Aerobic and anaerobic biodegradation of natural estrogens in continuous flow sediment mud columns

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1. Introduction

Endocrine disrupting activity in water and wastewater sources is caused mainly by natural estrogens such as estrone (E1), 17β-estradiol (E2) and estriol (E3). E2 and E1 in the final effluent of sewage treatment plants (STPs) were measured in levels from tens to hundreds nanograms per liter (Tanaka et al., 2003). Due to the merging of the final wastewater effluent into rivers and lakes, their presence has been also confirmed in water and sediment mud phases of natural water environment systems. Natural estrogens may change their forms and features due to various biochemical interactions through suspended and sediment microorganisms. To obtain more information related to the fate and behavior of estrogens in relatively closed water environment systems, continuous flow experimental approaches are necessary. Li et al. (2006) and Reni et al. (2007) showed that the degradation of E2 and E1 by sediment in batch experiments under anaerobic conditions is lower than that under aerobic conditions.

The aim of this study is to examine the behavior of E2 and its byproduct E1 and the effect of influent E2 concentrations in continuous flow sediment columns using four sediment columns, which were formed by undisturbed sediment mud phase and an overlying water phase, and were operated under well-controlled aerobic and anaerobic conditions.

2. Materials and Methods

2.1 Sediment and overlying water

Source of sediments from Ushikubiri Reservoir, a natural pre-reservoir of the Miharu Dam was located in the northeastern prefecture of Fukushima, Japan. Two sampling sites, referred as St. A and St. B, were designated along the flow direction of the reservoir. The distance between these two sites was about 100 m (Li et al., 2006) and Nagara River water that has similar physicochemical features of the reservoir water was used as the overlying water supplied to the columns.

2.2 Experiments

The schematic diagram of the experimental setup is displayed in **Fig. 1.** Columns, referred as OC-A and AC-A, and OC-B and AC-B in this figure, received sediment columns from St. A and St. B, respectively.

Two series of continuous flow experiments were performed. The first series of the experimental runs were carried out by varying the influent E2 concentrations at 15, 30 and 50 μg l^{-1}, respectively, to examine the likely effects of influent E2 load on the effluent E2 and its byproduct E1. The hydraulic retention time (HRT) was controlled identical at 4 hours. The second series of experimental runs were devised for investigating the degradation behavior of influent E1 for comparison. Intermittent monitoring of dissolved oxygen (DO) in the overlying water of all columns showed a small DO fluctuation at around 8.5 mg l^{-1} for aerobic columns (OC-A and OC-B), and about zero for anaerobic columns (AC-A and AC-B). E2 and E1 were analyzed using an Agilent 1100 series LC/MSD system (HP1100MSD).

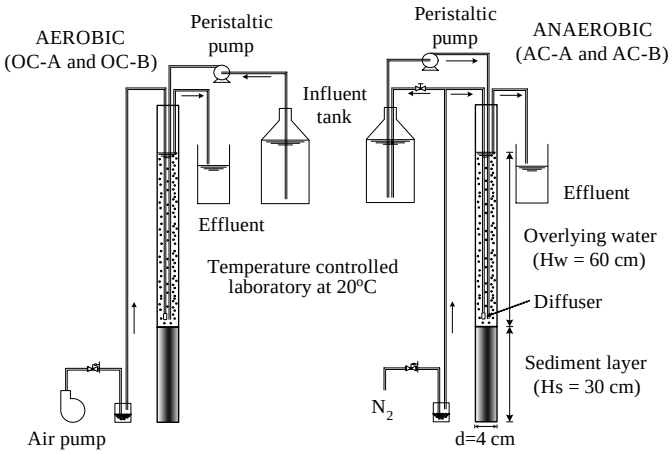

Fig. 1. Schematic diagram of the continuous flow sediment column experiments.

3. Results and Discussion

3.1 Biodegradation behavior of E2 and E1

The concentration profiles of E2 and E1 in continuous flow sediment columns where E2 and E1 were separately spiked are displayed in **Fig. 2a and 2b,** respectively. As shown in **Fig. 2a**, the effluent E2 increased with time over the initial running period, with the period length being found to be equivalent to the designated HRT. After the initial period, apparent changes in the effluent concentration of E2 were not appeared, indicating that the biological reaction had reached the steady state. Following the concentration increases of E2, its byproduct E1 emerged.

When E1 was spiked, its concentration profile as shown in **Fig. 2b** displayed a trend in close similarity with that of the above-mentioned E2 (**Fig. 2a**). However, its concentration level in the effluent was higher than the effluent level of E2 when E2 was spiked. The computed average effluents E2 and E1 at steady state are summarized in **Table 1.** The higher the influent E2 and E1 were the higher the effluent E2 and E1. A general trend of increases in the residual percentage of E2 and E1 with the influent E2 and E1 concentrations was confirmed existent. In addition, the residual percentages of E2 and E1 under aerobic condition were lower than those under anaerobic ones.

Table 1. Influent and effluent concentrations of E2 and E1 after reaching the steady state, and their apparent first-order degradation constants (k) when spiked separately.

Series I	Spiking of 17β-estradiol (E2)					Series II	Spiking of estrone (E1)			
Condition	Column	Influent E2[a]	Effluent E2[b]	Residual E2[c]	k_{E2}[d]	Influent E1[a]	Effluent E1[b]	Residual E1[c]	k_{E1}[d]
		μg l^{-1}		%	h^{-1}	μg l^{-1}		%	h^{-1}
Aerobic	OC-A	15.24 ± 0.18	0.70 ± 0.07	4,59	5,19	14.71 ± 0.59	3.09 ± 0.16	21,01	0,94
		30.93 ±1.07	3.20 ± 0.13	10,35	2,17	30.87 ±1.11	4.87 ± 0.33	15,78	1,33
		49.08± 1.67	13.33 ± 0.49	27,16	0,67	49.83± 1.13	13.89 ± 0.83	29,16	0,61
	OC-B	15.24 ± 0.18	0.32 ± 0.07	2,10	11,66	14.71 ± 0.59	3.09 ± 0.17	21,01	0,94
		30.93 ±1.07	2.06 ± 0.14	6,66	3,50	30.87 ±1.11	3.91 ± 0.31	12,67	1,72
		49.08± 1.67	9.63 ± 0.57	19,62	1,02	49.83± 1.13	9.99 ± 1.19	21,21	0,93
Anaerobic	AC-A	15.24 ± 0.18	0.77 ±0.08	5,05	4,70	14.71 ± 0.59	4.35 ± 0.17	29,57	0,60
		30.93 ±1.07	3.92 ±0.09	12,67	1,72	30.87 ±1.11	10.33 ± 0.36	33,51	0,50
		49.08± 1.67	20.54 ±1.53	41,85	0,35	49.83± 1.13	21.95 ± 0.69	41,64	0,35
	AC-B	15.24 ± 0.18	0.63 ± 0.11	4,13	5,80	14.71 ± 0.59	4.18 ± 0.31	28,42	0,63
		30.93 ±1.07	5.62 ± 0.35	18,17	1,13	30.87 ±1.11	8.80 ± 0.43	28,52	0,63
		49.08± 1.67	12.21 ± 1.05	24,88	0,75	49.83± 1.13	15.80 ± 0.57	31,71	0,54

[a] the measured values are given in the form of the mean value±the standard deviation over the whole running period

[b] the measured values are given in the form of the mean value±the standard deviation after reaching the steady state (7 data)

[c] Residual E2 or E1 = ($C_{eff.\ E2\ or\ E1\ average}$/ $C_{inf.\ E2\ or\ E1\ average}$) x 100 %

3.2 Apparent first-order constants (k) of E2 and E1

To further assess the behavior of influent E2 and E1 within the continuous flow sediment columns, their apparent disappearance rates (k_{E2} and k_{E1}) were calculated from the mass balance in the system as described below:

$$V\frac{dC_{(eff)}}{dt} = QC_{(\inf)} - QC_{(eff)} + V\left[-kC_{(eff)}\right]$$

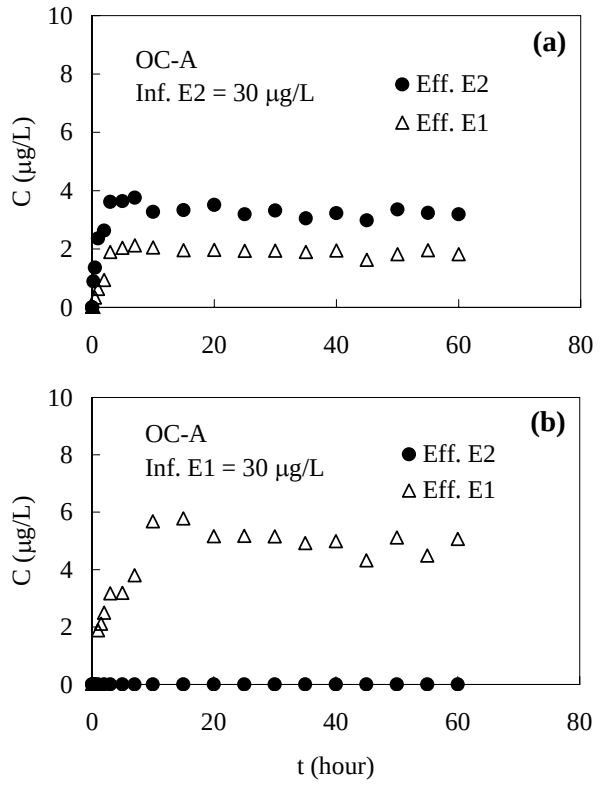

Fig 2. Concentration profiles of E2 and E1 under aerobic conditions. HRT was controlled at 4 hours.

Where $C_{(inf)}$ and $C_{(eff)}$ is the concentration (μg l^{-1}) in the influent and effluent, respectively, t is time (h) and k is the first order rate constant (h^{-1}). k was approximated when the accumulation flux dC/dt was given as zero, i.e., using the average effluent concentration after reaching the steady state. As shown in **Table 1**, a trend of decreases of k_{E2} with increasing the influent E2 was obtained. From this table, it was clear that k_{E1} was generally lower than k_{E2}. The obtained results showed E2 disappeared from sediment mud columns in a pace much faster than E1.

4. Conclusion

Continuous flow experiments using sediment mud columns were performed to investigate the behavior of E2 and E1 under aerobic and anaerobic conditions. The obtained results indicated that the effluent E2 and E1 concentrations at the steady state shown an increasing trend as the influent E2 and E1 concentration increased. The effluent E2 and E1 were generally higher in anaerobic columns than in aerobic ones. E2 disappeared from sediment mud columns faster than E1.

References

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