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Adsorption and biotransformation of 17β-estradiol in biological activated carbon adsorbers

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Abstract As the first systematic study dealing with the adsorption of estrogens by granular activated carbon (GAC), the removal behavior of 17β-estradiol (E2) and its biotransformation product of estrone (E1) in fixed GAC columns was examined using four biological activated carbon (BAC) columns (BAC-1∼BAC-4) generated by coating four GAC columns with detached microorganisms from the riverbed sediment of a representative drinking river water source containing lower content of natural organic matter (NOM). For comparison, parallel adsorption experiments were also performed using another four GAC columns (GAC-1∼GAC-4) packed by strictly following the configurations of four BAC columns. Adsorption experimental results obtained by intermittently spiking E2 over a total running period about 350 days into the river water mixed with or without a peaty water containing higher content of NOM showed that E2 was readily removed by adsorption and the combined adsorption/biodegradation. The vertical profiles of E2 and E1, which have great significance for better understanding and optimization of the adsorption process for removal of human estrogens, were also obtained.

Keywords Estrogens · Hormones · NOM · Adsorption · Biodegradation

1 Introduction

Natural and synthetic estrogens (including 17β estradiol, estrone, estriol, nonylphenol and 17α ethinylestradiol) are greatly concerned due to their likely estrogenic impacts on humans and wild lives (Routledge et al. 1998). Among such compounds, 17β estradiol (E2) and estrone (E1) are found responsible for a major proportion of endocrine disrupting effects identified in aquatic environmental systems (Routledge et al. 1998; Chistianshen et al. 2002).

The presence of natural steroid estrogens has been confirmed in aquatic environment systems (Belfroid et al. 1999). In Japan, the Ministry of the Environment conducted monitoring studies at chosen 124 river sites and from 54 sites, E2 was detected. Monitoring studies were also performed for 6 lakes, 17 coastal water bodies and 24 groundwater sources, and the existence of E2 was confirmed from 2, 10 and 3 sites, respectively. Even if certain percentages of the discharged E2 into natural water resources may get dissipated due to various physicochemical and biological reactions occurring therein (Chistianshen et al. 2002; Holthaus et al. 2002; Lai et al. 2000), the remaining percentages will enter drinking water treatment plants in its original form or the biological derivative form as E1. Like pesticides, odors and smells found in trace levels from most natural water resources, E2 and E1 are small molecules and can hardly be removed through conventional water purification systems comprising mainly of coagulation, sedimentation and sand

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filtration. To eliminate their presence in produced drinking water, the combined application of activated carbon adsorption, ozonation or some other advanced treatment processes is necessary.

With respect to activated carbon adsorption of estrogens, a limited number of studies on the adsorption capacity of E2, E1 or both have been conducted (Zhang and Zhou 2005; Cheong et al. 2005; Fukuhara et al. 2006). For instance, in a batch equilibrium study, Cheong et al. (2005) investigated the adsorption isotherms of E2 and E1 onto a coal-based activated carbon pulverized to particle size below 47 μm. It was found that the adsorption capacity of both E2 and E1 was relatively large and could be described by the single-solute Freundlich isotherm expression. In another batch study conducted using several activated carbon types with different pore size distribution, Fukuhara et al. (2006) investigated the adsorption capacity of E2 and E1. The observed differences in the adsorption capacity of these two adsorbates were further discussed based on their hydrophobicity, the specific surface area and the mean pore diameter of the adsorbents, and the presence of coexisting dissolved organic matrices. These studies have provided basic information on the removal of E2 and E1 by activated carbon adsorption and have considerable reference value when the adsorption capacity of these natural estrogenic compounds are compared with that of other micropollutants present also in drinking water resources. However, since the breakthrough of organic compounds through fixed granular activated carbon adsorbers is a complex adsorption behavior, which is controlled not only by the adsorption equilibrium but also by the adsorption kinetics and the operational conditions of the adsorbers, as well as the biological activities occurring within the adsorbers through attached microorganisms, fixed bed adsorption studies that could generate valuable breakthrough information are highly expected.

As the first systematic study dealing with the adsorption of estrogens in granular activated carbon (GAC) adsorbers, the removal of E2 by adsorption and biodegradation in fixed GAC columns was examined, and the vertical profiles of E2 and its biotransformation product E1 along the bed depth were presented. To achieve these, column studies using four biological activated carbon (BAC) columns (BAC-1∼BAC-4) generated by coating four packed GAC columns with microorganisms detached from the riverbed sediment of a representative drinking river water source that contains lower content of natural organic matter (NOM) were performed. The GAC columns were prepared by strictly following the configurations of another four GAC columns (GAC-1∼GAC-4) designed for comparisons with the performance of all four BAC columns. The particle size ranges of the packed GAC were 0.5–0.59 and 1.0–1.19 mm, which were obtained by pulverizing and sieving the well-used F400 (Filtrasorb/USA), and the packed bed depths were $L = 10$ and 20 cm, respectively. River water after removing suspended solids through filtration with a 0.45 μm membrane filter was consistently introduced into the columns as the base influent containing lower NOM content and E2 was intermittently added into the base influent with/without the addition of a peaty groundwater that contained higher content of NOM.

2 Materials and methods

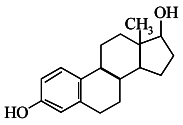
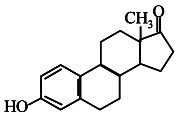
2.1 Stock solution of 17β-estradiol (E2)

The stock solution of E2 (about 0.9 mg/L) was prepared by dissolving a weighted amount of E2 (Wako Pure Chemical Co., Osaka, Japan) in Milli-Q water. Organic solvent was not used in order to eliminate its likely impact on the adsorption of E2 and NOM. To obtain the stock solution, 10 mg of E2 powders was added to a glass water container filled with about 5 L of Milli-Q water to make an initial E2 suspension at about 2 mg L^{-1}. After stirring for more than 24 hours, the suspension was filtered using a pre-washed 0.2 μm PTFE membrane filter to remove the E2 fraction not dissolved, and the filtrate was then stored refrigerated at dark at 5 °C as the stock solution. Major physicochemical features of E2 and its biodegradation byproduct E1 are displayed in Table 1.

2.2 Influent water containing natural organic matter (NOM)

Nagara River water (NRW) containing relatively lower content of natural organic matter (NOM) was used as the influent water to be consistently supplied into the fixed bed adsorbers for the present study. This water source was chosen because it is representative of most natural river water sources that are less polluted by human and social activities, and thus contain lower content of organic species. The average total dissolved organic carbon (DOC) in the NRW over the past two years is 0.53 mg L^{-1}, a value considerably lower than most urban river waters that generally receive wastewater discharges from sewage treatment plants. Nagara River is located within the territory of the central Japan Gifu Prefecture, and is one of the well-known and relatively well-conserved river water systems in the whole country. The mainstream length of the river is 166 km and the basin area developed along this river extends for 1985 km^2 and is covered mainly by vegetation (approximately 80% of the whole area is covered by a variety of forest types). The river water was sampled once for every two weeks and was stored refrigerated at 5 °C in the dark after being filtered through 0.45 μm membrane filters (Toyo Roshi, Japan) to remove suspended solids including microorganisms. The stored river water was added into the influent water tank

Table 1 Physicochemical features of 17β-estradiol and estrone (Johnson et al. 2000; Lai et al. 2000)

Compound	Formula	Molecular weight ($g\,mol^{-1}$)	Structure	$\log K_{OW}$
17β-estradiol (E2)	$C_{18}H_{24}O_2$	272.4		3.1
Estrone (E1)	$C_{18}H_{22}O_2$	270.4		3.4

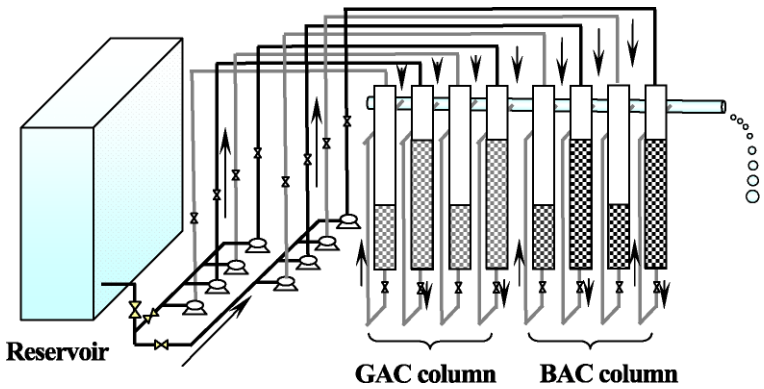


Fig. 1 The schematic setup of the fixed bed adsorption experiments

(with a storage volume of about 50 L) every day after reaching the controlled room temperature of 20 °C, under which the adsorption experiments were conducted.

In addition to the river water source, a peaty field groundwater (GW) containing relatively higher content of NOM was also used (the total DOC of 8.2 $mg\,L^{-1}$). This water was collected from a shallow well at the Kitamura village of Hokkaido and is frequently used by researchers for characterizing the behavior of naturally occurring humic substances during different water treatment processes. After reaching the laboratory where this study was conducted, the water was filtered through 0.45 μm membrane filters to remove suspended solids and then stored refrigerated at 5 °C in the dark for use. This water was used only at times when the effect of the enhanced NOM presence upon the removal of the intermittently spiked E2 was examined, for which the stored GW was added to the base influent of NRW for only a designated short period (about 5 hours) each time.

2.3 Granular activated carbon

Filtrasorb 400 (Calgon Co., USA), a well-used granular activated carbon (GAC) that has major physical characteristics as documented elsewhere (Kilduff et al. 1996), was chosen as the adsorbent. The representative carbon particles of this adsorbent were pulverized and sieved, and particles in the size ranges of 0.5–0.59 mm and 1.0–1.19 mm were collected. After washing with distilled water to remove fines, the collected carbon samples were dried at 105 °C overnight before being packed into respective columns.

2.4 Fixed bed adsorption experiments

The schematic setup of the laboratory scale fixed bed adsorption system is displayed in Fig. 1. Four biological activated carbon (BAC) columns (BAC-1∼BAC-4) were generated by coating four GAC columns with microorganisms detached from the riverbed sediment of the Nagara River. The sampling site for the riverbed sediment was the same as the site used for sampling of the river water. These GAC columns were packed by strictly following the packing conditions of another four GAC columns (GAC-1∼GAC-4) designed for comparisons with above-mentioned two categories of GAC in the size ranges of $d = 0.5$–0.59 and 1.0–1.19 mm. The packed bed depths of these columns were $L = 10$ and 20 cm, respectively.

The coating of the microorganisms for four BAC columns was achieved by circulating 500 mL of the detached riverbed

Table 2 Fixed bed conditions for all GAC and BAC columns used in this study

Column	GAC size (mm)	GAC weight (g)	Bed depth (cm)	Apparent porosity (%)	Empty bed contact time (min)
GAC-1	0.5−0.59	25	10	32.1	19.5
GAC-2	0.5−0.59	50	20	32.1	39.0
GAC-3	1.0−1.19	32	10	13.0	19.5
GAC-4	1.0−1.19	64	20	13.0	39.0
BAC-1	0.5−0.59	25	10	32.1	19.5
BAC-2	0.5−0.59	50	20	32.1	39.0
BAC-3	1.0−1.19	32	10	13.0	19.5
BAC-4	1.0−1.19	64	20	13.0	39.0

suspension (the suspended solid (SS) concentration was 5100 mg L^{-1}) to each column at a flow rate of 9.0 mL min^{-1} for about 48 hours. Measurement of the differences between the concentration of the suspended solids before and after circulation indicated that the quantities of SS coated onto the activated carbon particles were 58.8, 29.1, 59.7 and 27.1 mg-dry SS g^{-1}-GAC for BAC-1, BAC-2, BAC-3 and BAC-4, respectively. A preliminary batch degradation study conducted by spiking E2 and glucose (a well used easily-biodegradable substrate) to respectively reactors containing the same detached riverbed sediment suspension showed that the spiked E2 (30 μg L^{-1}) and glucose (10 mg L^{-1}) disappeared gradually from the reactors, with the half-life of E2 and glucose being determined as 1.6 and 3.8 hours, respectively. This thus proved that the detached riverbed sediment contained microorganisms that could readily degrade the spiked carbon sources. The fixed bed conditions for all GAC and BAC columns are briefly described in Table 2.

Adsorption experiments were commenced by supplying the Nagara River water in the influent reservoir to all columns in a down-flow mode with pumps at a constant flow rate of 2.5 ml min^{-1}. During experiments, E2 was intermittently spiked into the influent for several times in order to investigate the behavior of E2 in both GAC and BAC columns where adsorbable NOM molecules contained in the river water were continuously adsorbed. The spiking time length for each spiking experiment was about five hours. In addition, to examine the column response to higher influent NOM concentrations, following each short experiment of spiking E2 to the river water, a subsequent experimental run by adding E2 together with the higher NOM-containing GW to the base influent river water was also implemented for about five hours. The total NOM concentration in the mixed influent of GW and NRW was several times higher than that in the NRW alone.

From all columns, water samples were collected at designated sampling times and then subjected to quantitative analysis for NOM and targeted estrogens after filtering through 0.45 μm membrane filters (Toyo Roshi, Japan). NOM was quantified using the indices of total dissolved organic carbon (DOC) and UV-absorbance at 260 nm (UV260), for which a total organic carbon (TOC) analyzer (model TOC-Vws, Shimazu Co., Japan) and a UV-visible spectrophotometer (model U-3210, Hitachi Co., Japan) were used, respectively. The targeted estrogens (E2 and its biodegradation byproduct E1) were quantified using an Agilent 1100 series LC/MSD system. To obtain higher quantification precision, the internal standard analytical method with 17β-estradiol-C4 and estrone-C4 as the respective internal standards for E2 and E1 was employed and the detection limit for both E2 and E1 was determined as 0.01 μg L^{-1}.

3 Results and discussion

3.1 Adsorption behavior of NOM contained in the Nagara River water

The observed concentration profiles of the NOM in the NRW assessed with the quality indices of UV260 and DOC are displayed in Fig. 2, by using the results obtained for the BAC column with the packed bed depth of 10 cm (BAC-3) as examples. The bed volume was defined as the treated water volume divided by the packed bed volume. As displayed, even if influent and effluent NOM concentrations fluctuated over the total running period of about 350 days, the removal for NOM was apparent for both indices of UV260 and DOC. However, compared to the removals of DOC, the removals of UV260 were markedly higher, thus indicating that for all organic constituents contained in the river water source, the constituents assessed by UV260 were more favorably removed, while some constituents not detected by UV260 but detected by DOC were less favorably removed.

The time profiles of UV260 and DOC also showed the emergence of a general trend of increases in the effluent NOM content with the increases in the running time. This trend was especially obvious for the index of UV260 after running for nearly 125 days, which corresponded to the bed

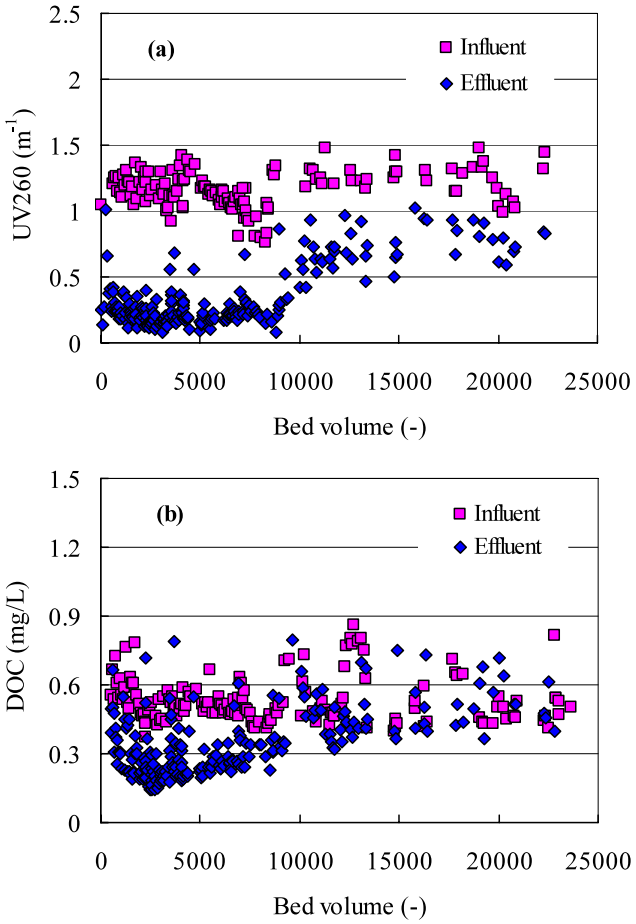


Fig. 2 The concentration profiles of NOM in the NRW supplied consistently into the column of BAC-3 by the indices of (**a**) UV260 and (**b**) DOC

volume of about 8500, indicating that breakthrough of organic constituents was occurring after running for this time length. Even from the early beginning of the adsorption runs, NOM was detected in the effluent from the outlet of all columns as could be seen from Fig. 2. The effluent ratios (about 20% with the index of UV260) did not change with the used columns even if the bed depth and the particle size of the granular activated carbon packed in these columns were different. It is thus reasonable to infer that the effluent NOM constituents from the early beginning of the experiments were consisted of those not adsorbable by activated carbon. The existence of non-adsorbable constituents in this river water source was also confirmed in a batch equilibrium study of the adsorption isotherms of the river water NOM collected before, during and after a heavy storm of rain (Li et al. 2005).

3.2 Removal of E2 spiked intermittently into all columns

During the running period, E2 was spiked into the Nagara River water for several times after the columns had been running for different time lengths. In addition, to evaluate the impact of the coexistent NOM level on the removal efficiency of E2, another series of spiking experiments were also conducted by adding E2 to the influent Nagara River water together with the groundwater that contained a higher content of NOM as mentioned earlier. The enhanced presence of NOM in the influent water is generally detected at times when such natural phenomena as rainfall, typhoon and snow thawing occur. Investigation of the column response to higher influent NOM concentrations with respect to both the removals for NOM and E2 is thus important. For each addition that lasted for about 5 hours, since changes in the effluent concentrations of NOM and E2 from each GAC or BAC column were less apparent, averaged values were computed. The results are summarized in Table 3 and Table 4.

As shown in Table 3, although the influent concentrations of E2 spiked into the base influent of the NGW varied in the range of 17–30 $\mu g\,L^{-1}$, in the effluent from the outlet of all GAC and BAC columns E2 was not detected. For the river water NOM, however, compared to the influent DOC values in the range of 0.436–0.624 $mg\,L^{-1}$, the effluent DOC values varied in 0.18–0.896 $mg\,L^{-1}$. It was thus clear that the removal for E2 took place in a manner more favorable than that for NOM. When the influent concentration of NOM was increased with the addition of the GW to the levels of 1.7–3.5 $mg\,L^{-1}$ as DOC, its removals turned higher (50.3–94.7%), as could be computed from the results shown in Table 4. However, the removals were still lower than those of the spiked E2 (100%) as E2 was not found at all from the column effluent. For further comparison, the changes in the composition of NOM before and after treatment were investigated in terms of the apparent molecular weight distribution measured using a size-exclusion high performance liquid chromatography (SEHPLC) system calibrated with three polystyrene sulfonates (PSS) of known molecular weights. The measurement conditions are documented elsewhere (Li et al. 2003). The results obtained with the columns of GAC-3 and BAC-3 are displayed in Fig. 3 as examples. Compared to the molecular weight distribution in the influent (with molecular weights falling in the range of 1000–5200 $g\,mol^{-1}$ as PSS), the molecular weight distribution in the effluent shifted downwards in a parallel manner, suggesting that the NOM constituents were removed uniformly, where preferential removal for either larger molecules or smaller molecules did not occur. In addition, based on the number of peaks appeared, the NOM was divided into four fractions (F1, F2, F3 and F4) having the weight-averaged molecular weights of 4350, 3500, 2700 and 1600 $g\,mol^{-1}$ as PSS, respectively; apparent removal differences among all four fractions were not revealed either (plots not shown). These results, together with the distinct removal differences for E2 and NOM shown clearly in

Table 3 Influent and effluent E2 and NOM concentrations at times when E2 was spiked into the NRW after different running time lengths

No.	Running time length (h)	Influent DOC ($mg\,L^{-1}$)	Effluent DOC ($mg\,L^{-1}$)								Influent E2 ($\mu g\,L^{-1}$)	Effluent E2 ($\mu g\,L^{-1}$)
			GAC-1	GAC-2	GAC-3	GAC-4	BAC-1	BAC-2	BAC-3	BAC-4		
1	740	0.436	0.216	0.436	0.21	0.402	0.216	0.229	0.269	0.224	30	ND
2	1358	0.505	0.379	0.534	0.397	0.292	0.238	0.382	0.31	0.54	30	ND
3	2348	0.464	0.296	0.26	0.36	0.278	0.259	0.228	0.257	0.172	17	ND
4	4884	0.624	0.488	0.312	0.496	0.326	0.264	0.359	0.411	0.18	30	ND
5	5338	0.453	0.433	0.304	0.462	0.285	0.94	0.491	0.896	0.296	30	ND
6	5816	0.596	0.385	0.443	0.637	0.306	0.527	0.355	0.43	0.369	28	ND
7	7472	0.541	0.613	0.467	0.532	0.305	0.528	0.381	0.697	0.467	20	ND

Table 4 Influent and effluent E2 and NOM concentrations at times when E2 was spiked into the NRW with PW together after different running time lengths

No.	Running time length (h)	Influent DOC ($mg\,L^{-1}$)	Effluent DOC ($mg\,L^{-1}$)								Spiked E2 ($\mu g\,L^{-1}$)	Effluent E2 ($\mu g\,L^{-1}$)
			GAC-1	GAC-2	GAC-3	GAC-4	BAC-1	BAC-2	BAC-3	BAC-4		
1	851	3.015	0.391	0.363	0.258	0.684	0.268	0.209	0.209	0.16	30	ND
2	1151	2.956	0.389	0.247	0.395	0.323	0.247	0.289	0.289	0.26	30	ND
3	1363	3.128	0.481	0.263	0.434	0.294	0.356	0.331	0.331	0.257	30	ND
4	2352	3.495	1.503	0.427	0.642	0.379	0.413	0.605	0.605	0.31	14	ND
5	2922										160	ND
6	4889	1.696	0.387	0.314	0.622	0.358	0.256	0.669	0.669	0.213	20	ND
7	5343	2.91	0.529	0.413	0.913	0.386	0.49	1.047	1.047	1.445	35	ND
8	5821	2.802	0.444	0.624	1.011	0.408	0.462	0.729	0.729	0.424	30	ND
9	7477	3.385	0.599	0.394	0.858	0.306	0.426	0.394	0.921	0.404	23	ND

Table 3 and Table 4, could help draw an important inference that E2 was removed more favorably than the constituting components of the studied NOM with different molecular weights by fixed GAC and BAC adsorbers.

In simultaneous multicomponent adsorption systems, competitive adsorption occurs due to competition for adsorption sites among coexisting components, resulting in reduced adsorption capacity for components having weak adsorbabilities. When trace organic micropollutants are adsorbed in the presence of macromolecules like humic molecules, in addition to competition for adsorption sites, humic molecules may block the pathways for small micropollutants to reach micro pores where their adsorption takes place more efficiently (Ebie et al. 2001; Newcombe et al. 2002). In a previous study, the authors investigated the adsorption equilibrium of the NOM contained in the same river water and the groundwater sources of the present study (Li et al. 2005). The mean Freundlich constant K and $1/n$ (for DOC) determined by analyzing the observed isotherm data with a well-established fictive multicomponent approach were 48.2 $(mg\,g^{-1})/(mg\,L^{-1})^{1/n}$ and 0.154 for the river water NOM, and 37.0 $(mg\,g^{-1})/(mg\,L^{-1})^{1/n}$ and 0.354 for the groundwater NOM, respectively. By converting the DOC-based Freundlich K values using a conversion factor of 50%, the constituting mass ratio of organic carbon in humic molecules (Malcom and MacCarthy 1986; Goh and Stevenson 1971; Grigoropoulos and Smith 1971), and the mean molecular weights of 3390 and 3640 g mol^{-1} of these two NOM types, the molar concentration-based K values were estimated as 30.8 and 25.1 $(\mu mol\,g^{-1})/(\mu mol\,L^{-1})^{1/n}$, respectively. Comparison of these K values with the K value of E2 determined through a single-solute batch adsorption experiment with the same carbon type of the present study, $K = 950$ $(\mu mol\,g^{-1})/(\mu mol\,L^{-1})^{1/n}$ $(1/n = 0.227)$ (Cheong et al. 2005), indicated that the adsorptive strength of E2 was much stronger than the studied NOM matrices. This was probably the major reason that led to favorable removal for the estrogenic compound as discussed earlier.

In Table 3 and Table 4, larger DOC removals for the groundwater NOM than the river water NOM were revealed for all columns. This thus suggested that the groundwater contained larger percentages of NOM constituents that could be removed through adsorption. The results support the documented ones (Li et al. 2005) obtained previously through model analysis of the observed isotherm data for the groundwater and the river water NOM that the non-

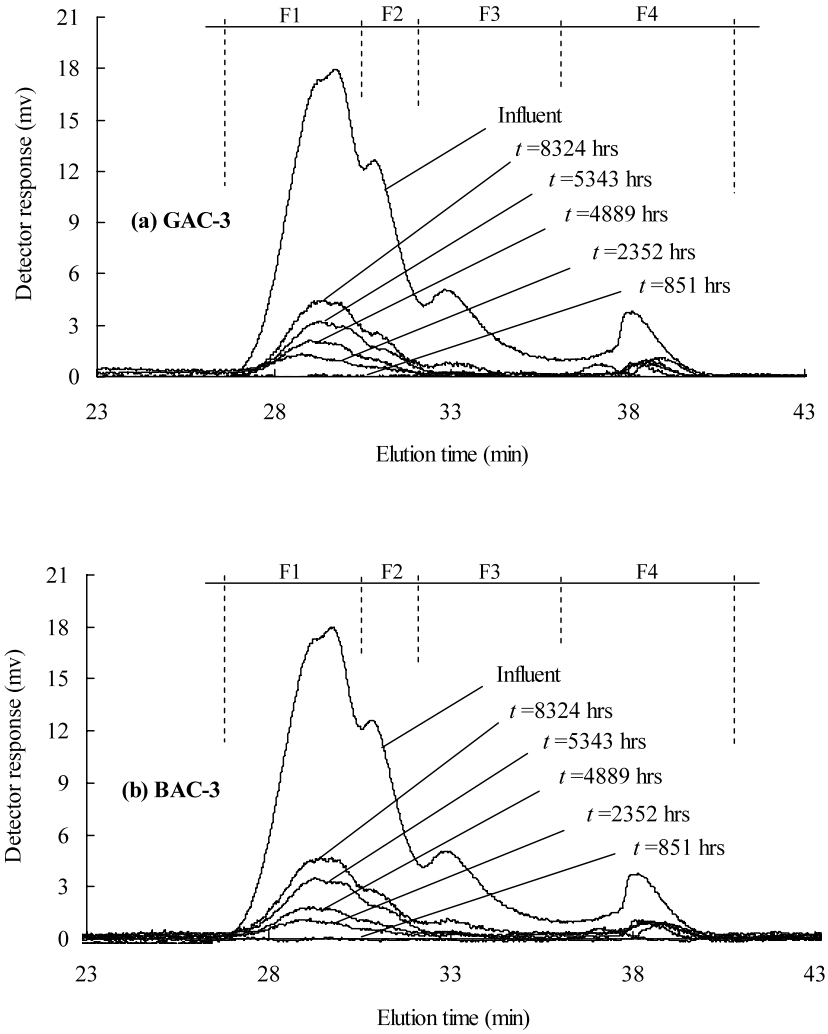


Fig. 3 Apparent molecular weight distribution of NOM in the effluent from the column outlet at times when E2 was spiked into the Nagara River water with the peaty groundwater for about 5 hours each time after consistent running of (**a**) GAC-3 and (**b**) BAC-3 for different time lengths. The apparent molecular weights are: total NOM = 3640, F1 = 4350, F2 = 3500, F3 = 2700 and F4 = 1600 g/mol as PSS

adsorbable DOC fraction in the groundwater (about 4%) was smaller than that in the river water NOM (about 15%).

3.3 Vertical concentration profiles of E2 along the packed bed of columns

The observed vertical profiles of E2 spiked to the Nagara River water supplied consistently to the columns of GAC-3 and BAC-3 for consecutively 2348 hours are displayed in Fig. 4. As water flowed towards the column outlet, the concentration of E2 decreased. The decreasing extent was markedly larger within the top 1 cm thickness of the packed bed, thus implying that the uptake rate for the targeted estrogen was relatively fast, a topic that will be further investigated in coming studies. For BAC-3, as the spiked E2 decreased, its biotransformation byproduct E1 emerged. This indicated that microorganisms that could degrade E2 were populated within the BAC columns. The result also supported the preliminary batch degradation study mentioned earlier for confirmation of the existence of microbes within the detached suspended solid suspension from the riverbed sediment of the Nagara River. In another batch study conducted using sediment mud from a natural water reservoir, the degradation of E2 under both aerobic and anaerobic conditions was also observed (Li et al. 2006). These results, together with limited literature information (Johnson et al. 2000; Lai et al. 2000; Ying and Kookana 2003), suggest that E2 degrading microorganisms probably exist in all natural water resources. It is thus reasonable to infer that when GAC adsorbers are applied for advanced treatment of such drinking water sources, the biodegradation of E2 is very likely to occur since E2 degrading microorganisms may attached onto GAC together with other suspended microbes to form microbial films.

The impact of the influent NOM concentration on the vertical distribution of E2 is displayed in Fig. 5. For GAC-3, where adsorption was the sole removal mechanism for organic adsorbates, the decreasing slope of E2 along the bed depth for the influent DOC of 3.5 $mg\,L^{-1}$ was not as sharp as that for the influent having a lower DOC value

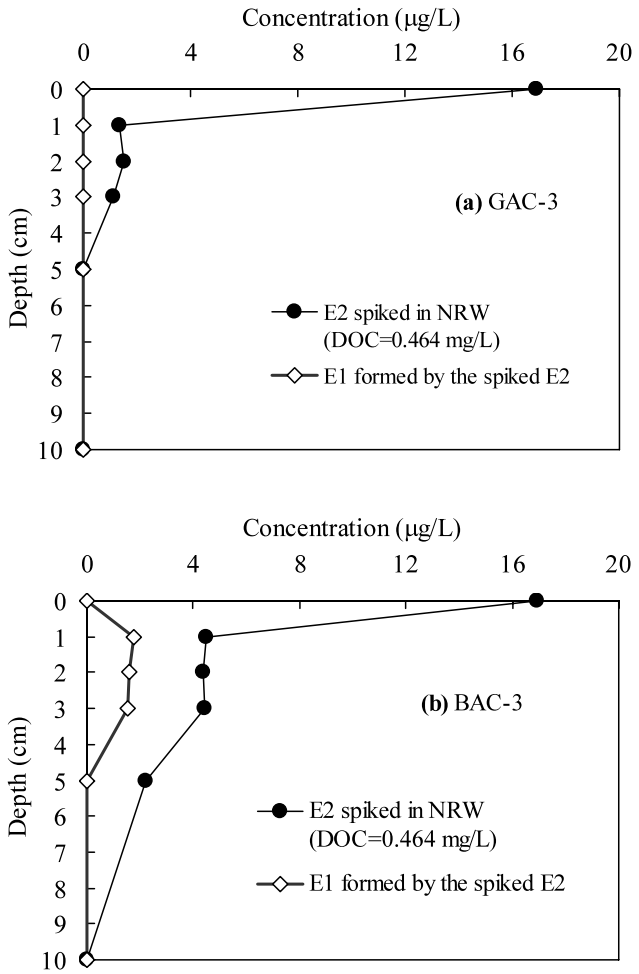


Fig. 4 Vertical profiles of E2 and its biodegradation byproduct E1 in fixed carbon bed columns when E2 was spiked into the Nagara River water for about 5 hours after consistent running of (**a**) GAC-3 and (**b**) BAC-3 for 2348 hours

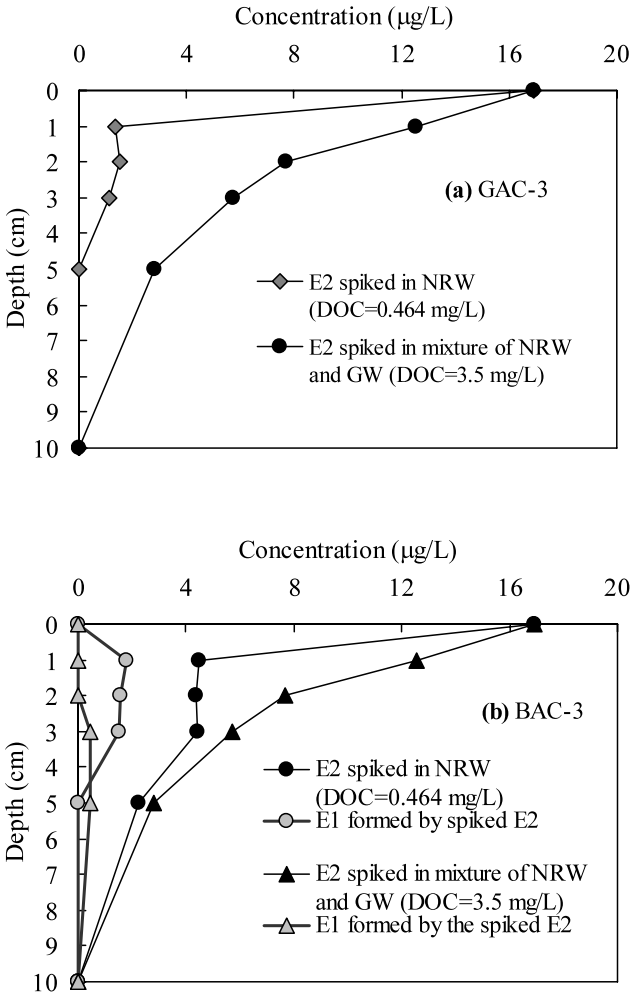


Fig. 5 The impacts of influent NOM concentration on the vertical distribution of E2 and its biodegradation byproduct E1 in fixed carbon bed columns when E2 was spiked into the Nagara River water together with and without the peaty groundwater for about 5 hours after consistent running of (**a**) GAC-3 and (**b**) BAC-3 for about 2350 hours

of 0.464 mg L^{-1}. This thus indicated that a higher influent NOM concentration would adversely affect the adsorption removal for E2 to an extent more apparent than a lower influent NOM concentration. Even if descriptive, the result could serve as an important evidence, from the aspect of column studies, in support of the ideal adsorbed solution theory that includes the concentration composition of coexistent adsorbates as a factor, in addition to another factor relating to the single-solute adsorption equilibrium, regulating their competitive adsorption isotherms. For BAC-3, where both adsorption and biodegradation were expected, the adversary impact caused by the increased NOM seemed to be alleviated a little bit due probably to the fact that biodegradation of E2 was less affected by the enhanced NOM presence, taking into account that most NOM constituents comprising mainly of humic molecules are generally considered biologically persistent. In this column, as the biotransformation byproduct of E2, the detected E1 also dissipated as water flowed downwards.

The vertical profiles of E2 in BAC-3 and BAC-4 with different packing depths ($L = 10$ and 20 cm) are displayed in Fig. 6. BAC-4 performed better than BAC-3 as the concentration of E2 in the longer column dropped more distinctly along the bed depth and its biotransformation byproduct E1 also disappeared faster. Although biodegradation of E2 occurred in all BAC columns as reflected by the confirmed existence of the biotransformation byproduct E1, its contribution was less significant than expected, judging from the observed removal differences of E2 in both GAC and BAC columns. For some runs, the removal of E2 in BAC columns was very close to that in GAC columns, exhibiting little merit with the biological columns. There were even a few cases where the removal by BAC turned to be slightly lower than GAC, as could be seen from the removal profiles of E2 displayed in Fig. 7 based on the results of GAC-3 and BAC-3. It was clear that even if the removal values of

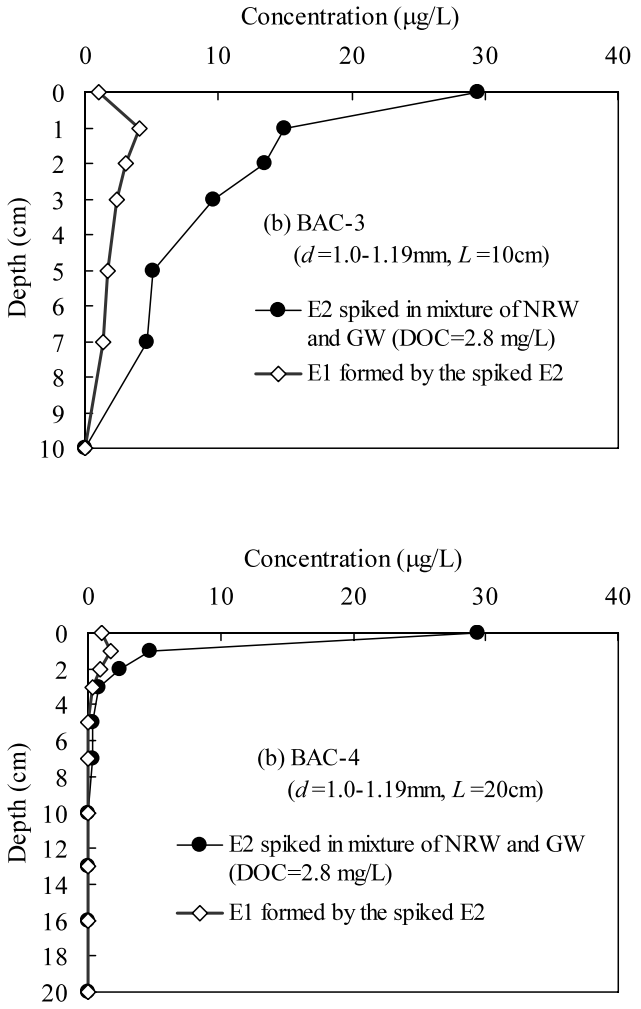


Fig. 6 Comparison of the vertical distribution of E2 and its biodegradation byproduct E1 in BAC columns with different bed depths: (**a**) $L = 10$ cm and (**b**) $L = 20$ cm, when E2 was spiked into the Nagara River water along with the peaty groundwater for about 5 hours after consistent running of the columns for 5821 hours

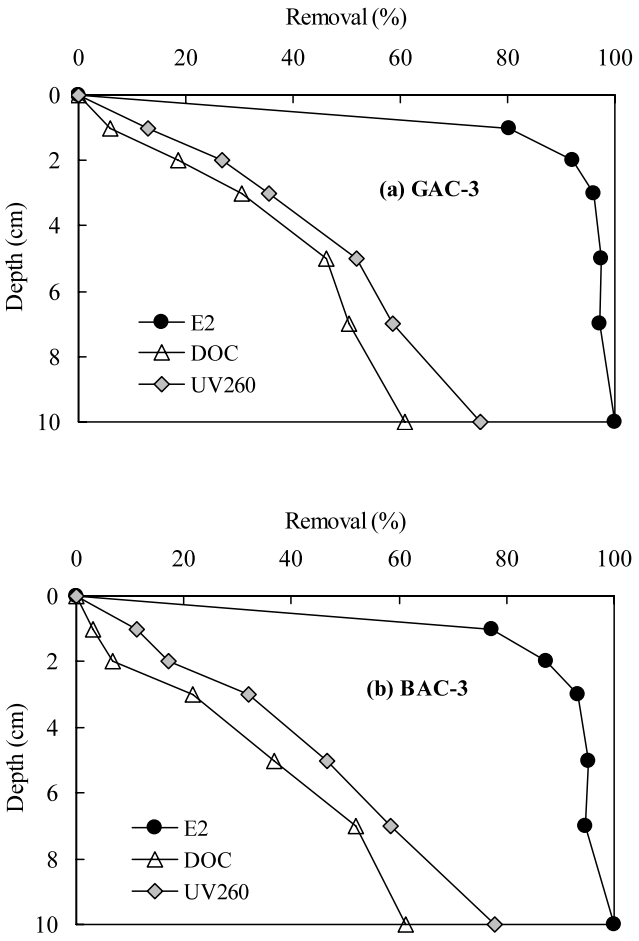


Fig. 7 Comparison of the vertical distribution of removals for E2 and NOM in fixed bed carbon columns when E2 was spiked into the Nagara River water together with the peaty groundwater for about 5 hours after consistent running of (**a**) GAC-3 and (**b**) BAC-3 for 10,000 hours. The spiked E2 concentration was 30 μg/L, and the NOM concentration was 3.07 mg/L as DOC and 9.981 m^{-1} as UV260

E2 at all examined bed levels were markedly higher than those of NOM assessed using the index of either UV260 or DOC, the removal values of E2 in BAC-3 were, by several percentage points, lower than those in GAC-3. The reason behind the lower E2 removals with the biological column is still not known; however, the blockage of the pore openings by biological films comprising microbes and some of their viscous metabolic macromolecular products, which may inhibit E2 access into pores where its adsorption takes place, is likely. The role of biodegradation may become eminent and could be easily distinguished from adsorption once the adsorption capability of activated carbon is nearly exhausted. For this, further investigation by continuously running the experimental systems of the present study is going on.

4 Conclusions

The removal behavior of E2 and its biotransformation product E1 in fixed GAC adsorbers were examined using four BAC and four GAC columns operated in the down-flow mode by intermittently spiking E2 to a representative river water containing lower content of NOM. In addition, to examine the impact of influent NOM concentration, experiments by elevating the influent NOM concentration with a peaty groundwater containing higher content of NOM were also performed. The spiked E2 was readily removed via adsorption (for GAC columns) and a combination of adsorption and biodegradation (for BAC columns). For both GAC and BAC columns, the removals of E2 were apparently larger than NOM assessed by both UV260 and DOC, indicating that E2 was removed more favorably than the larger molecular constituents of NOM. Further investigation is undertaken in order to quantitatively evaluate the role of

biodegradation involved in the biological activated carbon process.

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