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HPLC-fluorescence detection and adsorption of bisphenol A, 17β-estradiol, and 17α-ethynyl estradiol on powdered activated carbon

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Abstract

The adsorption of three estrogenic compounds (bisphenol A (BPA), 17β-estradiol (E2), and 17α-ethynyl estradiol (EE2)) on several powdered activated carbons (PAC) was investigated. Without preconcentration, method detection limits (MDL) using high-performance liquid chromatography (HPLC) with fluorescence detection at an excitation wavelength of 280 nm and an emission wavelength of 310 nm were 0.88, 1.15, and 0.96 nM for BPA, E2, and EE2, respectively. Compound recoveries were >90% in raw drinking water matrices. PAC screening studies (six PAC brands) indicated all three compounds were removed by PAC, but the percentage removal ranged from 31% to >99% based upon PAC type/dosage and presence/absence of natural organic matter. The order of removal (E2 > EE2 > BPA) corresponded with $\log K_{ow}$ values for the compounds (3.1–4.0, 3.7–3.9, 3.3, respectively). Kinetic and PAC dose–response experiments were conducted with the two best performing PACs. Increasing contact time and PAC dose improved compound removal. Freundlich isotherm parameters were fit to the experimental data. This study confirms that PAC treatment is feasible for >99% removal of three estrogenic compounds from raw drinking waters that may be at risk for containing such compounds, at least at initial concentration of 500 ng/L and higher.

Keywords: Powdered activated carbon; Adsorption; HPLC-fluorescence; Bisphenol A; 17β-estradiol; 17α-ethynyl estradiol; Treatment

1. Introduction

Adsorption processes employing powdered activated carbon (PAC) are widely used in drinking water to remove organic micropollutants [1–5]. Bisphenol A (BPA), 17β-estradiol (E2), and/or 17α-ethynyl estradiol (EE2) are endocrine-disrupting compounds (EDCs) that have been detected in drinking water, surface water, groundwater, and/or wastewater [6–11]. BPA, E2, and EE2 have been found in river water (ng/L) receiving sewage treatment work effluents (ng/L) and drinking water (pg/L) [6,8]. The analytical determination of BPA, E2, and EE2 from surface and wastewater commonly uses of gas chromatography-mass spectrometry (GC-MS or MS-MS) [6,7, 10–14], liquid chromatography-mass spectrometry (LC-MS or MS-MS) [12], and biological assays [7,9,12–13,15–17] following solid-phase extraction. These analytical techniques are expensive, time consuming, and require a high degree of analytical knowledge. High-performance liquid chromatography (HPLC) with ultraviolet (UV) or fluorescence detection has been also used to determine relatively high concentration (~μg/L) organic compounds (e.g., BPA, polychlorinated biphenyls, polyaromatic hydrocarbons, pesticides, surfactants, musk, and/or pharmaceuticals) from water supplies [9,18–28]. Each analytical technique

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has issues regarding pretreatment requirements, compound recoveries, detection limits, and compound specificities.

The purpose of this paper was two fold. First, a simple analytical technique for rapid determination of estrogenic compounds in drinking water matrices was developed using HPLC with fluorescence detection. Second, the feasibility for PAC addition to convention water treatment plants (WTPs) to remove selected estrogenic compounds was investigated. Batch PAC adsorption experiments were conducted in model (distilled) water and two raw drinking waters spiked with BPA, E2, and EE2.

2. Materials and methods

2.1. *PAC adsorption experiments*

Table 1 describes the characteristics of the EDCs used in this study. BPA (common plasticizer), E2 (natural estrogen), and/or EE2 (synthetic estrogen—oral birth control pharmaceutical) (initial concentration of 100 nM) were contacted with PAC in a model water and two raw drinking waters (SRPW and HRW). Applied PAC doses ranged from 1 to 50 mg/L. PAC brand screening experiments were conducted at two PAC dosages (5 and 15 mg/L) with a 4 h contact time. Kinetic experiments were conducted with 1, 4, and 24 h contact times. Duplicate experiments were conducted in HRW. Amber vials (40 mL) were used for the kinetic and isotherm experiments and were shaken on a wrist shaker (Multi-wrist® shaker, Lab-Line, Melrose Park, IL, USA) using a separate container for each duplicate. Control treatment contained BPA, E2, and EE2, but no PAC. Activated carbon was removed from the samples by filtering with a 0.7-μm (25 mm GF/F) glass-fiber filter.

Six powdered activated carbons, AC800 (AC800, Acticarb, Dunnellon, FL, USA), Hydrodarco-B #1033 (HDB-1033), Hydrodarco-B #1091 (HDB-1091), and PAC 20B (20B) (Norit Americas Inc., Atlanta, GA, USA), Picazine (Pica, Pica, France), and WPM (PAC form of F400, Calgon Carbon Corp., Pittsburgh, PA, USA) were used for the screening and/or kinetic and isotherm experiments. All the PACs are coal based except the wood-based Pica, respectively. All PACs were hydrated for 24 h in distilled water prior to use, and added as a slurry (1000 mg/L) to the samples.

2.2. *Determination by HPLC-fluorescence*

HPLC was performed on a Waters600 series (Milford, MA, USA) liquid chromatography. Detection was accomplished with a Waters2475 fluorescence detector at an excitation wavelength of 280 nm and an emission

Table 1
Characteristics of BPA, E2, and EE2

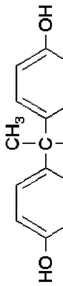
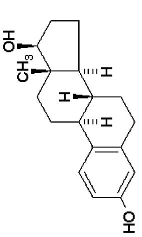
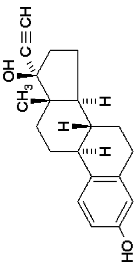
Common name (abbreviation) [full name]	Use	Molecular weight/mass	Log K_{ow}	pK_a	Structure
Bisphenol A (BPA) [2,2′-bis-(4-hydroxyphenyl)propane]	Plasticizer	228.1	3.3	9.6–10.2	
17*β*-estradiol (E2) [1,3,5(10)-estratriene-3,17*β*-diol]	Reproductive hormone	272.3	3.1–4.0	N/A	
17*α*-ethynylestradiol (EE2) [17*α*-ethinyl-1,3,5(10)-estratriene-3,17*β*-diol]	Ovulation inhibitor	296.2	3.7–3.9	N/A	

Table 2
Characteristics of source waters

Source water	DOC (mg/L)	UVA_{254} (1/cm)	SUVA (L/mg-m)	Conductivity (mS/m)	pH	BPA, E2, and EE2 spiked (nM)
Model water	N/A	N/A	N/A	108[a]	8.3[b]	100
SRPW	3.9	0.051	1.3	108	8.3	100
HRW	7.7	0.244	3.2	83	8.4	100

N/A = not available.

[a] Conductivity was adjusted by adding NaCl solution after pH was buffered by 5 mM $NaHPO_4$.

[b] pH was buffered by 5 mM $NaHPO_4$.

wavelength of 310 for all the compounds used in this study. Fluorescence detector wavelengths were selected based upon fluorescence peaks observed during excitation–emission matrix (EEM) analysis of the compounds in the HPLC eluent. Most EDCs contain aromatic moieties and should be amendable to fluorescence detection. The EEM measurements were conducted using a Perkin-Elmer LS-50 luminescence spectrometer. The excitation source was a 150-W xenon lamp. Excitation and emission slits were maintained at 10 nm and scan speed was set at 1000 nm/min during all measurements. A Waters 5-μm LiChrosorb® RP18 analytical column (4.6 mm × 100 mm) connected to a Waters 5-μm LiChrosorb® RP18 guard column (4.6 mm × 10 mm) was used for reverse-phase separations with a 200-μL sample loop. The mobile-phase solvent profile was 45% deionized (DI) water acidified with 10 mM H_3PO_4 and 55% MeOH for 30 min at a constant flow rate of 1 mL/min. The method was isocratic and the column was restabilized to the run time by passing the same mobile-phase solvent for 5 min. BPA and EE2 eluted from the columns at 7.5 and 17.5 min, respectively. E2 showed similar retention (elution time = 17 min) as EE2. Therefore, separate experiments were conducted to obtain adsorption characteristics of E2 and EE2; BPA and EE2 were studied as a mixture.

Stock solutions of BPA, E2, and EE2 (Sigma, St. Louis, MO, USA) were initially prepared in methanol at 1 mM and were subsequently diluted with DI water to four different concentrations of 1, 5, 10, and 50 nM for the calibration run. HPLC analysis was conducted for 30 min, with peaks for BPA and EE2 eluting at 7.5 and 17.5 min, respectively. Separate test solutions and analyses were conducted for experiments containing E2, because E2 showed a similar retention time of 17 min compared to EE2. MDLs using the HPLC with fluorescence detection were 0.88 nM (201 ng/L), 1.15 nM (313 ng/L), and 0.96 nM (283 ng/L) of DI water for BPA, E2, and EE2, respectively. MDLs were determined for these compounds by reverse-phase HPLC with fluorescence detection by injecting 200 μL of a 0.7 nM of each of these compounds eight times and reported with 99% confidence based upon the calculation of variance and standard deviation of the replicate measurements following United State Environmental Protection Agency MDL method (Revision 1.11).

Spike/recovery experiments were performed to determine the effects of inorganic salts and/or natural organic matter (NOM) on the detection of the compounds in two natural waters. Eight 1-L glass flasks were spiked with a mixture of BPA and EE2, or E2 only of four different concentrations of 1, 5, 10, and 50 nM and mixed for at least 4 h. Average recoveries were 96%, 95%, and 95% in the SRPW and 93%, 92%, and 90% in the HRW for BPA, E2, and EE2 at various concentrations. The two natural waters were selected to represent a relatively hydrophilic NOM showing lower SUVA (Salt River Project water (SRPW)) versus a relatively hydrophobic NOM showing higher SUVA (Huron River water (HRW)). The characteristics of source waters used in this study are described in Table 2.

Dissolved organic carbon (DOC) was measured using a combustion/non-dispersive infrared gas analysis method (Shimadzu Model TOC-5050A). UV absorbance at a wavelength of 254 nm (UVA_{254}) was measured with a Shimadzu UV/VIS 1601 spectrophotometer. The UV absorbance of NOM is ascribed exclusively to aromatic chromophores and the SUVA ($SUVA = UVA_{254}/DOC$) is considered a measure of the relative aromatic content of NOM. The natural source waters were prefiltered using a 0.7-μm (47 mm GF/F) ashed glass-fiber filter (Whatman® International Ltd., Maidstone, England) prior to use.

3. Results and discussion

3.1. PAC screening experiments

The relative performance of different PAC brands for removing estrogenic compounds was screened. Two dosages (5 and 15 mg/L) of each PAC were added to a model and two raw drinking waters spiked with BPA, E2, and EE2 at an initial concentration of 100 nM. This initial concentration was selected such that 99% removal (2-log) of the compounds could be quantified above the MDLs. A 4 h contact time was used. BSA, E2,

Table 3
Removal of BPA, E2, and EE2 by PAC (contact time = 4 h) in screening experiments

Type	PAC dose (mg/L)	Remaining (C/C_0)% in model water			Remaining (C/C_0)% in SRPW			Remaining (C/C_0)% in HRW[a]		
		BPA	E2	EE2	BPA	E2	EE2	BPA	E2	EE2
Norit 20B	5	10.5	<1.0	2.7	12.4	1.5	1.4	26.9 (±1.3)	6.4 (±0.1)	21.9 (±0.3)
AC800	5	1.4	<1.0	<1.0	17.3	11.2	2.9	34.5 (±1.1)	12.2 (±0.4)	28.9 (±1.1)
Pica	5	3.8	2.0	<1.0	23.9	1.5	<1.0	42.5 (±1.6)	3.6 (±0.1)	11.1 (±0.2)
WPM	5	2.5	<1.0	<1.0	37.1	2.2	8.4	47.0 (±1.6)	3.7 (±0.1)	27.3 (±1.1)
HDB-1091	5	9.5	2.7	3.1	49.1	4.2	11.1	61.4 (±2.2)	13.4 (±0.4)	49.6 (±1.0)
HDB-1033	5	6.7	4.6	2.7	52.8	4.9	12.6	66.7 (±3.0)	10.9 (±0.5)	45.7 (±0.7)
Norit 20B	15	3.4	<1.0	1.5	1.5	<1.0	<1.0	4.8	<1.0	4.5
AC800	15	<1.0	<1.0	<1.0	1.9	<1.0	<1.0	5.6	<1.0	3.8
Pica	15	2.6	1.8	<1.0	4.9	<1.0	<1.0	13.4	<1.0	1.8
WPM	15	1.2	<1.0	<1.0	5.9	<1.0	<1.0	14.5	<1.0	4.8
HDB-1091	15	6.3	2.0	1.2	12.8	2.6	4.9	21.5	5.9	19.4
HDB-1033	15	6.0	3.3	2.4	13.4	2.8	5.4	18.7	5.6	18.5

[a] The numbers in parenthesis are standard deviation calculated with duplicates.

and EE2 concentrations decreased upon PAC addition (Table 3). Greater than 99% of E2 and EE2 were removed from the model water on addition 15 mg/L for most PAC brands except the HDB-series (HDB-1033 and HDB-1091). Compound removals were lower in SRPW and HRW than the model water without NOM, percentage removal ranging from 31% to >99% depending on PAC types/dosages and water quality conditions. The lowest removals were observed in the HRW having the highest hydrophobic NOM content and DOC concentration. NOM molecules block pores in the activated carbon, reducing the surface area available for the adsorption of organic compounds, and competes with the specific compounds for adsorption sites [1, 29–31]. In rank order from highest to lowest compound removal by PAC (log K_{ow} values in parentheses: E2 (3.1–4.0) > EE2 (3.7–3.9) > BPA (3.3). Numerous studies showed that adsorption capacity increased with increasing octanol–water partitioning coefficient (K_{ow}) of organic compounds [32–34]. This observation, based largely upon low molecular weight organic compounds, appears valid for the three higher molecular weight EDCs studied herein.

Unique differences in the relative ranking of PAC performance for the three compounds in the model and raw drinking waters were observed (Table 3). For example, in the model water Norit 20B was the least effective PAC brand for BPA removal. In contrast, in the two raw drinking waters Norit 20B was among the best performing PAC brands for BPA, E2, and EE2. In the raw drinking water, AC800 was effective for BPA, but relative to other PAC brands was not as effective for E2 or EE2 removal. This implies that source water characteristics affect EDC removal by PAC. Two of among the better performing PAC brands (AC800 and Norit 20B) were selected from the screening experiments for additional kinetic and PAC dose–response studies.

3.2. *Kinetic and PAC dose–response experiments*

Kinetic experiments were monitored by collecting samples after 1, 4, and 24 h of contact with either AC800 or Norit 20B. Representative PAC dose–response data for EE2 with AC800 is shown in Fig. 1. Approximately 45 mg/L of AC800 was required to achieve 99% EE2 removal from SRPW with a 1 h contact time, whereas 15 and 9 mg/L were required for contact times of 4 and 24 h, respectively. Similar results were obtained for all three compounds in SRPW and HRW; lower PAC doses were required in the model water.

Freundlich isotherm values (K, $1/n$) were calculated from batch dose–response relationships (e.g., Fig. 1). Based upon Fig. 1, contact times of up to 24 h are inadequate for representing equilibrium. However, Freundlich isotherm values were calculated to allow comparison of adsorption capacity terms (K) among different experimental conditions. Example data for all three compounds in SRPW with a 1 h contact time are presented in Fig. 2. Calculated values for all experiments at 1 and 4 h contact times are presented in Table 4. K values were 8.1, 3.2, and 2.3 in the SRPW and 4.1, 2.7, and 1.7 in the HRW for E2, EE2, and BPA on AC800 at a 4 h contact time (Table 4). Norit 20B showed slightly higher K values than AC800. The Freundlich isotherm values were not calculated for the 24 h samples due to lack of data for most of the model water because all the compounds were removed below detection limit. The average $1/n$ value from all experiments was 0.34 and would be higher for the raw drinking waters than model (NOM-free) water. Adsorption capacity terms (K)

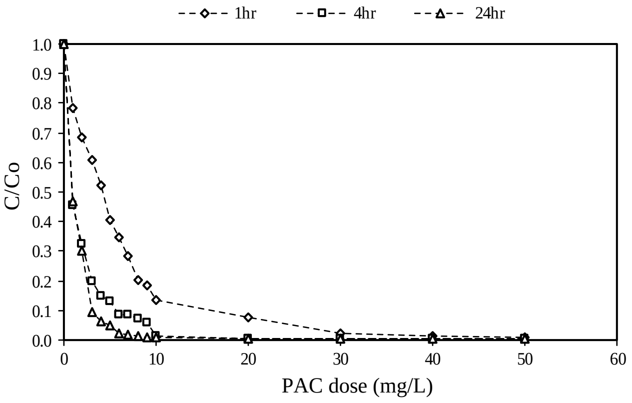


Fig. 1. Effect of contact time on EE2 removal from SRPW on AC800.

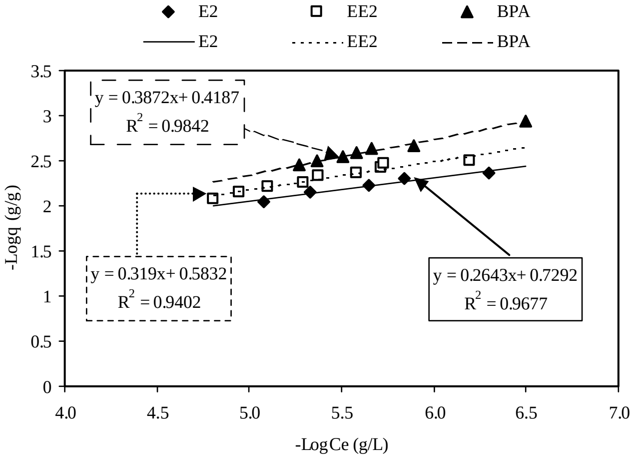


Fig. 2. Freundlich isotherm fits of experimental data on AC800 in SRPW (contact time = 1 h).

Table 4

Summary of K and $1/n$ values from PAC dose–response experimental data: pseudo-equilibrium parameters

Compound	Water	Norit 20B				AC800			
		1 h		4 h		1 h		4 h	
		K (g/g) (L/g)$^{1/n}$	$1/n$	K (g/g) (L/g)$^{1/n}$	$1/n$	K (g/g) (L/g)$^{1/n}$	$1/n$	K (g/g) (L/g)$^{1/n}$	$1/n$
E2	Model water	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	SRPW	5.36	0.26	10.9	0.14	4.80	0.30	8.11	0.22
	HRW	6.16	0.31	12.3	0.21	2.91	0.40	4.12	0.31
EE2	Model water	N/A	N/A	N/A	N/A	4.03	0.32	4.78	0.25
	SRPW	3.83	0.32	5.34	0.27	2.75	0.41	3.16	0.33
	HRW	1.61	0.45	3.10	0.34	1.76	0.47	2.73	0.37
BPA	Model water	N/A	N/A	N/A	N/A	2.87	0.39	4.60	0.27
	SRPW	2.62	0.39	4.48	0.30	1.86	0.47	2.32	0.38
	HRW	1.56	0.47	2.85	0.37	1.55	0.43	1.66	0.42

N/A = not available due to lack of data detected above detection limit.

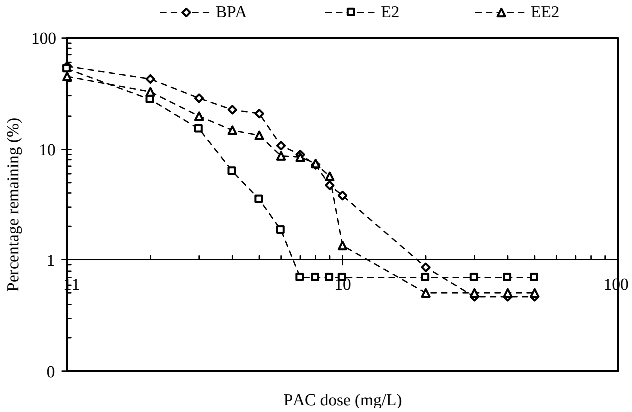


Fig. 3. Effect of PAC (AC800) dose on BPA, E2, and EE2 removal in SRPW (contact time = 4 h).

ranged from 1.55 to 10.9 (g/g)(L/g)$^{1/n}$. Although in our study, the parameters were calculated in pseudo-equilibrium with a relatively high initial concentration, the pseudo-equilibrium isotherm parameters would still be valid for determining PAC dosages. A previous study investigated the adsorption kinetics of E2 in batch experiments at a low dosage ranging from 0.5 to 100 ng/L to simulate a realistic range of contaminated ground water or surface water as a drinking water [2]. In that study, E2 was quickly adsorbed and a free hormone concentration close to the equilibrium concentration assuming a pseudo-first-order reaction was reached within a 50–180 min. Another study showed that the removal percentage of micropollutants (2-methylisoborneol and geosmin occurring at nanogram per liter levels compared to dissolved organic carbon at milligram per liter level) by PAC was independent of their initial concentration [31]. In addition, as a part of the Investigators' recent study (American Water Works Associated Research Foundation #2758 entitled *Evaluation of Conventional and Advanced Treatment Processes to Remove Endocrine Disruptors and Pharmaceutically Active Compounds*), PAC adsorption studies were conducted with two PACs, AC800 and WPM, at an initial concentration of 500 ng/L of E2 and EE2 in a model water. An applied PAC dosage was 5 mg/L at pH 5.8. The experiments were performed in a six-place gang stirred and 2-L glass beakers filled with a 1.5 L model water for reactors with a contact time of 4 h prior to sampling. MDLs using LC/MS/MS were 0.5 ng/L for E2 and 0.25 ng/L for EE2, respectively. Both E2 and EE2 percentage removal was greater than 99.5%. The practicality for these non-equilibrium Freundlich isotherm parameters is their potential usage with determination of PAC doses (D_0, mg/L), under non-equilibrium contact times:

$$D_0 = \frac{C_0 - C_{\text{eff}}}{K C_{\text{eff}}^{1/n}}, \tag{1}$$

where C_0 and C_{eff} are the raw and finished compound concentrations.

The dose–response removal of BPA, EE2, and E2 are presented in Fig. 3, with associated K and $1/n$ values reported in Table 4. The results indicate a higher adsorption capacity by PAC for E2 than EE2 or BPA, respectively, over the entire PAC dose range. Similar results were found for all 1, 4, and 24 h contact times in all waters. Based upon K values for E2, EE2, or BPA at any contact time, removal would be lowest in HRW (lowest K value), followed by SRPW (intermediate K values) and model water (highest K values). As with the screening experiments, competition for adsorption sites and pore blockage by NOM in HRW was responsible for lower adsorption capacity values.

4. Conclusions

HPLC with fluorescence detection proved to be a simple and useful tool for conducting controlled experiments with several estrogenic compounds. Method detection limits using HPLC with fluorescence detection were 0.88, 1.15, and 0.96 nM of model water for BPA, E2, and EE2, respectively, without preconcentration. Compound recoveries of >90% were achieved in raw drinking water matrices, indicating limited interference from NOM. HPLC-fluorescence analysis could be used to screen technologies for their ability to removed EDCs, since most EDCs contain aromatic moieties. Occurrence and low-level treatability of EDCs would require more advanced analytical instrumentation and preconcentration strategies.

PAC removed three estrogenic compounds (BPA, E2, EE2) from raw drinking waters. Although experiments were conducted at concentrations orders of magnitude above most reported occurrence levels, the results were useful as a PAC technology-screening tool. PAC removal of micropollutants at the part-per-billion and parts-per-trillion levels has been shown to be independent of initial concentration [31]. Preference for EDC compound removal paralleled $\log K_{ow}$ values; highest removal corresponded to largest $\log K_{ow}$. The PAC brand with the lowest removal capability (HDB brands) had the lowest point of zero charge (pH_{ZPC}) values (~ 3.5) compared against other PAC brands ($6 < pH_{ZPC} < 8$) [35]. PACs with a pHZPC near the natural water pH will have less ionization and potentially have a greater affinity for hydrophobic compounds (e.g., MIB or Geosmin) [36]. Thus PAC materials, in addition to EDC structure (e.g., $\log K_{ow}$) affected PAC removal efficiencies for three estrogenic compounds. The adsorption coefficient values ($1 < K < 10\,(\mathrm{g/g})(\mathrm{L/g})^{1/n}$ PAC) are lower relative to many polycyclic aromatic hydrocarbons and nitroamines [37–38]. Typically K values greater than 200 represent favorable adsorption properties.

A recent United State Geology Survey (USGS) report claims that there is an alarming level of uncertainty in reported $\log K_{ow}$ values [39]. For example, in the USGS study, there was a significant different range of more than two orders of magnitude between $\log K_{ow}$ values of DDT and DDE ($\log K_{ow}$ DDT, 4.9–6.9; $\log K_{ow}$ DDE, 4.3–7.0). The results suggest that K_{ow} measurements sound simple but turn out to be tricky: mix water, octanol, and the chemical of concern, wait a while, and then measure the contaminant, usually in both phases [40]. However, in our study, the authors consider that the order of removal of E2 and EE2 from water by powered activated carbons found by the authors did correspond with the $\log K_{ow}$ values obtained from previous studies [41, 42].

Many full-scale WTPs that use PAC have contact times of 1–5 h and apply PAC dosages of 5–50 mg/L. Previous work has shown that laboratory batch contact times represent full-scale basin contact times quite well [35]. Therefore, it would appear that PAC addition would be feasible for WTPs at risk of having estrogenic compounds in their raw waters. Elevated risk of estrogenic compounds in raw drinking water supplies could occur due to a combination of the following watershed factors: (1) upstream wastewater discharges, (2) low stream flow that reduce dilution of upstream pollutants, and/or (3) increased runoff from animal feedlots. Therefore, the use of PAC for these three representative estrogenic compounds control may only require seasonal PAC addition, based upon periods of elevated risk. In addition, more investigation is required for the broader classes of EDCs. PAC is already widely used as a seasonal treatment for pesticides or taste and odors (T&O). In at least one study involving SRPW for removal of two T&O compounds (MIB and Geosmin), a PAC brand screening indicated that AC800 and Norit 20B were among the best performing brands while HDB brands were among the lowest, analogous to the findings for the three EDCs [35]. This may suggest that PAC currently being used for T&O control would also be effective for removing estrogenic compounds, if the compounds were present.

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