Analysis of EDCs by Mass Spectrometry and their Removal by Membrane Filtrations

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(Rceived October 12, 2005, Accepted December 16, 2005)

Abstract: As a number of potential endocrine disrupting compounds (EDCs) are released into the environment, recently growing attention has been drawn to them. Therefore sensitive and reliable analytical methods are essential to monitor those compounds. In this study, complementary GC-MS and LC-MS were employed to analyze the endocrine disrupters, and the results of two methods were compared for di(2-ethylhexyl)phthalate (DEHP), benzylbutylphthalate (BBP), pentachlorophenol (PCP), and 4,4′-isopropylidenediphenol (Bisphenol-A, or BPA). The results indicate that it was possible to lower the detection limits of EDCs by LC-MS. Also, LC-MS enabled to identify the EDCs as almost intact molecules. Furthermore, this study presented a nanofiltration membrane (MWCO 250) and a ultrafiltration membrane (MWCO 1,000) filtration system as methods for removing EDCs from drinking water containing γ-BHC, p,p′-DDE, BBP, p,p′-DDT, DEHP, PCP, and BPA. Cross-flow type nanofiltrations showed 100% removal of EDCs, and the result implies that MWCO 250 nanofilter was sufficient for treatment of EDCs. The ratio of permeate flux to mass transfer coefficient of nanofiltration, high flux ultrafiltration, and low flux ultrafiltration with ultrapure water were 0.67, 3.4, and 0.44, respectively. It was found that nanofiltration and low flux ultrafiltration were operated at a diffusion dominant condition, and the high flux ultrafiltration was operated at a convection dominant condition. Furthermore, a diffusion dominant process attained reasonable rejection of EDCs. The removal in the ultrafiltration was depending on the molecular weight of an EDC, and the filtration was governed by diffusion-dominant hydrodynamic conditions.

Keywords: EDCs, Endocrine disrupting compounds, GC-MS, LC-MS

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1. Introduction

The endocrine system—also referred to as the hormone system—is made up of glands located throughout the body, hormones which are synthesized and secreted by the glands into the bloodstream, and receptors in the various target organs and tissues which recognize and respond to the hormones [1,2]. In recent years, researchers have reported that chemicals might be disrupting the endocrine system (glands and hormones) of humans and wildlife [3]. However, the effects of endocrine disrupting compounds (EDCs) in human may not come out until long after exposure [4,5]. The concerns about the effect of EDCs have grown more serious and endocrine disruption by EDCs is becoming more evident. Since the physiological processes of the endocrine (hormonal) system can be disrupted by a number of artificially and naturally occurring chemicals [6], most studies have focused on xenoestrogens or estrogen-like compounds that mimic the biological activities of the female endogenous estrogen, causing a feminizing or estrogenic effect [7-9]. The toxic potential of EDCs cannot be derived from their chemical structure, especially if they occur in complex mixtures containing unidentified compounds that are able to produce larger combination effects than each EDC alone.

EDCs are frequently found in wastewater released from various industries. For example, Pentachlorophenol (PCP) was used as an insecticide for termite control, a re-harvest defoliant, and herbicide. It is also used in the preservation of wood products, starches, dextrins, and glues [10,11]. PCP has been reported to induce the production of vitellogenin, a fish egg protein produced by female fish, in the male rainbow trout [4]. Di(2-ethylhexyl)phthalate (DEHP) has been used as a plasticizer for polyvinyl chloride and is often included in toys and households goods and butylbenzylphthalate (BBP) has been used as a plasticizer for both polycarbonate resins and cellulose ester plastics. It is widely known that DEHP and BBP could involve the depletion of testicular Zn and testicular germ cells [12].

Phthalates are also commonly found in groundwater, rivers and drinking water due to their persistence in the environment [13]. Bisphenol-A (BPA) is also known as a potential EDC. BPA is mainly applicable to the manufacture of durable plastic materials, food packaging, dental sealants and the epoxy coatings on the inside of food and drink cans. BPA is estrogenic to human breast cancer cell cultures [4].

Owing to the great number of such synthetic organic chemicals released into the environment reported as potential EDCs, strict characterization of contaminated effluents is needed [4]. In fact, like hormones EDCs exert their effects at very low concentrations. Thus, very sensitive and reliable analytical methods are essential to monitor those compounds. Common methods for identifying organic pollutants in contaminated industrial effluents generally involve the use of either liquid-liquid extraction or solid phase extraction, followed by gas chromatography-mass spectrometry (GC-MS) techniques. By this approach a variety of non-polar compounds in wastewater and effluents can be easily identified [14,15]. However, many polar, ionic, heavy and thermally unstable compounds cannot be analyzed by GC-MS techniques. An advanced technique is therefore necessary for these pollutants, which usually comprise more than 95% of the organic content [16-18]. Liquid chromatography-mass spectrometry (LC-MS) is a powerful analytical tool determining the non-volatile low concentrations of EDCs.

This study describes the analyses of endocrine disrupters by the complementary use of GC-MS and LC-MS, and compares the results of the two methods. Further, for production of safer drinking water and future regulations, the removal of EDCs from drinking water is needed [19]. Therefore, the feasibility of EDC removal was investigated in terms of their transport phenomena through membrane pores. It was considered that EDCs (Mw. 200~400 in this study) could be efficiently removed by nanofiltration membranes (molecular weight cut-off, MWCO, 250) [20-24] and low molecular weight cut-off (MWCO) ultrafiltration
Table 1. Membrane Characteristics [31]

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Material</th>
<th>Nominal MWCO</th>
<th>Zeta potential (mV) with latex solution</th>
<th>Zeta potential (mV) with NOM solution</th>
<th>i.e.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESNA</td>
<td>Thin Film Composite</td>
<td>250</td>
<td>-15.0</td>
<td>-21.9</td>
<td></td>
</tr>
<tr>
<td>T-1000</td>
<td>Titania (TiO₂)</td>
<td>1,000</td>
<td></td>
<td></td>
<td>6.25</td>
</tr>
</tbody>
</table>

Fig. 1. A schematic diagram of cross-flow membrane filtration apparatus.

[25-27] through size exclusion mechanisms. In this study, hydrodynamic conditions were varied to compare the diffusion dominant filtration and the convection dominant filtration.

2. Experimental

2.1. Apparatus

Grab sample bottles (1 L, amber glass) that were fitted with a screw cap lined with teflon and Erlenmeyer flasks (500 mL) were used. The extraction system used comprised of one body reactor (1.5 L, Pyrex) with 3 head holes and a separating pinch cock, funnel (300 mL, Pyrex) with a vent air arm and a separating pinch cock, and an overhead stirrer, a MS 3040 (TOPS company, Korea) with a teflon seal impeller. The rotary evaporator (RE 200A-WJ) with a 500 mL evaporative flask was purchased from Yamato, Japan. A one-milliliter syringe (Hamilton, USA) was used for collecting the concentrates. The microfilter system (MFS), an all-glass filter set, with a 1 L flask was purchased from Advantech in Japan. The 0.45 μm membrane filters and mixed cellulose ester were also purchased from Advantech in Japan. The 0.22 μm GV membrane filters were obtained from Durapore in Ireland. The diameter of the membrane filters was 47 mm.

Two membrane filtration units were used for removing the EDCs from water. A flat-sheet type of membrane filtration apparatus, Minitan II (Millipore, USA), accommodated polymeric nanofiltration membranes (Hydranautics, USA). A tubular type filtration holder and ceramic ultrafiltration membranes were purchased from TAM in France. The test membranes were selected based on MWCO of membranes in consideration of molecular weight of EDCs. The characteristics of the tested membranes are listed in Table 1. The membrane filtration unit was composed of nanofiltration and ultrafiltration membranes with an active filtration area of 58.9 cm² and 95.2 cm², respectively, and a membrane holder, pumps with a gear type pump head, needle valves (for the feed, retentive, and permeate streams), and pressure and flow meters. A schematic diagram of two membrane filtration apparatus is shown in Fig. 1. Either varying the pump head speed or controlling the needle valve in the retentive stream controlled the feed flow rate, the corresponding cross-flow velocity and the trans-membrane pressure. The experiments were carried out at room temperature.
Table 2. The Structure of EDCs Targeted for Analysis

<table>
<thead>
<tr>
<th>Target compounds</th>
<th>Molecular weight</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEHP [117-81-7]</td>
<td>390.56</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>BBP [85-68-7]</td>
<td>312.37</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>p,p'-DDT [50-29-3]</td>
<td>354.49</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>p,p'-DDE [72-55-9]</td>
<td>318.03</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>γ-BHC [58-89-9]</td>
<td>290.83</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>PCP [87-86-5]</td>
<td>266.34</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>BPA [80-05-7]</td>
<td>228.29</td>
<td><img src="image" alt="Structure" /></td>
</tr>
</tbody>
</table>

2.2. Reagents and Solutions

Di(2-ethylhexyl)phthalate (DEHP, 99%) and benzylbutylyphthalate (BBP, 98%), 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (p,p'-DDT, 98%), 2,2-bis(4-chlorophenyl)-1,1-dichloroethylene (p,p'-DDE, 99%), and 1,2,3,4,5,6-Hexachlorocyclohexane, γ-isomer, (γ-BHC or lindane, 97%) and 4,4'-Isopropylidenediphenol (Bisphenol-A, or BPA, 99+%) were purchased from Aldrich (USA). Pentachlorophenol (PCP, 98%) was purchased from Sigma (USA). Table 2 shows the structure of the EDCs targeted for this study.

Anhydrous sodium sulfate (granular, 99+%) and dichloromethane (PRA grade, 99.9%), used for GC-MS analysis, were purchased from Aldrich. Sodium hydroxide (96%) was obtained from Oriental Chemical Industry (Japan) and sulfuric acid (96~97%) was purchased from Merck (Germany). Anhydrous sodium thiosulfate (95%) was purchased from Junsei Chemical Co. Ltd. (Japan). HPLC grade water, acetonitrile, and methanol for LC-MS analysis were obtained from Fisher Scientific (USA). Acetic acid (99.5%) was purchased from Oriental Chemical Industry (Japan) and ammonium hydroxide (NH₃ 28%) was obtained from Junsei Chemical Co. Ltd. (Japan).

2.3. Gas Chromatography–mass Spectrometry

2.3.1. Extraction and Concentration

A sample volume of 1 L was prepared and the entire
sample was transferred into a 1.5 L separatory reactor. The pH of the sample adjusted to pH >11 with a 10 N sodium hydroxide solution. A 100 mL volume of dichloromethane (DCM) was added to the sample bottle, sealed, and shaken for 30 sec to rinse the inner surface. The solvent was poured to the separatory reactor and then the sample was extracted by stirring the reactor for 2 min at 1000 rpm with an overhead stirrer. The organic layer was separated from the water phase for a minimum of 10 min. The DCM extract was collected in a 500 mL Erlenmeyer flask. A second 100 mL of DCM was added to the sample bottle and the extraction procedure was repeated twice, combining the extracts in the Erlenmeyer flask. A third extraction was performed in the same manner. It was labeled as the combined extract as the base/neutral fraction.

The aqueous phase pH was adjusted to lower than 2 using a sulfuric acid (50%, v/v). The acidified aqueous phase was serially extracted three times with 100 mL aliquots of DCM. The extracts were collected and combined in a 500 mL Erlenmeyer flask and the total extract was labeled as the acid fraction [28]. The extract was mixed with 10 g of anhydrous sodium sulfate and well stirred. Subsequently, a MFS was assembled and the sample was filtered through 0.22 μm GV membrane filters. The filtrated extract was transferred to a 500 mL evaporative flask and then evaporated. When the volume of liquid reached approximately 1 mL, the evaporative flask was removed from water bath, and allowed to drain and cool for 10 min. A 1.0 mL syringe was used for the concentrates collected in 2 mL GC-MS vials.

2.3.2. Analytical Conditions

The GC-MS used was a HP 6890 series GC system with a mass selective detector (MSD) and a HP Vectra XM PC. An HP-5MS capillary column coated with 5% diphenyl and 95% dimethylpolysiloxane (30 m × 0.25 mm × 0.25 μm) was used. Helium was used as the carrier gas at 1 mL min⁻¹. The injection temperature was 280°C and the oven temperature was programmed from 80°C (4 min) to 310°C (5 min) at 7°C min⁻¹. The on-column mode was used for injecting the 1 L sample using a HP 10 L syringe. The mass selective detector was operated in the scan and selected ion monitoring (SIM) mode. Data collection and progressing were performed with HP MSD Chemstation software including the Willey Library.

2.4. Liquid Chromatography-mass Spectrometry

The LC-MS used in this study was a SSQ 710 single quadrupole instrument (Finnigan MAT, USA) with a Digital Unix Workstation. DEHP and BBP analyses were carried out in positive ionization mode with a methanol-water-acetic acid mixture (50:50:0.5, v/v). PCP and BPA analyses were conducted in negative ionization mode with an acetonitrile-water-ammonium hydroxide mixture (50:50:0.5, v/v). The following electrospray ionization (ESI) conditions were applied: the ESI spray needle voltage was either +4.5 kV or -4.5 kV, the sheath gas (nitrogen) pressure was 50 psi, the heated capillary voltage was either +42.9 V or -44.9 V, the heated capillary temperature was 200°C, and the electron multiplier voltage was 1000 V. The scan mass spectra were chosen in the range of 200–500 amu. Direct injection of a single pure sample in 20 μL min⁻¹ of mobile phase was applied without chromatographic separation. A 250 μL syringe (Hamilton, USA) and a syringe pump (Havard, USA) were used for LC-MS analysis.

The grab samples were collected in refrigerated glass containers. All samples were iced or refrigerated at 4 °C from the time of collection until extraction. The sample bottles were filled and, if any residual chlorine was present, 80 mg sodium thiosulfate per liter of sample was added and well mixed. All samples were extracted within seven days of collection and completely analyzed within 40 days of extraction. Extraction, concentration and analysis were performed as described in the gas chromatography-mass spectrometry section.

2.5. Membrane Filtration for Removing EDCs

Membrane filtration samples were prepared by dis-
solving 11.8 mg of DEHP, 15.4 mg of BBP, 7.4 mg of DDT, 7.4 mg of DDE, 16.2 mg of γ-BHC, 9.5 mg of PCP, and 14.2 mg of BPA in 11.8 mL, 15.4 mL, 7.4 mL, 7.4 mL, 16.2 mL, 9.5 mL, and 14.2 mL of methanol, respectively. An 80 μL volume of each sample was mixed with 4 L of tap water. A tap water sample of 4 L was additionally prepared in the same manner. Two tap water samples of 3 L were used for the membrane filtration with the nanofiltration membrane and the ultrafiltration membranes. The two remaining samples of 1 L were filled up to the feeds whenever the volume of permeates was approximately 250 mL. Extraction, concentration and analysis were performed by the same procedure in the gas chromatography-mass spectrometry.

3. Results and Discussion

3.1. Analyses of Some EDCs

3.1.1. DEHP and BBP

Fig. 2(a) shows that the retention time of DEHP (Mw. 390.56) is 29.02 min. Since the peak was not found for 1.0 g injection, the detection limit of DEHP was considered as 2.0 g under the conditions tested. The primary 149 m/z and secondary 167 m/z for the characteristic masses of DEHP were monitored in Fig. 2(b). The 149 m/z and 167 m/z indicated dehydrated phthalic acid and hydrated phthalic acid, respectively. The 391.4 m/z for (DEHP+H)⁺ (see Fig. 2(c)) was not found in the GC-MS spectrum. When 100 ng was injected into the LC-MS, 391.4 m/z was identified at a low level. Consequently, a LC-MS detection limit of DEHP was 250 ng in terms of solute mass.

The retention time, 26.79 min, of BBP (Mw. 312.37) is shown in Fig. 3(a). After injecting 3.0 μg, a small peak at 26.79 min was detected, but the mass spectrum (Fig. 3(b)) was not identified from the library. Therefore, the BBP detection limit in the GC-MS was 4.0 μg of the solute mass. The primary 149 m/z and secondary 91 m/z and 206 m/z for the characteristic BBP masses were observed in Fig. 3(b). The 149 m/z, 91 m/z, and 206 m/z indicated a dehydrated form of phthalic acid, a dehydrogenated form of toluene, and a deoxygenated form of monobutyl phthalate, respectively. The 313.3 m/z for (BBP+H)⁺ (see Fig. 3(c)) was not found in the GC-MS spectrum. The 331.4 m/z
indicated a hydrated form of \((\text{BBP}+\text{H})^+\). When 1.0 \(\mu\text{g}\) was injected into the LC-MS, 313.3 m/z and 331.4 m/z were spotted at a low level. Accordingly, the detection limit of BBP in the LC-MS was about 2.0 \(\mu\text{g}\) of the solute mass.

3.1.2. PCP and BPA

The PCP (Mw. 266.34) peak at 18.97 min is shown in Fig. 4(a). Injecting 6.0 g PCP, its mass spectrum was identified from the library. Peaks at 266, 202, 165, 132, and 96 m/z revealed the presence of PCP,
trichlorophenol, dichlorophenol, monochlorophenol, and phenol, respectively, as shown in Fig. 4(b). On the other hand, Fig. 4(c) shows only the 265.3 m/z for a dehydrogenated form of PCP, PCP was not detected obviously after injecting 75 ng of sample even if the peak at 265.3 m/z was found at a low level. Using a direct injection method, the PCP detection limit in the LC-MS was 100 ng in terms of solute mass.

Fig. 5(a) shows that the retention time of BPA (Mw. 228.29) is 24.72 min. Injecting 13.0 g, a small 24.72 min peak was found but its mass spectrum (Fig. 5(b)) was not identified from the Wiley library. Therefore, a BPA detection limit in the GC-MS was considered as 13.8 g under the conditions tested. Peaks at 213, 228, and 119 m/z revealed the presence of 4,4'-ethyldenebisphenol, BPA, 4-ethylphenol, respectively, as shown in Fig. 5(b). On the other hand, Fig. 5(c) shows only the 227.9 m/z for a dehydrogenated form of BPA. After injecting 0.5 g, BPA was not detected clearly even though the 227.9 m/z were found at a low level. When a direct injection method was used, a BPA detection limit in the LC-MS was found to be 1.0 µg.
of the solute mass. The summary of analyses of some EDCs is listed in Table 3.

3.2. Membrane Filtration for Removing EDCs
In order to remove the EDCs from drinking water, cross-flow type filtrations were performed. Considering the molecular weights of EDCs investigated in this study, nanofiltration was chosen initially. Table 4(a)

Table 4(a). Nanofiltration

<table>
<thead>
<tr>
<th>EDCs</th>
<th>Mw.</th>
<th>(D_w (\text{cm}^2/\text{s}))</th>
<th>R.T. (min)</th>
<th>Feed ((\mu\text{g}/\text{L}))</th>
<th>Permeate ((\mu\text{g}/\text{L}))</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma)-BHC</td>
<td>290.83</td>
<td>(0.59 \times 10^{-5})</td>
<td>18.98</td>
<td>19.1</td>
<td>ND</td>
<td>100</td>
</tr>
<tr>
<td>p,p'-DDE</td>
<td>318.03</td>
<td>(0.46 \times 10^{-5})</td>
<td>24.74</td>
<td>16.1</td>
<td>ND</td>
<td>100</td>
</tr>
<tr>
<td>BBP</td>
<td>312.37</td>
<td>(0.48 \times 10^{-5})</td>
<td>26.79</td>
<td>17.9</td>
<td>ND</td>
<td>100</td>
</tr>
<tr>
<td>p,p'-DDT</td>
<td>354.49</td>
<td>(0.37 \times 10^{-5})</td>
<td>26.79</td>
<td>18.4</td>
<td>ND</td>
<td>100</td>
</tr>
<tr>
<td>DEHP</td>
<td>390.56</td>
<td>(0.39 \times 10^{-5})</td>
<td>28.91</td>
<td>16.4</td>
<td>ND</td>
<td>100</td>
</tr>
<tr>
<td>PCP</td>
<td>266.34</td>
<td>(0.49 \times 10^{-5})</td>
<td>18.88</td>
<td>15.8</td>
<td>ND</td>
<td>100</td>
</tr>
<tr>
<td>BPA</td>
<td>228.29</td>
<td>(0.68 \times 10^{-5})</td>
<td>24.67</td>
<td>19.4</td>
<td>ND</td>
<td>100</td>
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</table>

Table 4(b). Results of Ultrafiltration (convection)

<table>
<thead>
<tr>
<th>EDCs</th>
<th>Mw.</th>
<th>(D_w (\text{cm}^2/\text{s}))</th>
<th>R.T. (min)</th>
<th>Feed ((\mu\text{g}/\text{L}))</th>
<th>Permeate ((\mu\text{g}/\text{L}))</th>
<th>Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma)-BHC</td>
<td>290.83</td>
<td>(0.59 \times 10^{-5})</td>
<td>18.97</td>
<td>11.8</td>
<td>6.8</td>
<td>43</td>
</tr>
<tr>
<td>p,p'-DDE</td>
<td>318.03</td>
<td>(0.46 \times 10^{-5})</td>
<td>24.73</td>
<td>7.5</td>
<td>2.8</td>
<td>63</td>
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<tr>
<td>BBP</td>
<td>312.37</td>
<td>(0.48 \times 10^{-5})</td>
<td>26.73</td>
<td>8.9</td>
<td>5.9</td>
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</tr>
<tr>
<td>p,p'-DDT</td>
<td>354.49</td>
<td>(0.37 \times 10^{-5})</td>
<td>26.73</td>
<td>6.0</td>
<td>5.3</td>
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<tr>
<td>DEHP</td>
<td>390.56</td>
<td>(0.39 \times 10^{-5})</td>
<td>28.89</td>
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<td>4.4</td>
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<tr>
<td>PCP</td>
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<td>18.86</td>
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<tr>
<td>BPA</td>
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<td>24.65</td>
<td>9.7</td>
<td>ND</td>
<td>100</td>
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</tbody>
</table>

Table 4(c). Results of Ultrafiltration (diffusion)

<table>
<thead>
<tr>
<th>EDCs</th>
<th>Mw.</th>
<th>(D_w (\text{cm}^2/\text{s}))</th>
<th>R.T. (min)</th>
<th>Feed ((\mu\text{g}/\text{L}))</th>
<th>Permeate ((\mu\text{g}/\text{L}))</th>
<th>Removal (%)</th>
</tr>
</thead>
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<tr>
<td>(\gamma)-BHC</td>
<td>290.83</td>
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<td>19.1</td>
<td>9.9</td>
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<tr>
<td>p,p'-DDE</td>
<td>318.03</td>
<td>(0.46 \times 10^{-5})</td>
<td>24.74</td>
<td>16.1</td>
<td>4.1</td>
<td>74</td>
</tr>
<tr>
<td>BBP</td>
<td>312.37</td>
<td>(0.48 \times 10^{-5})</td>
<td>26.79</td>
<td>17.9</td>
<td>ND**</td>
<td>100</td>
</tr>
<tr>
<td>p,p'-DDT</td>
<td>354.49</td>
<td>(0.37 \times 10^{-5})</td>
<td>26.79</td>
<td>18.4</td>
<td>ND</td>
<td>100</td>
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<td>DEHP</td>
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<td>PCP</td>
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<td>(0.49 \times 10^{-5})</td>
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<td>24.67</td>
<td>19.4</td>
<td>11.4</td>
<td>41</td>
</tr>
</tbody>
</table>

** Not Detected

shows 100% removal of the EDCs contained in the feed water.

The result implies that MWCO 250 nanofilter was sufficient for treatment of EDC contaminated drinking water. Usually nanofiltration requires a high-pressure pump to increase the flux. Ultrafiltration may increase the flux at the sacrifice of the selectivity. Two different operating conditions were examined for effects.
Table 5(a). Equilibration with Ultra Pure Water in Nanofiltration

<table>
<thead>
<tr>
<th>Time</th>
<th>ΔP (psi)</th>
<th>Q₁* (mL/min)</th>
<th>Q₁** (mL/min)</th>
<th>Q₁*** (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 min</td>
<td>42</td>
<td>2.60</td>
<td>260</td>
<td>263</td>
</tr>
</tbody>
</table>

\[ F = \frac{Q_p}{\Delta P \times 58.9} \times 2088.7 = 2.2 \text{ (L/day} \cdot \text{m}^2 \cdot \text{kPa)} \]

\[ J_0 = \frac{Q_p}{58.9 \times 60} = 0.000736 \text{ (cm/s)} \]

\[ U = \frac{Q_p}{0.57 \times 60} = 7.7 \text{ (cm/s)} \]

\[ k = 1.62 \left( \frac{7.7 \times (4.9 \times 10^{-5})^2}{2 \times 0.06 \times 6.2} \right)^{0.33} = 0.0011 \text{ (cm/s)} \]

\[ J_0/k = 0.67 \]

Table 5(b). Equilibration with Ultra Pure Water in Ultrafiltration (convection)

<table>
<thead>
<tr>
<th>Time</th>
<th>ΔP (psi)</th>
<th>Q₂* (mL/min)</th>
<th>Q₂** (mL/min)</th>
<th>Q₂*** (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min</td>
<td>35</td>
<td>8.60</td>
<td>231</td>
<td>240</td>
</tr>
</tbody>
</table>

\[ F = \frac{Q_p}{\Delta P \times 55.2} \times 2088.7 = 5.4 \text{ (L/day} \cdot \text{m}^2 \cdot \text{kPa)} \]

\[ J_0 = \frac{Q_p}{55.2 \times 60} = 0.00151 \text{ (cm/s)} \]

\[ Re = 261.0, \quad Sc = 2049.0, \]

\[ k = 1.62 \times \frac{4.9 \times 10^{-6}}{0.36} \left( \frac{261.0 \times 2049.0 \times 0.36}{23.0} \right)^{0.33} = 0.00045 \text{ (cm/s)} \]

\[ J_0/k = 3.4 \]

Table 5(c). Equilibration with ultra pure water in ultrafiltration (diffusion)

<table>
<thead>
<tr>
<th>Time</th>
<th>ΔP (psi)</th>
<th>Q₃* (mL/min)</th>
<th>Q₃** (mL/min)</th>
<th>Q₃*** (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 min</td>
<td>30</td>
<td>2.47</td>
<td>310</td>
<td>312</td>
</tr>
</tbody>
</table>

\[ F = \frac{Q_p}{\Delta P \times 55.2} \times 2088.7 = 1.8 \text{ (L/day} \cdot \text{m}^2 \cdot \text{kPa)} \]

\[ J_0 = \frac{Q_p}{55.2 \times 60} = 0.000432 \text{ (cm/s)} \]

\[ Re = 990.40, \quad Sc = 7106.2, \]

\[ k = 1.62 \times \frac{4.9 \times 10^{-6}}{0.36} \left( \frac{990.40 \times 7106.2 \times 0.36}{25.4} \right)^{0.33} = 0.00098 \text{ (cm/s)} \]

\[ J_0/k = 0.44 \]

*Flow of permeate  
**Flow of retentate  
***Total flow

of the mass transfer on the selectivity. Table 4(b) and Table 4(c) present the removal of EDCs at a high flux and a low flux condition in ultrafiltration. Except PCP and BPA, removal of EDCs was improved at a low flux condition. Table 5 shows the hydrodynamic and mass transfer characteristics for three filtration experiments. Under the hydrodynamic conditions with \( J_0/k < 1 \), transport by diffusion dominant, while transport by convection is dominant for \( J_0/k > 1 \) [29]. The \( J_0/k \) (permeate flux/mass transfer coefficient) ratio of nanofiltration, a high flux ultrafiltration, and low flux ultrafiltration were 0.67, 3.4, and 0.44 respectively, which
were obtained by equilibration with ultrapure water. Since the $J_0/k$ ratio indicates the mass transfer mechanism in membrane, it was found that nanofiltration and low flux ultrafiltration were operated at a diffusion dominant condition, and the high flux ultrafiltration was operated at a convection dominant condition.

From Table 4 and 5, a diffusion dominant process attained reasonable rejection of EDCs. The percentage removal in the diffusion dominant ultrafiltration was correlated with the molecular weight of in EDC. Fig. 6 shows that the EDC removal decreased with the increasing diffusion coefficient of the EDC in water. This result also indicates that the filtration was governed by diffusion. Therefore, EDCs can be removed from drinking water using membranes when the hydrodynamic operating conditions ($J_0/k$ ratio) is adjusted so that transport by diffusion is dominant ($J_0/k < 1$). Since the molecular volume of PCP (134.7 cm$^3$ mol$^{-1}$) is smaller than that of BBP (279.7 cm$^3$ mol$^{-1}$) and both have similar diffusion coefficients, the removal efficiency with ultrafiltration membrane filtration was lower for PCP than for the other EDCs. The $D_0$ of BPA was estimated from an empirical expression [30]:

$$D_0 = \frac{13.25 \times 10^{-5}}{1.14 \times (\frac{\mu}{1000})^{0.085}} \text{ (cm}^2 \text{s}^{-1})$$  \hspace{1cm} (1)

where $\mu$ is the viscosity of water (0.894) at 25°C, and

$\overline{V}$ is the molecular volume of BPA (191.0 cm$^3$ mol$^{-1}$).

Removal of target EDCs in a convection-dominated ultrafiltration showed a reversed tendency except PCP (as shown in Fig. 6) which is a polar organic compound. BPA was not detected in a convection-dominated ultrafiltration since detection limit of BPA was higher than that of the other ECDs.

4. Conclusions

In this study, the extraction and analytical methods for mass spectrometry of EDCs were investigated, and GC-MS and LC-MS were compared in determination of EDCs. The results showed that LC-MS enabled to lower the detection limits of EDCs and to identify the EDCs as almost intact molecules. Both nanofiltration and ultrafiltration methods removed about 16 \( \mu \text{g L}^{-1} \) of DEHP. Studies on determination of more EDCs combining analytical approaches such as GC-MS and LC-MS are in progress. Also, this research demonstrated that a membrane process could remove EDCs effectively.

Acknowledgment

This work was supported in part by a grant from Sustainable Water Resource Research Center (SWRRC) through the Water Reuse Technology Center (WRTC) in Gwangju Institute of Science and Technology (GIST), and in part by the National Research Laboratory (NRL) Program of Korea Institute of Science and Technology Evaluation and Planning.

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