic matter were examined. First, the relationship between the concentration of generated O₃ gas and dial scale (for setting O₃ gas concentration) was examined with potassium iodide solution (JWWA, 2001). From the obtained results, the following experiments were conducted at 0.0, 2.1 (only for examination with humic acid), 4.0 or 6.5 mg-O₃/L-gas. Second, the relationship between O₃ introduction time into water (distilled water) and dissolved O₃ concentration was determined by the indigo method (Bader and Hoigne, 1982). Lastly, humic acid decomposition capacity was determined by evaluation of TOC reduction. After introduced O₃ gas reached equilibrium, humic acid (Wako Pure Chemical Industries) was added to the water (distilled water) at about 50 mg-C/L as TOC (t = 0). O₃ gas was introduced

continuously and a small volume of water sample was collected at certain elapsed times, and TOC was measured.

Second, an experiment using O_3 gas and H_2O_2 was conducted using leachate samples to which EDCs were added. Filtrates of AW_E and BW_E were used as leachate samples. The concentrations of O_3 gas were set at 0 and 6.5 for AW_E , and 0, 4.0, and 6.5 mg- O_3 /L-gas for BW_E . O_3 gas was introduced into 3 L of leachate sample for 30 min. After introduced O_3 gas reached equilibrium, DBP and DEHP standards (Acetonic solution; <100 μ L) were added to leachate sample at 10 μ g/L ($t = 0$). O_3 gas was introduced continuously with the addition of a certain volume of H_2O_2 solution every 20 min to the leachate sample in a gallon bottle. A small volume of leachate sample was collected at certain elapsed times, and DBP and DEHP concentrations were measured.

3. Experimental results

3.1. Aeration treatment

The overall oxygen transfer coefficient (k_La) was 19.2 h^{-1} by aeration for 35 h at 1.0 L/min flow rate and 1.0 kg/cm² pressure with stirring. TOC was approximately 170 mg-C/L and did not decrease in any runs. Changes in ORP (H), BPA, and DEHP are shown in Fig. 2 (average, $n = 3$).

BPA concentration was decreased for both Air/unsterilized (to below one hundredth) and Air/sterilized BW_I in 48 h, and to below one thousandth for Air/unsterilized and below one tenth for Air/sterilized BW_I in 96 h. BPA concentration was not decreased to below 90% of initial concentration for both N_2 /unsterilized and N_2 /sterilized BW_I . DEHP concentration was not decreased to below 90% of initial concentration after 96 h in any of the conditions examined. Similar to BPA, the concentrations of APs, DBP, and BBP were decreased for both Air/unsterilized and Air/sterilized BW_I , and to below one tenth in 48 h. In contrast, DEP, like DEHP, showed no significant decrease in concentration.

3.2. Coagulation and sedimentation treatment

From the results of preliminary experiment to determine the required amount of coagulant and agitation conditions to obtain

a pure supernatant at pH 4, 7 or 9, the conditions were set at 200 mg/L (AW_I) and 100 mg/L (BW_I) for the amount of coagulant, 10 rpm and 20 min for the rate and time of slow agitation, and 1 h for the standing time. The dry weight of generated sediment and the turbidity of supernatant in experiments with leachate sample to which EDCs were added are shown in Fig. 3 (average, n = 3). The more alkaline the leachate sample, the larger the quantity of sediment.

Solid-liquid distribution was determined by measuring EDC concentrations in sediment and supernatant, and the results are shown in Fig. 4 (average, n = 3) for BPA and DEHP. The concentrations in sediment (unit: µg/L) was expressed by EDC contents (µg) extracted from sediment per volume of leachate sample (L). The distribution ratio of BPA in sediment by coagulation was slightly increased to approximately 20% in AW_I. On the other hand, the distribution ratio of DEHP in sediment by coagulation was relatively high, i.e., 30% for control and 70% for coagulated samples in BW_I. In regard to the other EDCs, the distribution ratio of NP in sediment was above 90%, and that of 4tOP, 4nOP, DEP, DBP, and BBP was below 50% for coagulated samples (data not shown).

3.3. Activated carbon adsorption treatment

According to the results of preliminary experiment to determine the required contact time for equilibrium, each EDC in each leachate sample was found to reach equilibrium in 6 h. In the following experiment to obtain adsorption isotherms, contact time was set at 6 h. The obtained adsorption isotherms for BPA and DEHP are shown in Fig. 5 (average, n = 3).

The log-log plots form a straight line. Regression was applied following Freundlich's equation and isotherm constants were obtained (Table 3).

$$q_e = KC_e^{1/N} \quad (1)$$

where q_e is equilibrium solid phase adsorbate concentration [µg/mg]; C_e is equilibrium liquid phase concentration [µg/L]; and K [(µg/mg)(L/µg)^{1/N}] and N [-] are Freundlich isotherm constants.

3.4. Advanced oxidation processes

The introduction of O₃ gas into distilled water revealed that dissolved O₃ reached equilibrium in 30 min regardless of O₃ gas concentration. The dissolved concentration at equilibrium was about 2 and 5 mg-O₃/L using 4.0 and 6.5 mg/L-gas of O₃ gas,

respectively. TOC of humic acid solution was decreased more rapidly as O₃ concentration was increased, i.e., the introduction of O₃ gas at 6.5 mg-O₃/L-gas decreased TOC from 46 to 30 mg-C/L in 120 min (Fig. 6). In addition, the brown solution became clear.

DBP and DEHP concentration changes, the introduced O₃ concentration and the volume of added H₂O₂ are shown in Fig. 7 (average, n = 3). In regard to AW_E, the concentrations were decreased from 10 µg/L to approximately 0.2 µg/L in 40 min and to below 0.1 µg/L in 120 min for DBP, and to below 1.0 µg/L in 120 min for DEHP at 6.5 mg-O₃/L-gas, respectively. In regard to BW_E, different concentrations of O₃ gas and amounts of H₂O₂ were set. Both DBP and DEHP concentrations were decreased more rapidly as O₃ or H₂O₂ concentrations were increased. The required treatment times to decrease the concentration from 10 µg/L to below 0.1 µg/L were 60 min at 4.0 mg-O₃/L-gas and 40 min at 6.5 mg-O₃/L-gas for DBP; and 120 min at 4.0 mg-O₃/L-gas and 60 min at 6.5 mg-O₃/L-gas for DEHP. Comparing AW_E and BW_E at the same O₃ condition (6.5 mg-O₃/L-gas) revealed similar decreases in DBP concentration. On the other hand, the concentrations of DEHP at 120 min were different, i.e., approximately one tenth for AW_E and below one hundredth for BW_E.

4. Discussion of behavior of EDCs in leachate treatment process and evaluation of removal efficiency

4.1. Aeration treatment

BPA was hardly decomposed in anaerobic condition and hardly volatilized in air (the ratio of decrease was below 10% in 96 h). In addition, as the rate of concentration decrease was higher in Air/unsterilized than in Air/sterilized condition, the decrease could be due to decomposition mainly by aerobic microorganisms (Kang and Kondo, 2002; Sajiki and Yonekubo, 2002) and partly by chemical oxidation. BPA is thought to be decomposed relatively more easily than other organic matter contained in leachate since TOC was not decreased during the designated experimental period. The concentration of BPA was decreased to below one hundredth in 48 h, and is similar to that reported for actual leachate treatment facilities (Asakura et al., 2004, 2007). DEHP, which showed no significant decrease of concentration in any of the aeration conditions examined (the ratio of decrease was below 10% in 96 h), is considered to be hardly decomposed by aeration and to be difficult to volatilize.

4.2. Coagulation and sedimentation treatment

The effective removal, of which ratio is above 50%, of BPA by coagulation and sedimentation treatment could not be accomplished because most of BPA partitioned in the supernatant. The distribution ratio of DEHP in sediment was increased by coagulation. If the generated sediment were removed completely from AW_I or BW_I , the removal ratios would be approximately 50 to 70%. According to reports of actual facilities for leachate treatment (Asakura et al., 2004, 2007), DEHP removal ratio was below 50%. One of the reasons for the low treatment efficiency could be insufficient coagulation or separation of solid and liquid in actual facilities.

4.3. Activated carbon adsorption treatment

The q_e value of BPA followed the order $AW_E < BW_E < PW$ at the same C_e . The reverse order was observed for TOC in leachate samples (0 for PW, 406 for AW_E , and 143 mg-C/L for BW_E). Therefore, a larger amount of BPA was adsorbed when TOC was lower in leachate samples. In contrast, the q_e value of DEHP followed the order $PW < BW_E < AW_E$ at the same C_e , i.e., the order was the same as that for TOC and the reverse of the order of q_e value for BPA. The difference in adsorption tendencies between BPA and DEHP was considered as follows. Octanol-water partition coefficients ($\log P_{OW}$) are 3.32 for BPA (IPCS, 1989; Dorn et al., 1987) and 5.11 to 8.35 for DEHP (OECD, 1981; Howard et al., 1985; De Kock and Lord, 1987; De Bruijn et al., 1989; Klein et al., 1988; Brooke et al., 1990; Ellington and Floyd, 1996), i.e., that of DEHP is 1.5 to 2.5 times higher than that of BPA. Therefore, the distribution ratio of DEHP in organic matter such as humic substances in leachate should be higher than that of BPA, and DEHP in both liquid and humic substances is possibly adsorbed by activated carbon. On the other hand, the adsorption of BPA is possibly inhibited by the preferential adsorption of humic substances. The adsorption amount of trichloroethylene, of which $\log P_{OW}$ (2.42 reported by IPCS (1989)) is lower than that of DEHP, is also reduced by presence of humic substances (Kilduff and Karanfil, 2002).

The efficiency of activated carbon adsorption treatment for EDCs in leachate was considered with the following calculation. The removal ratio was estimated using equation (1) and the Freundlich isotherm constants in Table 3, assuming a complete mixing model that involved treatment of 100 $\mu\text{g/L}$ APs and BPA and 50 $\mu\text{g/L}$ PAEs in 100 m^3/d leachate with 100 kg of

activated carbon (Asakura et al., 2007). The removal ratios were above 90% for APs and BPA, and 50 to 90% for PAEs (in particular, 50 to 70% for DEHP).

4.4. Advanced oxidation processes

The concentration of DBP could be decreased to below one hundredth in 120 min. The removal efficiency of DEHP in AW_E was lower than that in BW_E . One of the reasons is possibly the consumption of hydroxyl radical that is necessary for advanced oxidation of organic matter, since TOC was higher in AW_E than in BW_E . At any rate, of all the experiments conducted in this study, only advanced oxidation processes could decrease the concentration of DEHP to below one tenth.

4.5. Summative evaluation of removal efficiency

The removal efficiencies of the treatment processes considered in this study are summarized in Table 4. The concentration in surface water (WMS, 1999) and the concentration ratio of leachate (Asakura et al., 2004) to surface water are also shown in Table 4. Symbols are defined as follows: ++ indicates above 99%; +, above 90%; -, above 50%; and --, below 50% removal efficiency, respectively. Among target EDCs, concentrations of BPA (1800 times), DBP (10 times), BBP (40 times), and DEHP (30 times) in leachate are more than ten times higher than those in surface water. The efficiency of aeration treatment of BPA is relatively high, i.e., its concentration can be decreased to below one hundredth in 48 h by aeration. Activated carbon adsorption decreases the concentration of BPA to below one tenth, and the concentration in treated leachate would be less than 10 times that in surface water. According to data from actual treatment facilities (Asakura et al., 2004, 2007), such aerobic biological treatments as rotating biological contactor and contact aeration were also effective for decreasing BPA concentration. Therefore, aeration and subsequent biological treatments such as rotating biological contactor process, could decrease BPA in treated leachate to less than 10 times that in surface water. Aeration decreases the concentrations of DBP and BBP to below one tenth in 48 h, and the concentration in treated leachate would be less than 10 times that in surface water. In contrast, the concentration of DEHP is decreased to below one tenth not by aeration, coagulation and sedimentation, or activated carbon adsorption treatment, but by advanced oxidation processes, and the concentration in treated leachate would be less than 10 times that in surface water.

5. Conclusions

An experimental study of the behavior of endocrine-disrupting chemicals (EDCs) in leachate treatment processes (aeration, coagulation and sedimentation, activated carbon adsorption, and advanced oxidation) was conducted and the removal efficiencies were evaluated. The following are the main findings, focusing on bisphenol A (BPA), dibutylphthalate (DBP), butylbenzylphthalate (BBP), and diethylhexylphthalate (DEHP). Among target EDCs, concentrations of BPA (1800 times), DBP (10 times), BBP (40 times), and DEHP (30 times) in leachate are more than ten times higher than those in surface water. BPA, DBP, and BBP can be treated by aeration and DEHP, by advanced oxidation processes.

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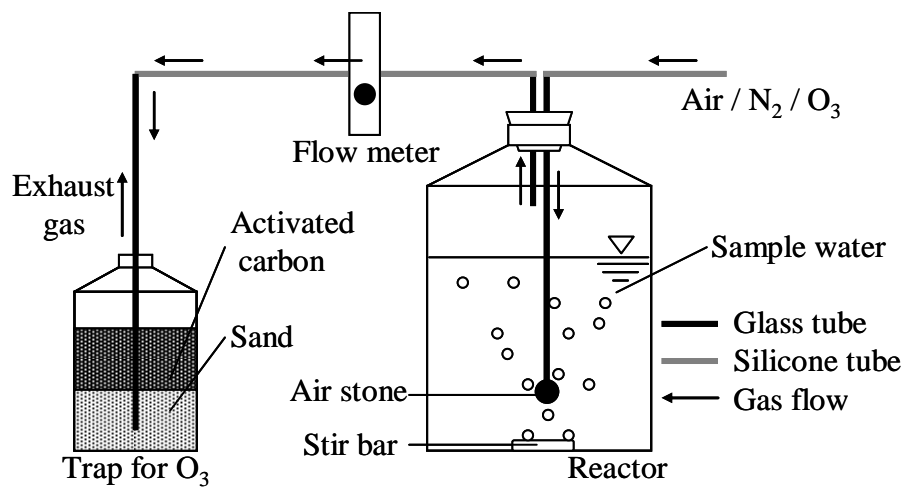


Figure 1. Schematic diagram of apparatus for aeration or advanced oxidation processes

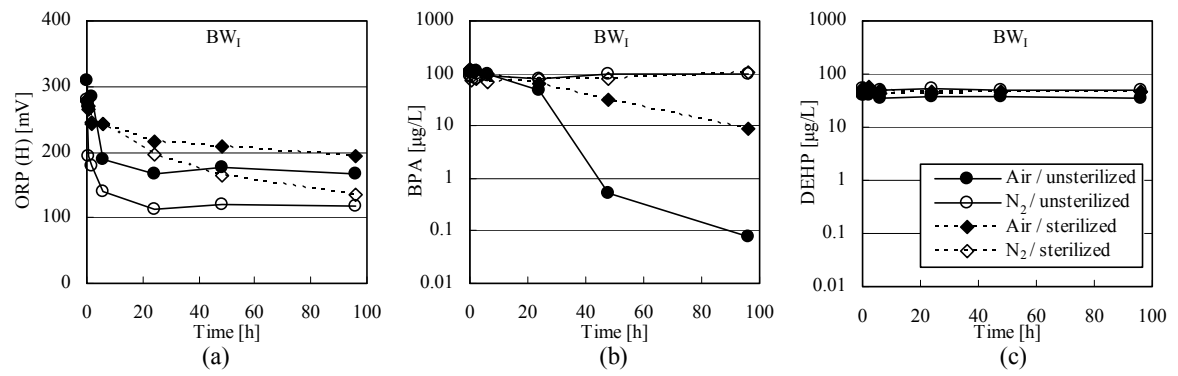


Figure 2. Changes of ORP (H) (a) and concentrations of BPA (b) and DEHP (c) in aeration experiment with BW₁ sample (average, n = 3)

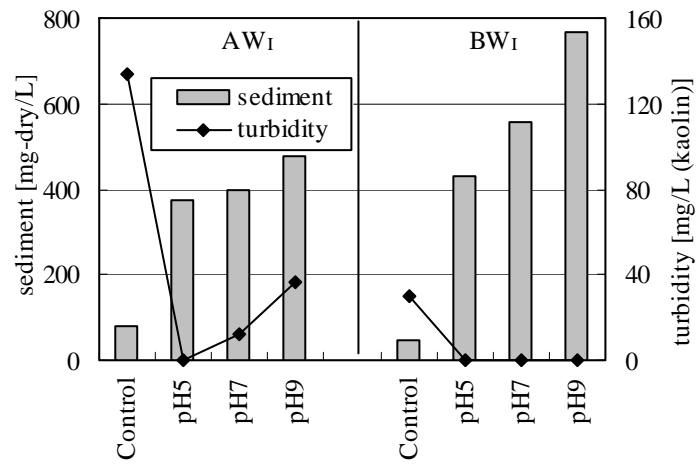


Figure 3. Generated sediment and turbidity in supernatant of AW_I and BW_I samples in coagulation and sedimentation experiment

(Control: 0, AW_I: 200, BW_I: 100 mg/L of coagulant) (average, n = 3)

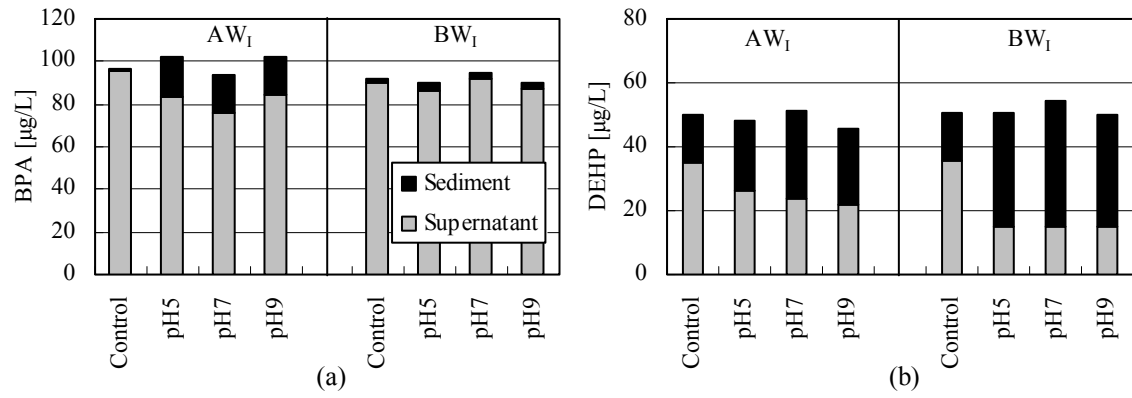


Figure 4. Distribution of BPA (a) and DEHP (b) in coagulation and sedimentation experiment

(Control: 0, AW₁: 200, BW₁: 100 mg/L of coagulant) (average, n = 3)

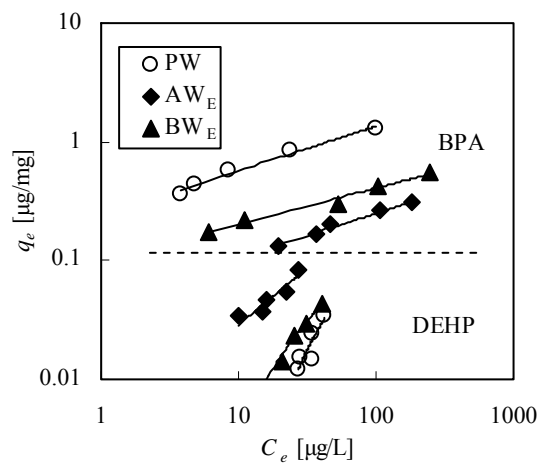


Figure 5. Adsorption isotherms of BPA and DEHP in aqueous solution onto activated carbon at 20 °C (adsorption conditions: carbon = 100 – 1300 mg / 500 mL, agitation rate = 180 rpm, agitation time = 6 h) (average, n = 3)

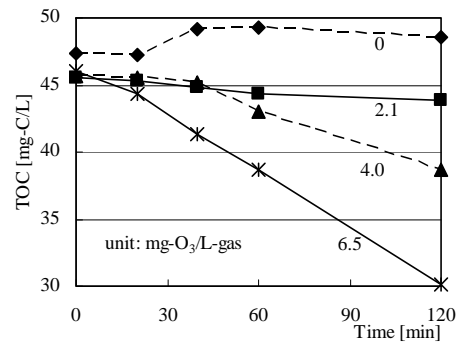


Figure 6. Change of TOC of humic acid solution using O₃ gas of different concentration

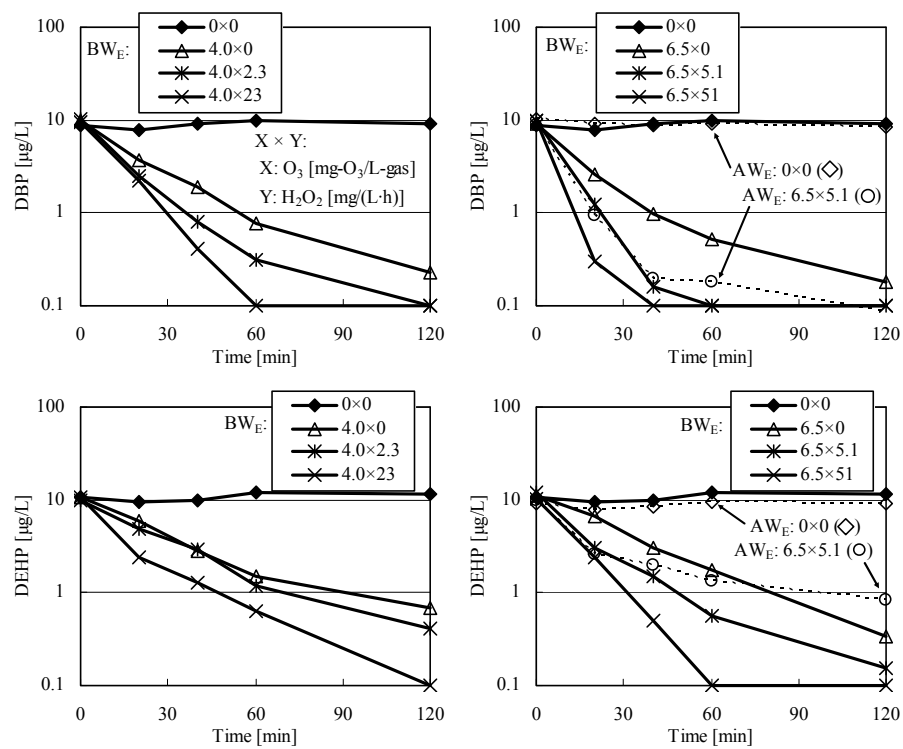


Figure 7. Changes of DBP (a, b) and DEHP concentrations (c, d) using O₃ gas of

4.0 mg-O₃/L-gas (a, c) and 6.5 mg-O₃/L-gas (b, d) (average, n = 3)

Table 1. Quality of leachate samples employed in the experiment of leachate treatment

Sample name	AW			BW		PW	
Landfill waste	Food waste, Incombustible waste			Incinerated residue, Incombustible waste		–	
Sampling point at coagulation tank	Influent	Effluent		Influent	Effluent	–	
Performed experiment ^a	AR	CS	AC & AOP	AR & CS	AC & AOP	AC	
Pre-treatment for experiment	–	Filtration		–	Filtration	–	
pH	–	–	8.3	8.3	7.6	6.8	7.2
EC	mS/cm	–	2.7	2.8	2.9	3.1	<0.01
ORP (H)	mV	–	–84	–82	310	269	320
SS	mg/L	–	92	37	34	15	<1
TOC ^b	mg-C/L	–	414	406	174	143	<1
COD _{Mn} ^b	mg-O ₂ /L	–	82	82	42	34	<1
Cl ^{–b}	mg/L	–	337	334	459	538	<1
NO ₃ ^{–b}	mg-N/L	–	<1	<1	21	22	<1
NH ₄ ^{+b}	mg-N/L	–	142	146	<1	<1	<1

^aAR: Aeration, CS: Coagulation and sedimentation,

AC: Activated carbon adsorption, AOP: Advanced oxidation processes

^bFiltrate

Table 2. Specifications of activated carbon

Model	Takeda Pharmaceutical Co. XS7100	
Specific surface area	m ² /g	1100–1200
Specific pore volume	mL/g	0.5
Nominal pore diameter	nm	1.70–1.80
Iodine adsorbability	mg/g	1050–1150

Table 3. Freundlich isotherm constants and correlation coefficients

for adsorption of EDCs onto activated carbon at 20 °C

		APs			BPA	PAEs			
		4tOP	4nOP	NP		DEP	DBP	BBP	DEHP
PW	K	1.3×10^{-1}	3.4×10^{-2}	5.1×10^{-3}	2.4×10^{-1}	8.1×10^{-2}	3.5×10^{-2}	2.6×10^{-2}	1.4×10^{-5}
	$1/N$	5.1×10^{-1}	7.1×10^{-1}	9.4×10^{-1}	3.8×10^{-1}	4.0×10^{-1}	3.8×10^{-1}	4.1×10^{-1}	2.1×10^0
AW _E	K	2.0×10^{-2}	1.8×10^{-2}	2.7×10^{-3}	4.5×10^{-2}	3.9×10^{-2}	1.5×10^{-2}	3.6×10^{-2}	4.5×10^{-3}
	$1/N$	4.4×10^{-1}	4.9×10^{-1}	7.9×10^{-1}	3.7×10^{-1}	4.7×10^{-1}	6.1×10^{-1}	4.3×10^{-1}	8.4×10^{-1}
BW _E	K	1.3×10^{-1}	4.7×10^{-2}	3.4×10^{-2}	1.0×10^{-1}	2.0×10^{-2}	7.7×10^{-3}	1.3×10^{-2}	1.3×10^{-4}
	$1/N$	2.1×10^{-1}	4.7×10^{-1}	4.6×10^{-1}	3.0×10^{-1}	3.6×10^{-1}	7.7×10^{-1}	5.8×10^{-1}	1.6×10^0

Freundlich isotherm model: $q_e = KC_e^{1/N}$

C_e : equilibrium liquid phase concentration [$\mu\text{g/L}$], q_e : equilibrium solid phase adsorbate concentration [$\mu\text{g/mg}$],

K [$(\mu\text{g/mg})(\text{L}/\mu\text{g})^{1/N}$], N [-]: Freundlich isotherm constants

Table 4. Removal efficiency to influent of 100 µg/L APs and BPA, and 10–50 µg/L PAEs
by different treatment processes

	Surface water in Japan ^a	Conc. ratio ^b	Removal efficiency				
			AR	CS	AC ^c	AOP	
APs	4tOP	0.03	<10	+	--	+	n.a. ^d
	4nOP	<0.01	<10	++	--	+	n.a.
	NP	0.19	<10	++	+	+	n.a.
BPA		0.04	1800	++	--	+	n.a.
PAEs	DEP	0.7	<10	-	--	-	n.a.
	DBP	0.5	10	+	--	-	++
	BBP	<0.1	40	+	--	-	n.a.
	DEHP	0.6	30	--	-	-	+
Treatment time [h]				50	2	3	2

Removal efficiency:

++: >99%, +: >90%, -: >50%, --: <50%

^aWMS (1999)

^bconcentration ratio of leachate to surface water
(Asakura et al., 2004)

^ccarbon: 100 kg, leachate: 100 m³/d

^dnot analyzed