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Removal efficiencies of endocrine disrupting chemicals by coagulation/flocculation, ozonation, powdered/granular activated carbon adsorption, and chlorination

Keun Joo Choi, Sang Goo Kim†, Chang Won Kim* and Jae Kwang Park**

Water Quality Institute, Busan City Waterworks, Maeri 421-1, Sangdong, Gimhaesi, Kyungnam 621-813, Korea
*Department of Environmental Engineering, Busan National University, 30 Jangjungddong, Gumjunggu, Busan 609-735, Korea
**Department of Civil and Environmental Eng., Univ. of Wisconsin-Madison, U.S.A.

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Abstract−Removal efficiencies of endocrine disrupting chemicals (EDCs), bisphenol A and nonylphenol, during various types of water treatment processes were evaluated extensively using laboratory- and pilot-scale experiments. The specific processes of interest were coagulation/flocculation sedimentation/filtration (conventional water treatment process), powdered activated carbon (PAC), granular activated carbon (GAC), ozonation and chlorination. Batch sorption tests, coagulation tests, and ozone oxidation tests were also performed at higher concentrations with 14 EDCs including bisphenol A. The conventional water treatment process had very low removal efficiencies (0 to 7%) for all the EDCs except DEHP, DBP and DEP that were removed by 53%, 49%, and 46%, respectively. Ozonation at 1 mgO$_3$/L removed 60% of bisphenol A and 89% of nonylphenol, while chlorination at 1 mg/L removed 58% and 5%, respectively. When ozone and chlorine doses were 4 and 5 mg/L, respectively, both EDCs were not detected. PAC removal efficiencies ranged from 15% to 40% at 3 to 10 mg/L of PAC with a contact time of 15 minutes. In the high concentration batch sorption tests, EDC removal efficiencies by PAC were closely related to octanol-water partition coefficient (K_{ow}). GAC adsorption was very effective water treatment process. The type and service time of GAC did not affect EDC removal efficiencies. The combination of ozonation and GAC in series appears to remove EDCs effectively to safe levels while conventional water treatment could not.

Key words: Activated Carbon, Water Treatment, Endocrine Disrupting Chemicals

INTRODUCTION

Endocrine disrupting chemicals (EDCs) consist of synthetic and naturally occurring chemicals that affect the balance of normal hormonal functions in animals and humans. Generally, depending on their activity, EDCs may be characterized as estrogen modulators or androgen modulators. Concern over EDCs has been growing since certain chemicals were found to mimic the sex hormones - estrogen and androgen (thereby producing similar responses). These chemicals may also block the activities of estrogen or androgen (i.e., become anti-estrogens or anti- androgens).

A wide range of chemicals are thought to be potential EDCs. Although several hundreds of chemicals are known to be EDCs, around 70,000 chemicals currently used in United States should be tested to screen potential EDCs [Zacharewski, 1998]. Based on Zacharewski's classification [1998], EDCs include: natural compounds (plant estrogens, e.g., genistein and coumestrol), pharmaceuticals (diethylstilbestrol and ethynylestradiol), environmental pollutants (DDT, polychlorinated biphenyls, dioxins, and polyaromatic hydrocarbons), and industrially relevant chemicals (alkylphenols and bisphenol A). EDCs can also be classified according to pollutant sources. Wastewater effluents were found to contain largely estrogen-disrupting chemicals such as nonylphenol, 17 β-estradiol, and ethynylestradiol and pharmaceuticals [Baronti et al., 2000; Svenson et al., 2003; Verstraeten et al., 2003]. Also detected in wastewater effluents were alkylphenol polyethoxylate along with its degradation products [Ahel et al., 1994, 2000; Fujita et al., 2000; Nasu et al., 2001; Rudel et al., 1998] and estradiol-related chemicals [Desbrow et al., 1998; Routledge et al., 1998]. Alkylphenols including nonylphenol, octylphenol, and nonylphenol ehoxylates are thought be degradation products of nonionic surfactants (alkylphenol polyethoxylates). In 1988, the United States purchased about 200 million kg of these chemicals.

They are discharged to wastewater plants from households and industries [Roefer et al., 2000]. Other estrogenic EDCs come from synthetic and endogenous estrogens. Ethynylestradiol (synthetic estrogen used in oral contraceptives) and 17 β-estradiol (natural estrogen) are excreted in urine and enter into municipal sewage treatment plants [Carballa et al., 2004; Roefer et al., 2000]. Bisphenol A and nonylphenol are reported to be one of the most commonly found EDCs in waterbodies [Rudel et al., 1998; Roefer et al., 2000; Yamamoto et al., 2000]. Nasu et al. [2001] found that EDCs detected in raw sewage were found to be removed during wastewater treatment from 7% for 17 β-estradiol to >99% for bisphenol A and nonylphenol. Anderson et al. [2003] claimed that a common municipal wastewater treatment plant with an activated sludge system can appreciably eliminate natural and synthetic estrogens. According to Carballa et al. [2004], activated sludge system showed the removal performance of approximately 65% for 17 β-estradiol. Svenson et al. [2003] reported that activated sludge treatment tended to be more effective than trickling filters, whereas chemical precipitation using iron or aluminium salts without biological treatment showed little effectiveness. A Japanese study reported detectable bisphenol A in 86 and nonylphenol in 53 of 171 water samples collected in 2001.

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†To whom correspondence should be addressed.
E-mail: sgkim0822@hanmail.net

The maximum level of bisphenol A and nonylphenol were in the range of 0.56-1.81 μg/L and 4.6-21 μg/L [Japan Environmental Protection Agency, 2002].

Nonylphenol is a high-volume chemical that has been used for more than 40 years as detergents, emulsifiers, and wetting and dispersing agents. Recent results from mesocosm experiments indicate moderate persistence of nonylphenol in sediments, with half-lives of 28 to 104 days [Maguire, 1999]. According to the study on sorption and degradation of bisphenol A, 17 beta-estradiol, 17 alpha-ethynylestradiol, 4-tert-octylphenol, and 4-n-nonylphenol, 4-n-nonylphenol degraded quickly under aerobic conditions with a half-life of 7 days while bisphenol A remained almost unchanged [Ying et al., 2003]. Kuramitz et al. [2002] developed a new treatment method for p-nonylphenol as well as phenol, o-chlorophenol, p-chlorophenol, 2,4-dichlorophenol, and 2,4,5-trichlorophenol by voltammetric techniques. Although there have been many studies on detection of EDCs in wastewater, rivers, and lakes and fates in the environment and wastewater treatment plants, few studies have been performed to assess the fate of EDCs during water treatment [Snyder et al., 2003]. It is necessary to evaluate removal efficiencies of EDCs by various water treatment processes and determine the most efficient method(s) of removing EDCs during water treatment. The principal objective of this study was to determine removal efficiencies of selected EDCs by chlorination, ozonation, and adsorption with powdered activated carbon (PAC) and granular activated carbon (GAC) as well as Coagulation/flocculation/sedimentation/filtration (conventional water treatment process) from a series of laboratory- and pilot-scale tests. This study was designed to screen technologies used in water treatment for various types of EDCs and to provide operational conditions for pilot testing.

MATERIALS AND METHODS

The Nakdong River is one of the most polluted rivers in Korea. Water samples were collected in the Nakdong River, at which 30 industrial complexes are located upstream and 7,725 factories are scattered along the river. Total volume of wastewater discharged into the Nakdong River was 760,000 m^3/day [Korea Ministry of Environment, 2004]. The characteristics of the raw river water are summarized in Table 1.

Bisphenol A and nonylphenol were dissolved in methanol and spiked in the raw water. Bisphenol A and nonylphenol were analyzed using solid phase extraction (SPE) (Oasis® HLB Cartridge Columns, Waters Corp., Milford, MA) and high-performance liquid chromatography (HPLC) [US EPA Method 555; Kawaguchi et al., 2004; Rodriguez-Mozaz et al., 2004]. The analytical conditions are shown in Table 2 and Fig. 1.

The LODs (limits of detection) of bisphenol A and nonylphenol were 18 and 46 ng/L and the LOQs (limits of quantification) 50 and 250 ng/L, respectively, and the standard deviation of three replicates was ±2% at the LOQs. At 500 ng/L, the recovery rate ranged from 97 to 110%. The retention time difference was within ±5 sec. Treatment methods tested in this study were conventional water treatment - coagulation/flocculation/sedimentation, oxidation - chlorination and ozonation, and adsorption - powdered activated carbon (PAC) and granular activated carbon (GAC). Coagulants tested were alum, polyaluminum hydroxychloride (PACl), polyaluminum silicate sulfate (PASS), polyaluminum chloride silicate (PACS), and $Fe_2(SO_4)_3$. Optimum coagulant doses for individual coagulants were determined first and then removal efficiencies by various coagulants were determined under optimum conditions. After 1 minute of rapid mixing at 120 rpm in a 2-L rectangular Plexiglas® container, the content was mixed at 60 rpm for 9 minutes. After 20 minutes of settling, the samples were filtered and analyzed for concentrations of bisphenol A and nonylphenol. The same laboratory configuration was used for each coagulation experiment. Ozone was generated using PCI G-1 (West Caldwell, NJ, USA) with air feeding. The ozone reactor was 6 m tall, 0.14-m diameter Plexiglas® with a water volume of 0.07 m^3. A fine bubble diffuser was installed at the bottom of the tank. The ozone transfer efficiency was approximately 97%.

Table 1. Characteristics of raw water in Nakdong River, Korea

pH	Turbidity, NTU	Alkalinity, mg/L as $CaCO_3$	TOC, mg/L	UV 254, cm^{-1}
8.2-8.5	5.1-9.4	38-42	2.5-3.1	0.0895-0.0951

Table 2. Analysis conditions of HPLC (Waters 486)

Items	Conditions
Column	Chromolith Columns Rp-18e 100-4.6 mm
Mobile Phase	A : pH 3.0 phosphate buffer (15 mM) B : acetonitrile
Gradient	60% A initial, then linear gradient to 100% B in 20 min
Flow rate	0.8 ml/min
UV detector	278 nm (0.02 AUFS)
Injection	250 μL

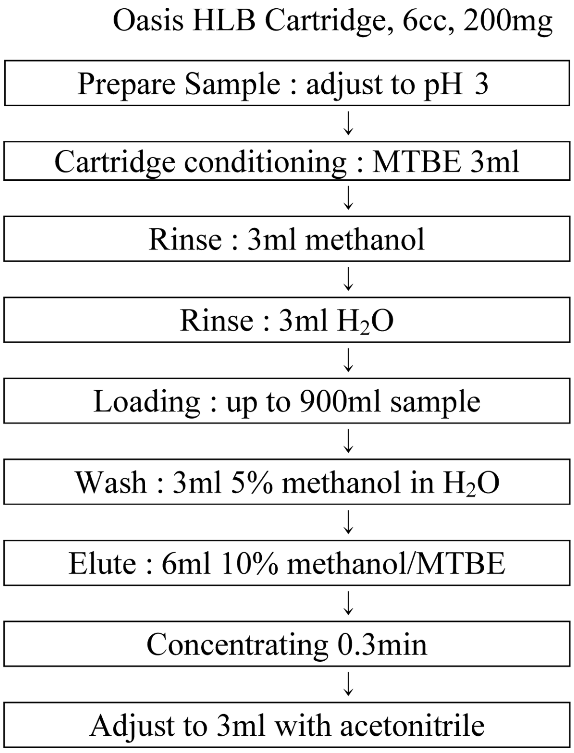

Fig. 1. SPE method (preparation).

The influent was fed into the top of the reactor, and effluent exited at the bottom, creating a counter-current flow pattern. Residual ozone in samples was removed by addition of 0.1 N $Na_2S_2O_3$ to stop further oxidation after sampling. Bisphenol A and nonylphenol were added with precision microinjection pumps while raw water was supplied. After 7 minutes of contact time, samples were taken for analysis. Target influent ozone concentrations were 1, 2, 4, 6, and 10 mg/L. The ozone concentration was measured with an ozone analyzer (PCI 90-400, West Caldwell, NJ). Residual ozone concentration was monitored using potassium iodide titration [APHA, 1998] and ozone kit (AccuVac® HACH, USA, Ozone Reagent, High Range 0-1.5 mg/L Ozone). Chlorination tests were conducted in a 1.5 L Erlenmeyer flask at chlorine doses ranging from 1 to 9 mg/L for one hour. In order to minimize the loss of chlorine, the flask was tightly sealed with Teflon cap. Powdered activated carbon (PAC) made from saw dust (Samchunri Inc., Seoul, Korea) was washed with distilled water and dried at 110 °C until there was no weight change. PAC was added at 1 to 10 mg/L to a 2-L rectangular Plexiglas® container and mixed at 120 rpm for 15 minutes. The concentration was measured after filtration with a Whattman® GF/C (1.2 μm) filter.

In order to evaluate removal efficiencies of various EDCs by PAC, a series of batch tests was performed at higher concentrations (10-100 mg/L). The EDCs tested include: bisphenol A, 2,4-dichlorophenol, bis(2-ethylhexyl) phthalate (DEHP), di-n-butyl phthalate (DBP), diethyl phthalate (DEP), 4-nitrotoluene, nonylphenol, 4-heptylphenol, 4-octylphenol, and 4-t-butylphenol, bezophenone, styrene monomer, and styrene trimer. Properties of the EDCs tested are summarized in Table 3. Thirteen EDCs were very insoluble. These insoluble EDCs were dissolved by boiling to increase their solubilities. Then, the dissolved EDCs were added to the Nakdong river water so that the EDC concentrations were approximately 10 mg/L. Concentrations were measured with a UV spectrophotometer at

Table 3. Properties of EDCs tested

Organic Compound	Formula	Henry's const. (dimensionless)	Vapor pressure, mm Hg	Solubility, mg/L	log K_{ow}	UV_{max} abs. wavelength, nm	Sources
Bisphenol A	$C_{15}H_{16}O_2$	$^{1}4.1\times10^{-10}$	$^{2}3.91\times10^{-7}$	$^{3}120$	$^{4}3.32$	278	Baby bottles, water bottles, epoxy resins, dental sealants, food can plastic lining, etc.
2.4-Dichlorophenol	$C_6H_4Cl_2O$	$^{5}2.25\times10^{-4}$	$^{6}1.16\times10^{-1}$	$^{7}4500$	$^{4}3.06$	292	Intermediate for dye-stuff and herbicides
4-Octylphenol	$C_{14}H_{22}O$	$^{1}2.88\times10^{-4}$	$^{8}4.78\times10^{-4}$	$^{9}5$	$^{10}5.28$	277	Detergents, binding polymer emulsion of water based paints, agricultural pesticides, emulsion polymers, epoxy resin, plastic stabilizer, leather processing, fuel and oil additives, photographic materials, textile processing, paint use, etc.
Nonylphenol	$C_{15}H_{24}O$	$^{5}4.51\times10^{-5}$	$^{11}2.36\times10^{-5}$	$^{12}6.35$	$^{10}5.99$	276	
4-Heptylphenol	$C_{13}H_{20}O$	$^{13}3.40\times10^{-1}$	$^{13}3.70\times10^{-1}$	$^{13}49.65$	$^{14}3.65$	278	
4-t-Butylphenol	$C_{10}H_{14}O$	$^{1}5.94\times10^{-5}$	$^{15}3.81\times10^{-2}$	$^{7}580$	$^{4}3.31$	276	
Benzophenone	$C_{13}H_{10}O$	$^{1}8.11\times10^{-5}$	$^{16}1.93\times10^{-3}$	$^{7}137$	$^{4}3.38$	258	Foundation, fragrances, UV absorbers, hair care products, insecticides, additive for plastics, coatings and adhesives, etc.
Styrene monomer	C_8H_8	$^{17}1.15\times10^{-1}$	$^{15}6.4$	$^{7}310$	$^{4}2.95$	248	Polymerizer for plastics, resins, coatings, and paints, disposable cups, etc.
4-Nitrotoluene	$C_7H_7NO_2$	$^{18}2.35\times10^{-4}$	$^{19}1.64\times10^{-1}$	$^{7}442$	$^{4}2.37$	284	Intermediates of colorants, agricultural, pharmaceutical, rubber chemicals, etc.
DEHP	$C_{24}H_{38}O_4$	$^{1}1.13\times10^{-5}$	$^{20}1.42\times10^{-7}$	$^{21}0.27$	$^{22}7.6$	244	Plasticizer for plastic food wraps and containers, PVC toys and medical devices, color stabilizer for manicure, mascara, eye liner, etc.
DBP	$C_{16}H_{22}O_4$	$^{23}7.57\times10^{-5}$	$^{24}2.01\times10^{-5}$	$^{25}11.2$	$^{26}4.50$	276	
DEP	$C_{12}H_{14}O_4$	$^{5}2.55\times10^{-5}$	$^{20}2.10\times10^{-3}$	$^{.54}1080$	$^{26}2.42$	276	

DEHP: di(2-ethylhexyl)phthalate; DBP: di-n-butyl phthalate; DEP: 4-heptylphenol

[1] Meylan and Howard [1991]; [2] Neely and Blau [1985]; [3] Dorn et al. [1987]; [4] Hansch et al. [1995]; [5] Paterson et al. [1990]; [6] Shiu et al. [1994]; [7] Yalkowsky and Dannenfelser [1992]; [8] Boublik et al. [1984]; [9] Meylan et al. [1996]; [10] Meylan and Howard [1995]; [11] Daubert and Danner [1989]; [12] Shiu et al. [1990]; [13] van Vlaardingen [2003]; [14] Talley [1993]; [15] Chao et al. [1983]; [16] Yaws [1994]; [17] Bocek [1976]; [18] Altschuh et al. [1999]; [19] Perry and Green [1984]; [20] Hinckley et al. [1990]; [21] Defoe et al. [1990]; [22] De Bruijn et al. [1989]; [23] Atlas et al. [1983]; [24] Donovan [1996]; [25] Howard et al. [1985]; [26] Ellington and Floyd [1996].

Table 4. Specifications of granular activated carbon used in testing

Item	Properties		
	Coal	Coconut	Wood
Apparent density, g/cm^3	0.43	0.47	0.23
Hardness number, %	98	99	98
Iodine value, mg/g	1,100	1,200	900
Methylene blue adsorption, mL/g	256	245	250
Residual material after 8×32 mesh	99.5	99	-
Specific surface area, m^2/g	1,100	1,230	1,611
Total pore volume, cm^3/g	0.61	0.54	1.21
Mean pore radius, Å	23	18	28

the wavelengths shown in Table 3 for three replicates.

The standard deviation of each EDC was ±5-10% at 0.1 mg/L. The wavelength of each EDC was determined from the water matrix containing only one EDC. The LOQ ranged from 0.1 to 1 mg/L, depending on EDCs. For the conventional water treatment test, the concentrations of PACl varied from 30 to 60 mg/L. After 1 minute of rapid mixing at 120 rpm, 10 minutes of flocculation at 60 rpm, and 30 minutes of settling, supernatant was collected for analysis. For ozonation tests, a 7-L column was used at an ozone concentration of 8.5 mg/L. Samples were collected at 1, 2 and 5 minutes. PAC sorption tests were performed at 10 to 100 mg/L of PAC at 25 °C for 30 minutes with a mixing speed of 220 rpm. The sample was filtered with a Whattman GF/C (1.2 μm) filter before analysis. A series of pilot tests was performed with granular activated carbon (GAC) columns with three types of GACs based on coal (Calgon Inc., Pittsburgh, PA), coconut (Samchunri Inc., Seoul, Korea), and wood (Picabiol Inc., France). The specifications of three GACs are summarized in Table 4. The operating conditions of the GAC columns were: 15 minutes of empty bed contact time (EBCT), 12 m/hr of approach velocity, and 2.5 m of bed depth. The experimental conditions of the GAC column tests are summarized in Table 5. In GAC columns #4 and #6, approximately 10% of the GACs were recharged with regenerated GAC.

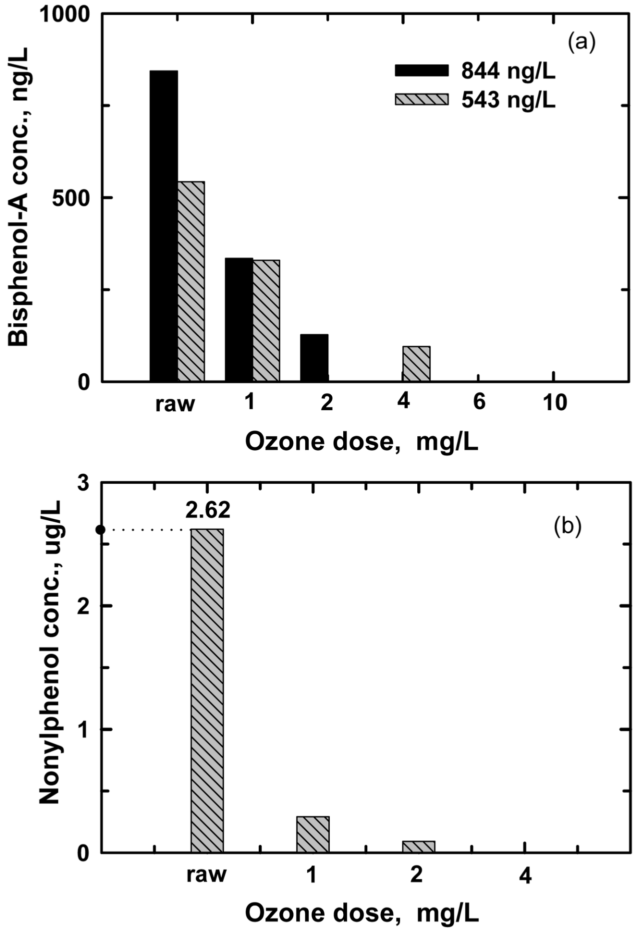

Fig. 2. Removal of bisphenol A (a) and nonylphenol (b) through ozonation.

RESULTS AND DISCUSSION

1. Low Level Bisphenol A and Nonylphenol Removal Efficiency

Results of conventional water treatment, using five different co-

Table 5. Experimental conditions for GAC pilot tests

Conditions	GAC #1	GAC #2	GAC #3	GAC #4	GAC #5	GAC #6	GAC #7
GAC type	Coal	Coal	Coal	Regenerated coal	Coconut	Regenerated coconut	Wood
GAC age	New	1 year	5.9 yrs	3.1 yrs	3.1 yrs	3.1 yrs	3.1 yrs
Bed volume, v/v	-	28,000	170,000	89,600	89,600	89,600	89,600

Table 6. Removal of bisphenol A and nonylphenol by coagulation/flocculation/sedimentation

Chemical	Initial conc.	Alum 50 mg/L	PACl 45 mg/L	PASS 45 mg/L	PACS 30 mg/L	$Fe_2(SO_4)_3$ 45 mg/L
Bisphenol A, μg/L	1.00	0.93	0.96	0.94	0.96	0.94
Turbidity, NTU	5.1	0.76	0.64	0.74	0.60	0.69
DOC, mg/L	2.16	1.53	1.64	1.59	1.62	1.67
Nonylphenol, μg/L	4.50	4.56	4.35	4.43	4.50	4.40
Turbidity, NTU	9.4	0.82	0.70	0.76	0.63	0.77
DOC, mg/L	2.25	1.62	1.50	1.58	1.60	1.57

agulants, are summarized in Table 6. The turbidity dropped from 5.1-9.4 NTU to 0.60-0.82 NTU and dissolved organic carbon (DOC) concentrations decreased from 2.16-2.25 to 1.5-1.67 mg/L. Despite the fact that DOC decreased by 26-30%, removal efficiencies of nonylphenol and bisphenol were 4-7% and 0-3%, respectively.

Spiked EDCs did not appear to be adsorbed onto natural organic matter (NOM) completely during 30 minutes of coagulation/flocculation/sedimentation. The type of coagulant used did not affect the EDC removal efficiency significantly. Chemical precipitation using iron and aluminum salts was found to be ineffective in removing estrogen [Svenson et al., 2003] and pharmaceuticals [Ternes et al., 2002]. Results of the ozonation experiments are shown in Fig. 2. In general ozone is effective method for DOC removal [Choi, 2004]. The removal efficiencies of bisphenol A and nonylphenol were 60% and 89%, respectively, at 1 mg/L of ozone concentration. When the ozone concentration was $\geq$4 mg/L, both EDCs were not detected. When chlorine was added, the removal efficiencies were 58% for bisphenol A and 5% for nonylphenol at a chlorine concentration of 1 mg/L, as shown in Fig. 3. When chlorine was added at $\geq$5 mg/L, neither EDC was detected at the initial concentration of 500 ng/L. At the chlorine dose of 1 mg/L, removal efficiencies were 58% for bisphenol A and 5% for nonylphenol. Oxidation with ozone and chlorine appears to be relatively effective in removing bisphenol A and nonylphenol at typical conditions encountered during water treatment as found by previous studies. For example, Komori et al. [2003] found that aerated gravel contact oxidation process removed 79% of bisphenol A and 76% of nonylphenol. Lee et al. [2003] found the removal of bisphenol A was increased with the increase in ozone dose and decrease in pH, and was not affected by the presence of hydroxyl radicals. Ternes et al. [2002] found that pharmaceuticals such as diclofenac, bezafibrate, and carbamazepine, were removed by 50->90% by ozonation and GAC was very effective in removing pharmaceuticals. Huber et al. [2003] claimed that ozonation and advanced oxidation processes were effective in removing pharmaceuticals.

PAC was added at 1, 3, 5, 7, and 10 mg/L. Results are shown in Fig. 4. At the initial bisphenol A concentration of 497 ng/L, removal efficiencies of PAC for the various PAC concentrations ranged from ~2% to 36%, while at 1,053 ng/L, removal efficiencies were between 15% and 39%. With an increase in PAC dose from 3 to 10 mg/L, removal efficiencies increased from 18% to 40%. PAC had limited removal efficiency for low level bisphenol A and nonylphenol at a contact time of 15 minutes and concentration of 10 mg/L. It is anticipated that the removal efficiency will improve with the increase in contact time as well as PAC concentration.

2. High Level EDC Removal Efficiency

When bisphenol A, benzophenone, 2,4-dichlorophenol, 4-hep-

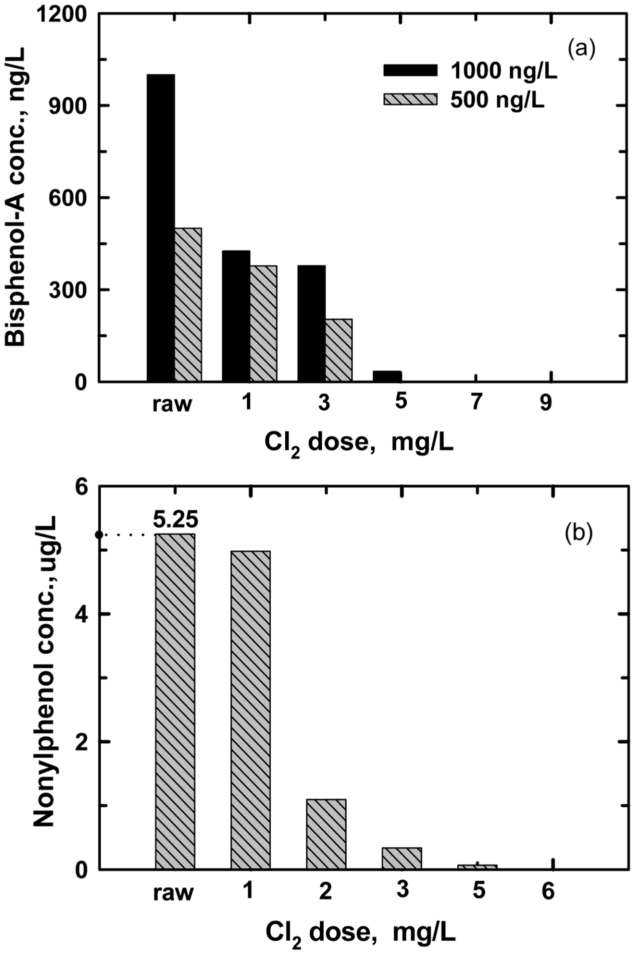

Fig. 3. Removal of bisphenol A (a) and nonylphenol (b) through chlorination.

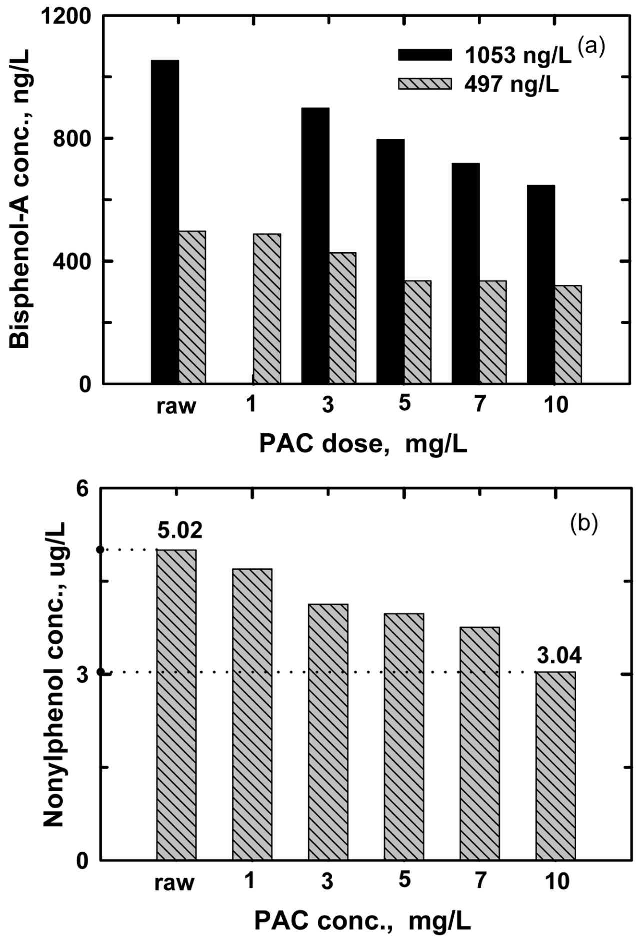

Fig. 4. PAC adsorptions of bisphenol A (a) and nonylphenol (b).

tylphenol, 4-nitrotoluene, DBP, and DEP were spiked in raw water at the concentration of 10.4, 10.0, 10.0, 10.0, 12.0, 13.0, and 10.0 mg/L, respectively, EDCs (except DEHP, DBP, and DEP) were not removed by the conventional water treatment process. DEHP, DBP, and DEP were removed by 53%, 49%, and 46%, respectively, probably due to removal of natural organic matter (NOM) that adsorbed these phthalates having high octanol/water partition coefficients.

Bisphenol A, benzophenone, 2,4-dichlorophenol, 4-heptylphenol, 4-nitrotoluene, DBP, and DEP were spiked in raw water at the concentration of 10.4, 10.0, 10.0, 10.0, 12.0, 13.0, and 10.0 mg/L, respectively, and ozone was supplied at 8.5 mg/L to evaluate the removal efficiencies of various EDCs by ozonation. After up to 5 minutes of contact time, the concentrations of these EDCs did not decrease, indicating that at high concentrations it may require a high ozone dose and longer contact time. Results of batch sorption tests with various EDCs at 10 mg/L of the initial concentration are shown in Figs. 5 through 8.

Fig. 5 shows the removal efficiencies of phthalate by PAC. DEHP had the greatest removal efficiency probably because DEHP has the largest K_{ow} value of 7.6 and thus the most hydrophobic among the EDCs tested. Although the K_{ow} value of DEP is 2.42 compared with 4.5 for DBP, the removal efficiency was similar. This was thought to be caused by the fact that DBP has four more aliphatic carbons that have weak reactivity structurally but has the same number of ester that has a charge.

Although bisphenol-A and 2,4-dichlorophenol have similar hydrophobic properties, the reason for the difference in removal efficiency by PAC as shown in Fig. 6 appeared to be due to high reactivity of chlorine attached to aromatic carbons in 2,4-dichlorophenol.

At the PAC concentration of 30 mg/L, nonylphenol of alkylphenols that has the greatest hydrophobicity had 100% removal efficiency and 4-t-butylphenol that has the lowest K_{ow} had the lowest removal efficiency, as expected. The removal efficiency of 4-octylphenol was not greater than 4-heptylphenol although 4-octylphenol has a greater K_{ow} value than 4-heptylphenol. This similar removal efficiency was thought to be caused by aliphatic carbon, CH_2, of 4-octylphenol located in the place in which the reaction is difficult to occur physically.

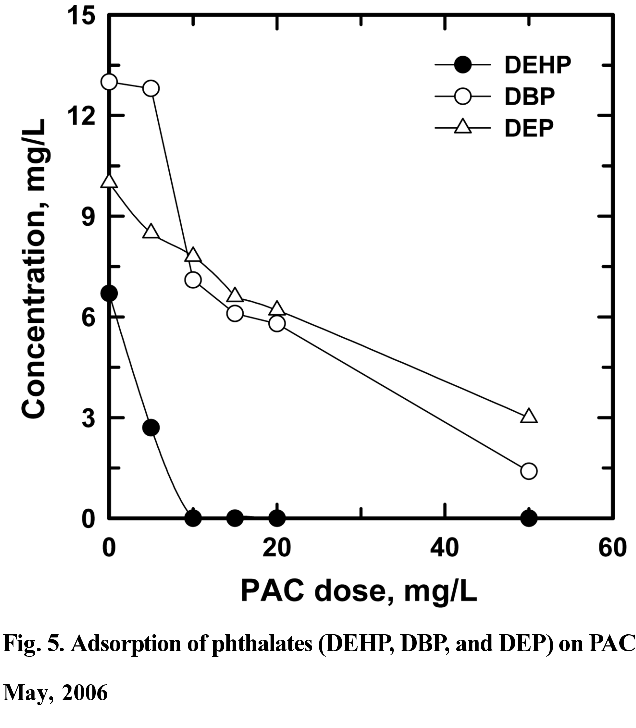

Fig. 5. Adsorption of phthalates (DEHP, DBP, and DEP) on PAC.

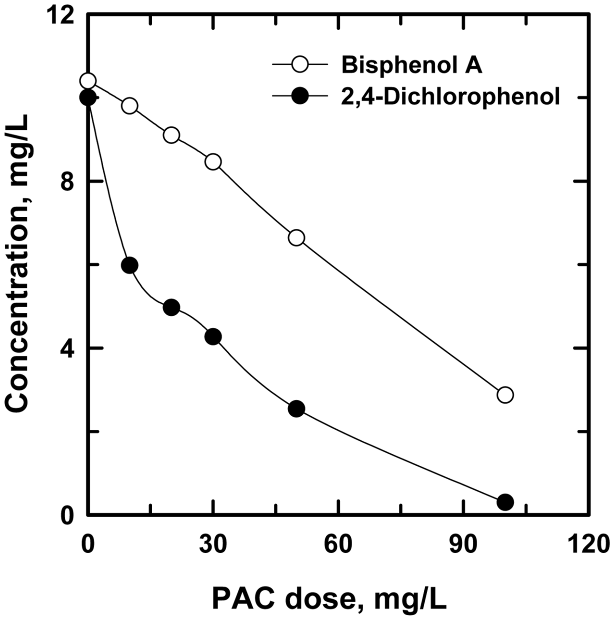

Fig. 6. Adsorption of bisphenol A & 2,4-dichlorophenol on PAC.

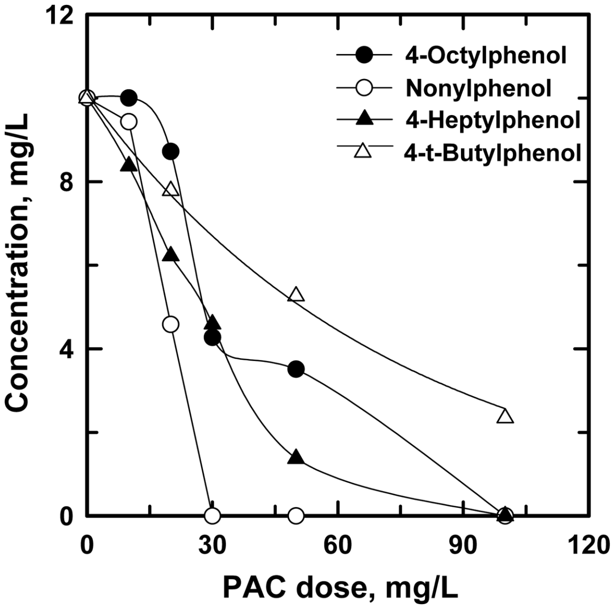

Fig. 7. Adsorption of alkylphenols on PAC.

Among the EDCs shown in Fig. 8, styrene had different sorption trend due to structural properties. Although carbon structure of aromatics strengthens the hydrophobicity, the sorption efficiency is slightly low due to low reactivity. It can be said that despite high hydrophobicity, PAC sorption efficiency becomes low if the accessability is low or the reactivity is low due to the absence of charge.

The partition coefficient, K_d, is defined as the ratio of the quantity of the adsorbate adsorbed per unit mass of solid to the amount of the adsorbate remaining in solution at equilibrium [US EPA, 1999].

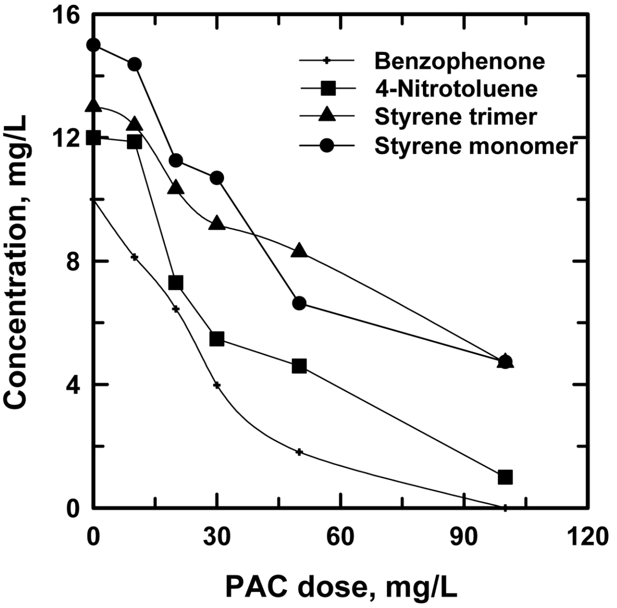

Fig. 8. Adsorption of aromatic compounds and VOCs on PAC.

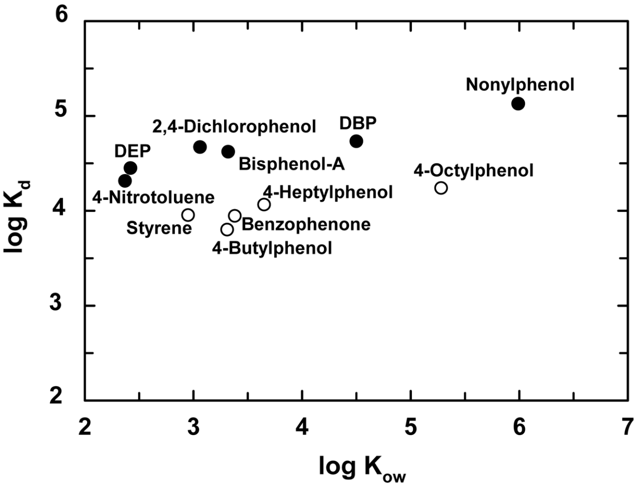

Fig. 9. Relationships between log K_{ow} and log K_d.

In this study, K_d was determined after 15 minutes of contact time not after equilibrium since jar tests were conducted not batch isotherm tests. The partition coefficient, K_d, is commonly correlated with the log K_{ow} (octanol-water partition coefficient) [Karickhoff et al., 1979]. The relationships between log K_{ow} and log K_d are shown in Fig. 9. The K_d value for DEHP was not plotted because the concentration was zero at 10 mg/L of PAC in the batch test. Poor relationship between log K_d and log K_{ow} may be due to the fact that the K_d values were not determined from typical batch isotherm tests but from the batch jar test with 15 minutes of contact time. DEHP, which has the highest log K_{ow} value of 8.39 among EDCs tested, was not detected at PAC concentration of 10 mg/L while nonylphenol with the log K_{ow} value of 5.99 was removed completely at PAC concentration of 30 mg/L. Bisphenol A, styrene monomer, and styrene trimer were adsorbed to PAC less than phthalates but greater than alkylphenols. The order of adsorption removal was in good agreement with the magnitude of log K_{ow} values of individual EDCs. It is anticipated that EDCs with the log K_{ow} value of >2.5 are easily removed at by activated carbon adsorption if the initial concentration is >10 mg/L.

3. GAC Adsorption Tests

Short-term granular activated carbon (GAC) adsorption tests were performed with seven different GACs to evaluate the effect of types of GACs and service time on EDC removal. All GAC columns had 15 minutes of EBCT and samples were collected at bed volumes of 36 and 64 for analysis of EDCs. GAC columns #1 and #2 were packed with the same GACs used in the Busan Water Treatment Plant, Korea. GAC columns #1 and #2 adsorbed 1 μg/L of bisphenol A and 2.5 μg/L of nonylphenol to below detection limits at bed volumes of 36 and 64. GAC columns #3 through #7 have been in service for 3 to almost 6 years. Therefore, these GACs are fully saturated with DOC. At the initial concentrations of bisphenol A and nonylphenol of 2.3 and 2.9 μg/L, respectively, none of the compounds were detected in the effluent. Despite the exhaustion of DOC sorption capability, EDCs were effectively adsorbed to GAC. There were no significant effects of types and service times (ages) of GACs tested on the removal of bisphenol A and nonylphenol. Long-term GAC column tests must be performed to determine the breakthrough time and GAC replacement period and those of the biodegradable portion [Rhim, 2006].

It should be noted that the chromatograms of HPLC analyses did not show any peaks with GAC treated samples but had small peaks near the retention times of bisphenol A and nonylphenol with ozonation. This indicates that ozonation or chlorination generated by-products while GAC removed EDCs below the detection limit without generating by-products. Itoh et al. [2000] found that chlorination amplified the estrogenic effect of nonylphenol and 17 beta-estradiol in natural water 2.3 times more than without chlorination. Ryoko et al. [2002] claimed that chlorinated bisphenols might be more severe endocrine disruptors than bisphenol A because polychlorinated bisphenols were not easily biodegraded. Therefore, it is recommended that EDCs be removed before chlorination due to potentially persistent and more toxic by-product formation. GAC adsorption appeared to be effective for EDC removal in drinking water treatment as found by Tanghe et al. [2001] and Ternes et al. [2002]. Biodegradation is expected to play a major role in the removal of bisphenol A from the environment. In the most common type wastewater treatment system, an activated sludge treatment process, 92-98% removal of bisphenol A was reported [Staples et al., 1997, 1998]. Therefore, it can be said that many EDCs are removed by operating GAC columns biologically-active after chemical oxidation such as ozonation and chlorination.

CONCLUSIONS

Extensive screening tests were performed in the laboratory using simulated conventional water treatment consisting of coagulation/flocculation/sedimentation/filtration, pre- and post-ozonation, prechlorination, PAC, and GAC to evaluate the removal efficiency of various water treatment processes. From batch and laboratory experiments, the following conclusions can be drawn:

1. The conventional coagulation/flocculation water treatment pro-

cess had very low removal efficiencies for bisphenol A (0-3%) and nonylphenol (4-7%).

2. Oxidation was effective for removing both bisphenol A and nonylphenol. The removal efficiencies of bisphenol A and nonylphenol were 60% and 89%, respectively, at 1 mg/L of ozone concentration with the contact time of 7 minutes. Ozone was much more efficient than chlorination. At the initial concentration of <3 μg/L, both EDCs were not detected when the ozone concentration was ≥4 mg/L and the chlorine concentration was ≥5 mg/L. The oxidation efficiency was lower at low initial EDC concentrations than at high concentrations.

3. PAC tested in this study had relatively low removal efficiencies (25-40%) for bisphenol A and nonylphenol at the contact time of 15 minutes. The adsorption of EDCs was closely related to log K_{ow} values. At the initial concentration of >10 mg/L, EDCs were effectively removed by PAC. However, at the EDC levels commonly detected in the environment, PAC may not be an acceptable alternative for removing EDCs.

4. GAC adsorption was effective in removing EDCs at the empty bed contact time of 15 minutes. A GAC column showing no DOC removal due to saturation was still able to remove EDCs to below detection limits. The type and service time (age) of GAC did not affect the removal of EDCs. Times to breakthrough and reach steady state must be determined with long-term GAC column tests.

5. The combination of ozonation and GAC in series during water treatment appears to be most effective in removing most EDCs to a safe level. If GAC is biologically active, EDCs with high solubilities or by-products formed during chemical oxidation of EDCs may be removed further and GAC service time may be increased significantly.

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