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(20) ADSORPTION BEHAVIOR OF ESTROGEN AND ANTIBIOTICS IN GRANULAR ACTIVATED CARBON COLUMNS

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The adsorption behavior of 17β-estradiol (E2), oxytetracycline (OTC) and tetracycline (TC) by granular activated carbon (GAC) was examined using four GAC columns packed with activated carbon having particle size of 0.5-0.59 and 1.0-1.19 mm to bed depths of 10 and 20 cm, respectively. The results obtained by intermittently spiking E2, OTC and TC, respectively, into river water mixed with or without peaty groundwater containing higher content of natural organic matter (NOM) over a total running period about 35000 hours showed that E2, OTC and TC were readily removed by adsorption. Significantly higher removals of E2, OTC, and TC than NOM (assessed by both UV260 and DOC) indicated that these three compounds were removed more favorably than larger molecular constituents of NOM. Observation of the vertical distributions of the residuals of E2, OTC and TC along the GAC bed depth revealed that the impact of the influent NOM concentration and the bed depth on the adsorption behavior of these three compounds was not obvious. However, NOM adsorbed before the targeted compounds flowed into the columns were found to cause reduction in the removal of all the compounds.

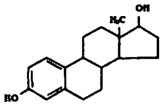
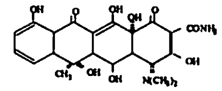
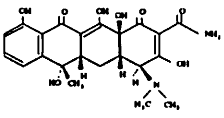
Key Words: *Estrogen, antibiotics, adsorption, NOM, activated carbon*

1. INTRODUCTION

As trace organic pollutants (TOPs), natural estrogens (including 17β-estradiol, estrone, and 17α-ethinylestradiol) and veterinary antibiotics are greatly concerned because of their potential adverse effects on ecosystems and human health.

The presence of steroid estrogens has been confirmed in aquatic environment systems [1)]. In Japan, the Ministry of the Environment conducted monitoring studies at chosen 124 river sites and from 54 sites, 17β-estradiol (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. It is also reported that, in Japan, more than 2200 tons of antibiotics are administered annually, with approximately 60% being used for veterinary purposes (including antibiotics used in animal feeds) and 30% for human purposes. For veterinary antibiotics, about a half of them are tetracycline related compounds such as oxytetracycline (OTC) and tetracycline (TC), which are primarily used in swine farming for prevention of infections [2)]. OTC and TC are released to the environment with animal waste through direct deposition, discharge from associated wastewater treatment facilities, and direct land application. OTC was detected up to the μg L^{-1} level in stream water in a small catchment area with many livestock farms [2)], and an agricultural watershed [3)]. In recent years, concerns have been raised regarding the public health impact of the occurrence of these antibiotics in the aquatic environment. There are indications of increased

Table 1 Physicochemical features of 17β-estradiol, oxytetracyclines and tetracyclines10)

Compound	Formula	Molecular weight ($g\ mol^{-1}$)	Structure	log Kow	pKa
17β-estradiol (E2)	$C_{18}H_{24}O_2$	272.4		3.94	na*
Oxytetracyclines (OTC)	$C_{22}H_{25}N_2O_9$	461.5		-1.19	3.27
Tetracyclines (TC)	$C_{22}H_{24}N_2O_8$	444.4		-1.22	3.30

*not available

bacterial resistance in wastewater from hospitals and pharmaceutical industry 4).

Even if certain percentages of discharged E2 into natural water resource may get dissipated due to various physicochemical and biological reactions occurring therein 5-7), the remaining percentages of E2 will enter drinking water treatment plants. Because of its small molecular size, E2 can hardly be removed by conventional water purification system comprising mainly of coagulation, sedimentation and sand filtration. Activated carbon adsorption, which is probably most effective for the removal of E2 from drinking water source, is necessary. A limited number of studies on the adsorption capacity of E2 have been conducted. For instance, in a batch equilibrium study, researcher investigated the adsorption isotherm of E2 onto a coal-based activated carbon pulverized to particle size below 47 μm 8). It was found that the adsorption capacity of E2 was relatively large and could be described by the single-solute Freundlich isotherm expression. Little work was done to investigate the adsorption of OTC and TC by activated carbon. It is also important that natural organic matter (NOM) existing in natural water sources can adversely affect the adsorption capacity of micro-pollutants 9). For fixed-bed GAC adsorption, the breakthrough of organic compounds is a complex adsorption behavior, which is controlled not only by the adsorption equilibrium but also by the adsorption kinetics. The operational conditions of adsorbers are also important controlling factors. A systematic fixed bed adsorption study that could generate valuable breakthrough information is highly expected.

As a systematic study dealing with the adsorption of estrogens and veterinary antibiotics, the removals of E2, OTC and TC in fixed GAC columns were examined. To achieve these, adsorption studies using four packed bed GAC columns were performed. In addition, to generate information on the adsorption zones and the uptake rates of these compounds within the carbon bed, samples from designated bed levels were also collected. 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 that contained lower NOM content, and E2, OTC and TC were intermittently added into the base influent with or without the addition of peaty groundwater that contained higher content of NOM.

2. MATERIALS AND METHODS

(1) Stock solution of E2, OTC and TC

The stock solutions of E2, OTC and TC were prepared by dissolving weighted amounts of E2, OTC, TC (Wako pure chemical Co., Osaka Japan) into Milli-Q water, respectively. Organic solvent was not used in order to eliminate its likely impact on the adsorption of E2, OTC, TC and NOM. For E2, after stirring for more than 24 hours, its suspension was filtered using a pre-washed 0.2 μm PTFE membrane filter to remove the fraction not dissolved, because its water solubility is low. The stock solutions of E2, OTC and TC were stored refrigerated at dark at 5 ° C. Major physicochemical features of these three compounds 10) are displayed in **Table 1.**

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

Column	GAC size (mm)	GAC weight (g)	Bed depth (cm)	Apparent porosity (%)	Empty bed contact time (min)	Flow rate (ml/min)	Vertical distance of sampling position from the bed surface (cm)
GAC-1	0.5-0.59	25	10	32.1	19.5	2.5	1, 2, 3, 5, 7, 10
GAC-3	1.0-1.19	32	10	13.0	19.5	2.5	
GAC-2	0.5-0.59	50	20	32.1	39.0	2.5	1, 2, 3, 5, 7, 10, 13, 16, 20
GAC-4	1.0-1.19	64	20	13.0	39.0	2.5	

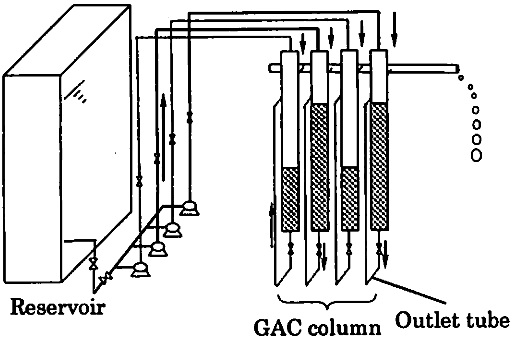


Fig. 1 The schematic setup of laboratory scale fixed bed adsorption system

(2) Influent water containing NOM

Nagara river water (NRW) containing relatively lower content of NOM was used as the influent water to be consistently supplied into the fixed bed adsorbers, because it represents most natural river water sources that are less polluted by human and social activities, and thus contain lower content of humic molecules. For the last two years, the average total dissolved organic carbon (DOC) in NRW is 0.53 mg L^{-1}, which is lower than most urban river water. The NRW was sampled every two weeks. For removing suspended solids including microorganisms, the water sampled was filtered with 0.45 μm membrane filters (Toyo Roshi, Japan), and the filtrate was stored refrigerated at 5°C in the dark to avoid biological activities. The stored water, flowing out from the water tank with a storage volume of about 50 L, was used as the influent water of the adsorption experiments conducted every day in a temperature controlled room at about 20°C.

In addition to the NRW, a peaty-field groundwater (GW) with relatively higher content of NOM was also used (the total dissolved organic carbon is 8.2 mg L^{-1}). This water was sampled from a shallow well at the Kitamura-Village of Hokkaido. After reaching the laboratory, it was filtered with 0.45 μm membrane filters (Toyo Roshi Japan) to remove suspended solids and stored refrigerated at 5°C in the dark. GW was added to the base influent water of NRW for 5 hours each time when intermittent spiking experiments for studying the effect of enhanced NOM presence on the removal of E2, OTC and TC were conducted.

(3) Granular activated carbon

Filtrasorb 400 (Calgon Co., USA), a well-used granular activated carbon (GAC), was chosen as the adsorbent. The carbon particles were pulverized and sieved into the size ranges of 0.5-0.59 mm and1.0-1.19 mm. After being washed with distilled water in order to remove fines, the pulverized and sieved carbon types were dried at 105°C overnight before being packed into respective columns.

(4) Fixed bed adsorption experiments

The schematic setup of the laboratory scale fixed bed adsorption system is displayed in **Fig. 1.** Four GAC columns (GAC-1~GAC-4) were designed for comparisons using 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 the columns were L=10 and 20 cm, respectively. The fixed bed conditions of all columns are briefly described in **Table 2.**

Adsorption experiments were commenced by supplying the NRW 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 or OTC and TC were intermittently spiked into the influent for several times (20 times for E2, 10 times for OTC and TC) with the concentrations about 30 μg L^{-1} in order to investigate the behaviors of them in all GAC columns where adsorbable NOM molecules contained in the river water were continuously adsorbed. The spiking time length for each spiking experiment was about 5 hours, since preliminary investigation test confirmed that the effluent concentration of each targeted compound reached the steady state after the time length equivalent to the empty bed contact time of each column and also because a shorter spiking time did not cause a larger load of the targeted compound on activated carbon that may obviously affect its adsorption behavior when spiked at other times. In addition, to examine

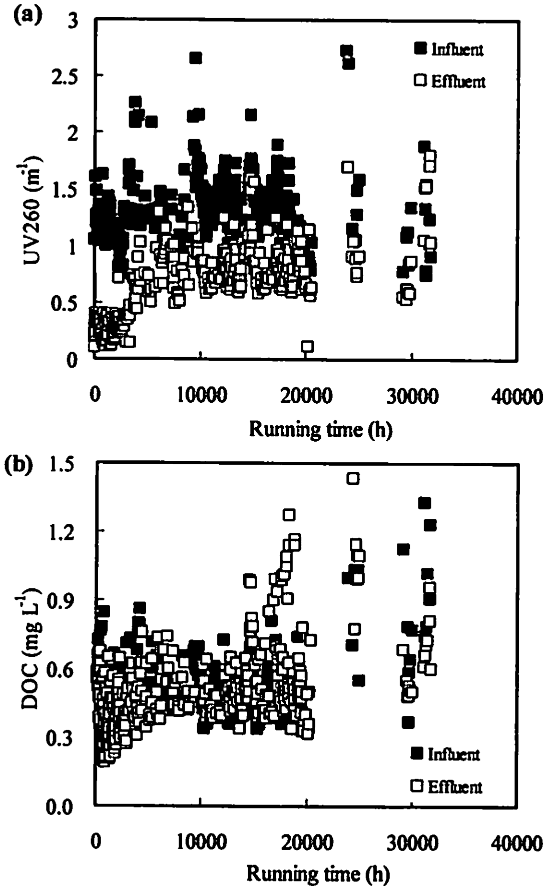


Fig. 2 The concentration profiles of NOM in the Nagara River water supplied consistently into GAC-3 by the indices of (a) UV260 and (b) DOC

the column response to higher influent NOM concentration, following each short experiment of spiking E2 or OTC and TC to the river water, subsequent experimental run by adding them together with the higher NOM-containing GW to the base influent river water was also conducted for 5 hours. The total NOM concentration in the influent mixed with GW (average DOC was 3.1 mg L^{-1}) was several times higher than that in the NRW alone (average DOC was 0.53 mg L^{-1}) .

For all columns, water samples were collected from the outlet at designated sampling times. In addition, samples from different bed depths were also collected using a special sampler that allowed insertion of a sampling needle (with a diameter of 0.3 mm and a length of 50 cm) to the designated levels [11]. After being filtered through 0.45μm membrane filters (Toyo Roshi, Japan) samples were subjected to quantitative analysis for NOM and targeted compounds. NOM was quantified using the indices of total dissolved organic carbon (DOC) and UV-absorbance at 260nm (UV260), for which a total organic carbon (TOC) analyzer (model TOC-V ws, Shimazu Co., Japan) and a UV-visible spectrophotometer (model U-3210, Hitachi Co., Japan) were used, respectively. The index of UV260 was used because, like UV-absorbance at 254 nm (UV254), it is capable of reflecting the presence of humic molecules in water environment systems, and the specific ultraviolet absorption (SUVA), a calculated parameter of UV260 or UV254 divided by DOC, has thus been used as an indicator of the humic content [11]. The targeted compounds (E2, OTC and TC) were quantified using an Agilent 1100 series liquid chromatography/mass spectrometry (LC/MSD) system (HP1100MSD; CA, USA). The identification and quantification were made in negative (E2) and positive (OTC and TC) mode by following the well-used internal standard methodology, respectively.

3. RESULTS AND DISCUSSIONS

(1) Adsorption behavior of NOM contained in the NRW

The concentration profiles of the NOM in the NRW assessed by the quality indices of the UV260 and DOC are displayed in **Fig. 2**. These results were obtained from the GAC-3 with the packed bed depth of L=10 cm. Even the influent and effluent NOM concentration fluctuated over the total running time for about 35000 hours, the removal for NOM was apparent, especially with the index of UV260. Compared to the removal for DOC, the removal for UV260 is observably higher, indicating that organic constituents assessed by UV260 were more favorably removed, and those not detected by UV260 but detected by DOC were not removed as favorably as those detected by UV260.

A general trend of increase in the effluent NOM with the increase of the running time are showed in the time profiles of UV260 and DOC. This trend was especially obvious for UV260 after running for about 5000 hours. This indicates that breakthrough of organic constituents was occurring after running for this time length. It is also obvious from **Fig. 2** that from the very beginning of the running time, NOM was detected in the effluent from the outlet of column GAC-3. Similar results were also observed for three columns (GAC-1, GAC-2, GAC-4) even if their bed depths and particle sizes of GAC packed were different. These results led to the inference that the effluent NOM constituents from the beginning of the experiment were consisted of those not adsorbable by activated carbon. The existence of non-adsorbable constituent 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 [12].

(2) Removal of E2, OTC and TC spiked intermittently into all columns

During the running period, E2, OTC and TC were spiked into the NRW for several times after the columns had been running for different time lengths. Another series of spiking experiment were also conducted by adding them into the influent NRW together with the GW that contained a higher content of NOM which was mentioned earlier. The higher content NOM in the influent water is generally detected at times when such natural phenomena as rainfall, typhoon and snow thawing occur.

Fig. 3 shows the reactions of the removal of NOM, E2, OTC and TC with the increases of accumulated amount of NOM adsorbed. Even if the effluent removal of NOM for both indices of UV260 and DOC decreased with continuous adsorption of NOM, none of E2, OTC and TC was detected from the effluent water. It was thus clear that the removal for E2, OTC and TC took place in a manner more favorable than that for NOM. When the influent concentration of NOM was increased for a short time length of 5 hours each time with the addition of the GW, the removals of UV260 and DOC turned higher than those when only NRW NOM was supplied. This suggested that NOM in GW contained higher percentage of constituents that can be adsorbed than that in the NRW. Similar results were also obtained for other columns (GAC-1, -2, -4) as summarized in **Table 3**.

In simultaneous multi-component adsorption systems, competitive adsorption occurs because of the competition for adsorption sites among coexisting components, leading to reducing

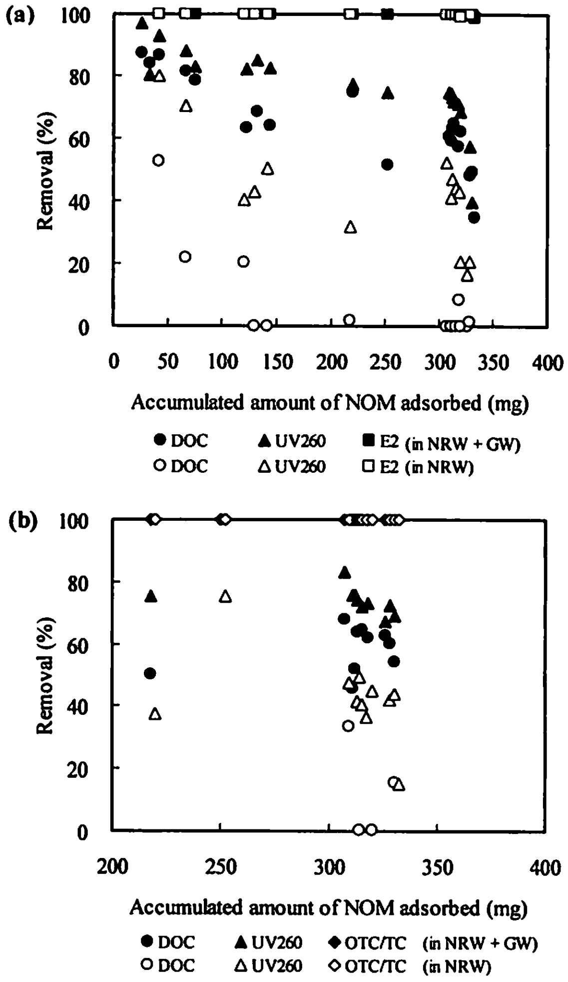


Fig. 3 The changes of the removals of NOM, E2, OTC and TC at the outlet of GAC-3 with the increases of accumulated amount of NOM adsorbed when (a) E2 and (b) OTC and TC were spiked into Nagara River water with and without the peaty groundwater

Table 3 Removal of NOM, E2, OTC and TC detected from the effluent water, when E2, OTC and TC were spiked into Nagara River water (a) without and (b) with the addition of peaty groundwater

Column	DOC (%)	UV260 (%)	E2 (%)	TC (%)	OTC (%)
			(a)		
GAC-1	1.0~52.7	36.1~81.9	100	100	100
GAC-2	10.3~53.9	6.5~84.5	100	100	100
GAC-3	0~52.7	6.4~81.9	100	100	100
GAC-4	0~53.9	2.2~81.6	100	100	100
			(b)		
GAC-1	58.7~87.5	66.6~97.2	100	100	100
GAC-2	73.5~91.9	64.6~98.2	100	100	100
GAC-3	34.8~87.5	39.6~97.2	100	100	100
GAC-4	71.2~91.9	72.2~98.2	100	100	100

adsorption capacity for component having weak adsorbabilities. In addition to competition for adsorption sites, humic molecules may block the pathways for small micro-pollutants to reach micro pores where their adsorptions take place more efficiently [13, 14]. Concerning the extent of effect caused by the competition for adsorption sites, two factors, namely, the single solute adsorptive strength represented by the Freundlich constant *K* and the initial concentration composition, reflected by the concentration ratio of each compound in the multi- solute adsorption system, are predominant. For a compound that has a higher *K* value and that has a higher initial concentration ratio, the adverse effect from other coexisting compounds on its adsorption capacity is smaller. This could be explained by the well-used competitive IAST (Ideal adsorbed solution theory)-Freundlich model, and was also verified by adsorption experimental results for simultaneously adsorption of NOM and trace organic compounds [15]. For NOM and the targeted compounds in this study, for instance the E2, the calibrated *K* values on molar basis is 30.8 and 25.1 (μmol g^{-1})/(μmol L^{-1})$^{1/n}$ for NOM in NRW and GW, respectively (Li et al., 2005); and is 950 (μmol g^{-1})/(μmol L^{-1})$^{1/n}$ [8]. The significantly higher value of *K* for E2 suggests that the adsorption for E2 is more favorable than that for NOM. On the other hand, the molar-based initial concentration of E2 (0.11 μmol L^{-1}) is lower than that of NOM (0.32 and 2.16 μmol L^{-1} for NOM in NRW and GW, respectively). The molar-based concentration of NOM was calibrated based on its approximate carbon content (50%) and mean molecular weight (3326 for NOM in NRW and 2865 for NOM in GW) [12]. This implies that, from the initial concentration composition viewpoint, the adsorption of E2 might have been affected by NOM. Judging from these two aspects, it is reasonable to infer that, the higher removal of E2 observed in the study was probably a result that the positive contribution effect of the larger *K* value of E2 exceeded the adversary effect of larger NOM initial concentration ratio.

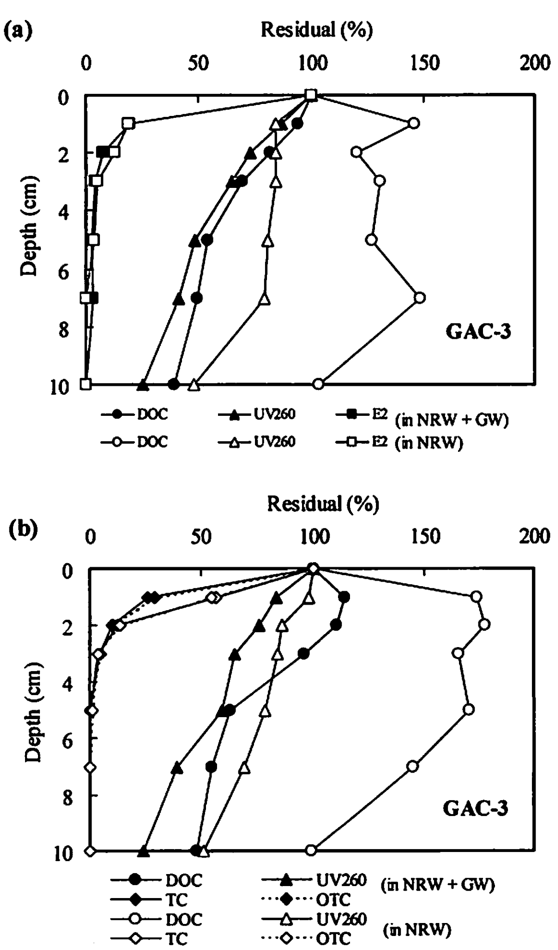


Fig. 4 Vertical distributions of residuals of NOM, E2, OTC and TC in GAC-3 when (a) E2 and (b) OTC and TC were spiked into the Nagara River water together with and without the peaty groundwater for about 5 hours after consistent running for (a) 12635, 12630 hours and (b) 12659, 12654 hours

If we consider the adsorption sites remaining after great occupation by adsorbed NOM molecules were available for both NOM molecules and E2 flowed simultaneously into the columns at the time when E2 was spiked, the lager pre-loading of NOM on the activated carbon would surely affect the removal of E2, however, such an adversary effect would also exist for the upcoming NOM molecules.

In **Table 3**, larger DOC removals for groundwater NOM than the river water NOM were revealed for the four columns. This could also be supported by previous results obtained through model analysis of the observed isotherm data for the groundwater and the river water NOM that the groundwater NOM contained less amount of non-adsorbable constituents than the river water NOM did [12].

(3) Vertical distributions of residual of NOM, E2, OTC and TC within columns

The vertical distributions of residuals of NOM, E2, OTC and TC in columns GAC-3 and GAC-4, with bed depth of 10 cm and 20 cm respectively, are displayed in **Fig. 4** and **Fig. 5**. As water flowed towards the column outlet, both of the estrogen and antibiotics decreased markedly within the top 2 cm thickness of the packed bed, thus implying that the uptake rates of both of them were relatively fast. In both GAC-3 and GAC-4, E2 disappeared in the bed depth at about 6 cm, and for OTC and TC, they

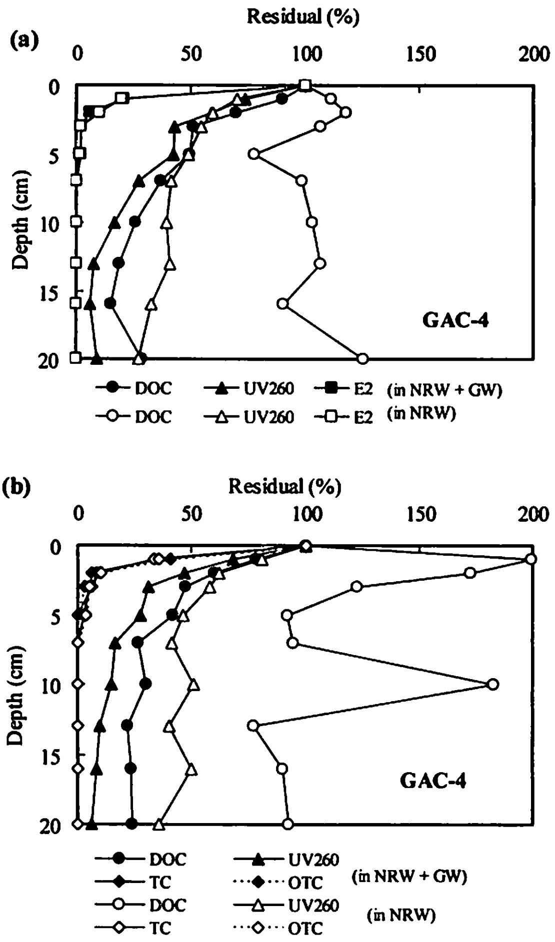


Fig. 5 Vertical distributions of residuals of NOM, E2, OTC and TC in GAC-4 when (a) E2 and (b) OTC and TC were spiked into the Nagara River water together with and without the peaty groundwater for about 5 hours after consistent running for (a) 12635,12630 hours and (b) 12659, 12654 hours

disappeared at the bed depth of about 5 cm, no matter the influent NOM concentration was lower or higher. This implied that the impact of the influent NOM concentration on the adsorption behavior of E2, OTC and TC in the column was not obvious. In regard of DOC and UV260, lower residuals along the bed depth were associated with the case when the groundwater NOM was mixed in the influent.

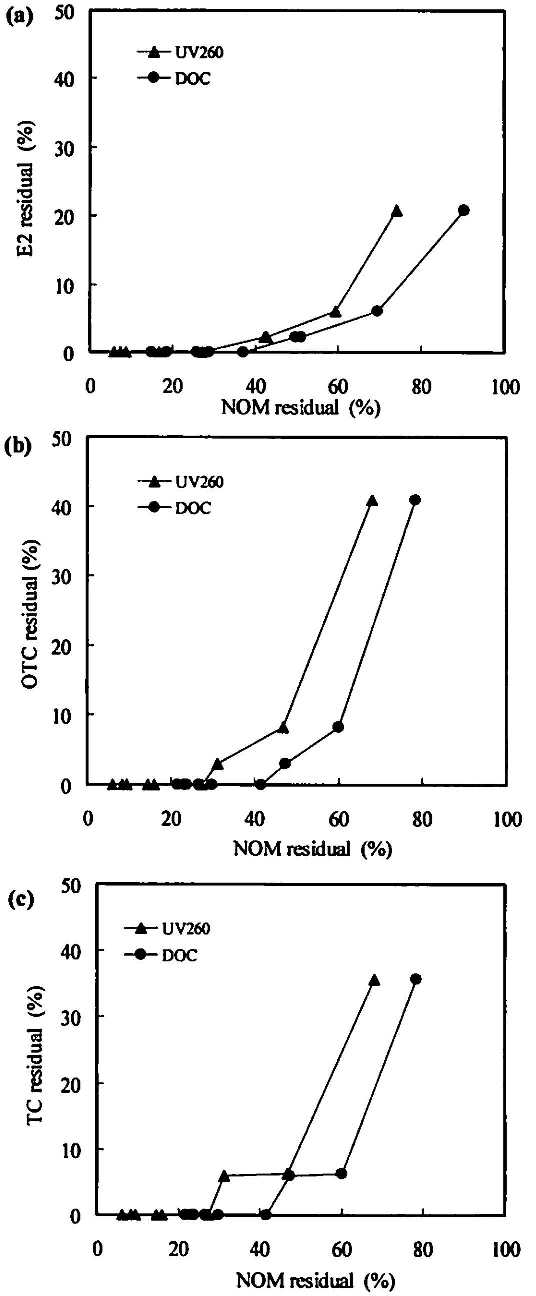


Fig. 6 The relationship between residuals of NOM with (a) E2, (b) OTC and (c) TC in GAC-4 when E2, OTC and TC were spiked respectively into the Nagara River water, with peaty groundwater after consistent running for about 12650 hours

The relationships between residuals for NOM and E2, OTC, TC in the column GAC-4 when E2, OTC and TC were spiked into the NRW along with peaty groundwater are shown in **Fig. 6.** The residuals of E2, OTC and TC increased with increases of both UV260 and DOC. However, the increasing slopes of OTC and TC were relatively sharper than those of E2. This indicated that at a given NOM residual (above about 30%), E2 was removed to a level higher than those of OTC and TC. What can be seen also from **Fig. 6** is that with the same residuals for

E2, OTC and TC, the residuals of UV260 were always lower than that of DOC, indicating that organic constituents assessed by UV260 were more favorably adsorbed than those were not detected by UV260 but detected by DOC, as mentioned earlier.

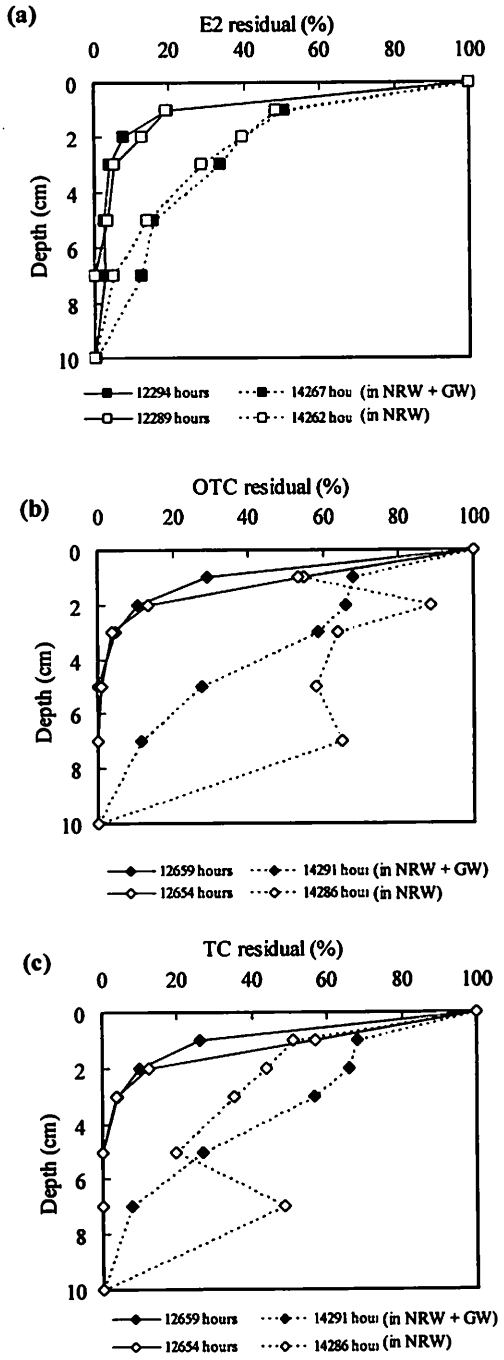


Fig. 7 Impacts of continuous adsorption time for NOM on the adsorption behavior of (a) E2, (b) OTC and (c) TC along the bed depth of GAC-3

The impacts of continuous adsorption time for NOM on the adsorption behavior of E2, OTC and TC along the bed depth are displayed in **Fig. 7.** For both the cases that E2, OTC and TC were spiked in NRW with and without the GW, their residuals increased with the time of adsorption for NOM, suggesting that NOM adsorbed adversely affected the adsorption for all three small compounds investigated in this study.

4. CONCLUSIONS

Based on the study, following findings were obtained:

(1) When E2, OTC and TC were intermittently introduced into the GAC columns, E2 was adsorbed more favorable than OTC and TC.

(2) The removals of E2, OTC and TC were significantly higher than NOM assessed by either UV260 or DOC, under the experimental conditions of the present study.

(3) Under the experimental conditions of this study, NOM concentration did not cause obvious differences in the removal of E2, OTC and TC when these compounds entered into the GAC columns together with NOM molecules.

(4) NOM adsorbed onto GAC reduced the adsorption performance for removal of the intermittently spiked E2, OTC and TC. A reduction of adsorption site for small compounds caused by NOM molecules adsorbed might be the mechanism involved.

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