Removal of endocrine disruptors in membrane separation activated sludge process

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Abstract

Removal of 17β-estradiol (E2), estrone (E1), 17α-ethynilestradiol (EE2) and Bisphenol A (BPA), which are possible endocrine disruptors and have relatively hydrophilic nature with LogK_{ow} of 3.1 to 4.0, was investigated in a laboratory membrane separation activated sludge process. The target solutes were removed biologically to a certain extent and they were not significantly retained by microfiltration membranes even after long-term operation which causes gel-layer formation on the membrane surface. A two-phase fate model was introduced to assess the effectiveness of complete solid-liquid separation on the removal by microfiltration membranes. The water-sludge partition coefficients (k_p), the water-sludge mass-transfer rate constants (k_b) and the deformation rate constants (k_1) in the reaction kinetic model were determined for these solutes by experiments. Calculation by the parameters determined in the model showed that higher MLSS operation in membrane separation activated sludge promotes the migration of these pollutants from the liquid phase to the sludge phase resulting in higher removals.

Keywords: endocrine disruptors; estrogen; membrane separation activated sludge process; reaction kinetic model; wastewater treatment

1. Introduction

Membrane separation activated sludge process is widely used for improving water quality in wastewater reclamation [1,2] and domestic [3] or industrial wastewater treatment. This technology can reduce BOD and nitrate in effluents. It is not clear the effectiveness of membrane separation activated sludge process on the removal of endocrine disrupting chemicals (EDCs).

Three advantageous factors can be considered for membrane separation activated sludge process. The first factor is complete solid-liquid separation which prevents the discharge of suspended matters which have higher concentrations of hydrophobic chemicals like dioxins. The second factor is the long SRT operation in membrane bioreactor which may result in the efficient removal or retention of COD [4,5], ammonia nitrogen [4], metals [6], and so on. Long SRT operation potentially cause retention of special bacteria which can degrade chemicals efficiently. The third factor is formation of membrane surface deposits which is reported to act as a barrier in the rejection of viruses [7] and in the removal of nitrate by denitrification bacteria [8]. However little is known about the contribution of the above factors in removing estrogens and other micropollutants.

Many models describing the fate of chemicals in wastewater treatment plant have been suggested so far. The target compounds are volatile organic compounds (VOCs) [9-11], nitrilotriactetic acid (NTA) [12], linear alkyl benzene sulfonate(LAS) [12], phosphorus [13], dioxin [10], PCBs [11] which have high hydrophobic property, 17α-ethynilestradiol [14] and so on. However there are few studies on modelling biodegradation with membrane separation and with model parameters determined. The quantitative estimation of the effectiveness of

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membrane separation activated sludge process is required.

In this study batch experiments were carried out in a laboratory scale activated sludge reactor to investigate the behavior of typical EDCs like estrogens and Bisphenol A by measuring the concentrations in water phase and sludge phase separately. Then a reaction kinetic model was introduced to determine the adsorption and deformation characteristics of the target compounds quantitatively. In addition, the effectiveness of membrane separation activated sludge process over conventional activated sludge process was evaluated by using numerical simulation and calculated parameters.

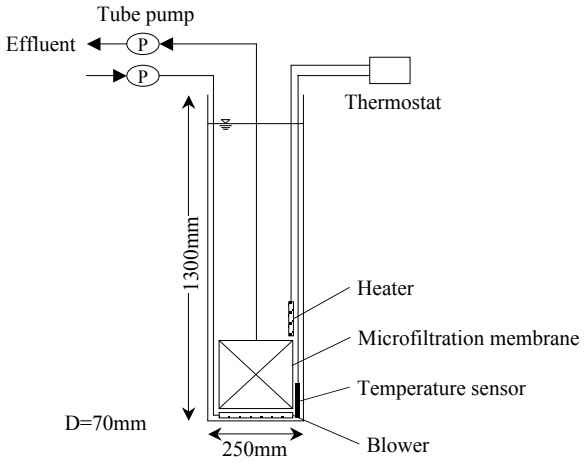

Fig. 1
A schematic diagram of the activated sludge reactor

2. Materials and Methods

Target compounds were 17β-estradiol (E2), estrone (E1), 17α-ethynilestradiol (EE2) and Bisphenol A (BPA). E2-d_4 was employed as a surrogate in the analysis. Activated sludge was collected at a wastewater treatment plant in Tokyo, Japan. The experimental set-up was consisted of an activated sludge reactor with the volume of 20*l* which was operated with 24 hours cycle batch condition as shown in Fig. 1. The reactor was operated for initial 60 days with fill and draw type activated sludge process and for successive 20 days with membrane separation. The microfiltration hollow fiber membrane (UMF 0234L1; Mitsubishi Rayon Co., Ltd.) made from polyethylene was immersed in the reactor. The nominal pore size of the membrane is 0.4μm and the surface area is 0.2m^2. Artificial wastewater (10*l*) with E2, EE2 and BPA (1m*l* of 20g/*l* acetone solution) were fed at a certain time everyday. The extraction of treated water through membrane began 3 hours after the feeding of the artificial wastewater. Permeate volume was controlled to reach 10*l* at 22 hours after the feeding. Treated water was collected in a tank. During the experiments, mixed liquor was sampled with the sampling volume of 80m*l*, subjected to immediate separation by using centrifuge and grass-fiber-filters with retention diameter of 1μm into water phase and sludge phase. Concentrations of target compounds were measured by GC/MS analysis after dimethyl derivatization. Extraction, derivatization and measurement procedures were based on a manual published by Japan Ministry of the Environment [15].

3. Results and discussion

3.1 Experimental Results

Typical results are shown in Fig. 2. E2 in the water phase was rapidly adsorbed to the sludge and the adsorbed E2 was rapidly biodegraded and partially converted to E1, which is one of the oxidation products of E2. Then E1 in the sludge phase was released to the water phase at a certain rate. Thereafter both concentrations of E1 in water phase and sludge phase were gradually decreased due to biodegradation. On the other hand, biodegradability of EE2 was lower than

Table 1
The additional removal due to membrane surface deposits

	Removal[%]
E2	20.2
E1	44.8
EE2	31.4
BPA	38.4

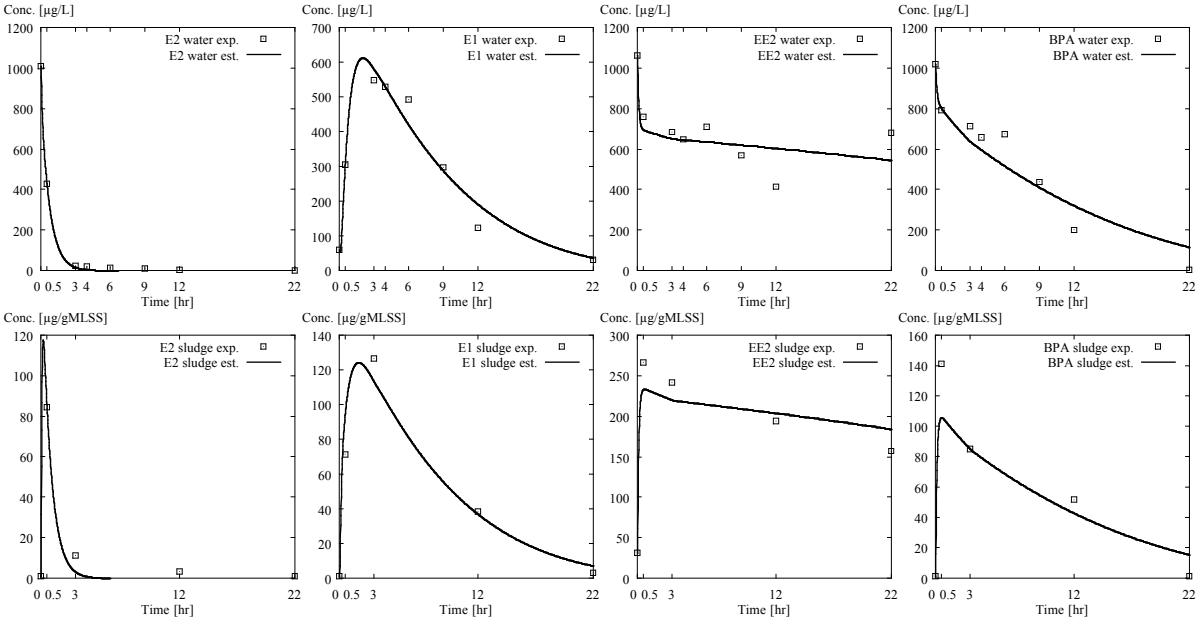

Fig. 2
The plots show experimental results on time dependent change in concentrations. Solid lines represent most probable fitting-curves. Upper figures show concentrations in water phase. Bottom figures show concentrations in sludge phase.

that of E2, E1 and BPA.

The effectiveness of membrane surface deposits was discussed in terms of removals of the target compounds, which was calculated from the removal ratio of the concentration of permeate over of water phase concentration in the reactor. Table 1 shows that the effectiveness remained below 45%.

3.2 Two-phase fate model

A two-phase fate model for the target compounds was introduced. The model contains adsorption and desorption of target compounds between water phase and activated sludge phase and deformation kinetics in activated sludge phase as shown in Fig. 3. The assumption of linear adsorption and desorption, and first order deformation in activated sludge phase led to the following expressions for mass transport shown in Fig. 3:

(in water phase) $$\frac{d(\theta C_W)}{dt} = -k_b\left(k_p C_W - C_S\right)X \qquad \text{(Eq. 1)}$$

(in activated sludge phase) $$\frac{d(C_S X)}{dt} = k_b\left(k_p C_W - C_S\right)X - k_1 C_S X \qquad \text{(Eq. 2)}$$

where C_W is concentration in water phase [μg/l], C_S is concentration in activated sludge phase [μg/gMLSS], X is mixed liquor suspended solid (MLSS) [gMLSS/l], θ is volume correction factor [-], k_p is water-sludge partition coefficient [l/gMLSS], k_b is water-sludge mass-transfer rate constant [hr^{-1}], and k_1 is deformation rate constant [hr^{-1}].

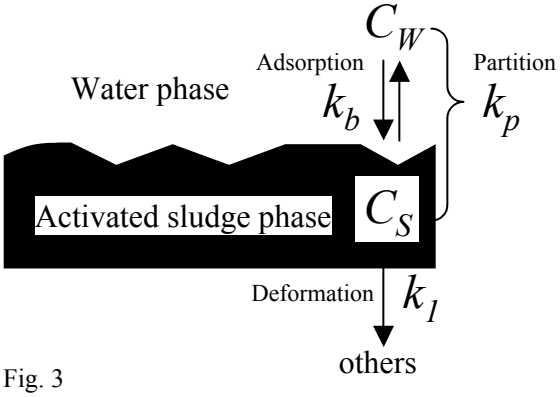

Fig. 3
A conceptual diagram of the two-phase fate model

Table 2
Operational conditions and calculated model parameters

		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8
COND	Acclimatization time [d]	1	20	24	35	60	67	73	80
	Water temp. [°C]	16.6	14.0	14.3	11.6	8.5	15.0	15.0	15.0
	MLSS [gMLSS/*l*]	3.000	2.216	1.990	1.886	4.754	5.086	5.000	1.680
	Influent DOC [mg/*l*]	100	200	200	400	400	400	400	400
E2	k_b [hr^{-1}]	0.771	0.366	0.100	>10	>10	1.422	4.070	5.466
	k_p [*l*/gMLSS]	1.603	1.818	4.664	0.497	0.214	0.929	0.599	0.336
	k_1+k_2 [hr^{-1}]	0.960	1.301	0.918	3.367	4.388	7.430	7.359	5.081
	k_1 [hr^{-1}]	-0.651	0.443	-1.629	1.633	1.329	2.264	0.996	-0.160
	k_2 [hr^{-1}]	1.611	0.858	2.547	1.734	3.059	5.166	6.363	5.241
E1	k_b [hr^{-1}]	>10	>10	>10	>10	>10	>10	>10	>10
	k_p [*l*/gMLSS]	0.818	0.102	0.234	0.151	0.141	0.179	0.384	0.201
	k_1 [hr^{-1}]	0.259	0.286	0.049	0.533	0.496	1.308	0.874	0.536
EE2	k_b [hr^{-1}]	>10	>10	—	0.009	1.368	0.938	1.456	5.589
	k_p [*l*/gMLSS]	1.184	0.332	—	0.749	0.367	0.435	0.654	0.341
	k_1 [hr^{-1}]	0.085	0.024	—	0.005	0.027	0.000	0.034	0.069
BPA	k_b [hr^{-1}]	0.010	>10	>10	0.079	1.247	0.947	0.413	7.161
	k_p [*l*/gMLSS]	2.503	0.137	0.228	0.465	0.209	0.332	1.169	0.142
	k_1 [hr^{-1}]	0.072	0.089	0.047	0.130	0.324	0.847	0.567	0.387

3.3 Estimation of the parameters

Model parameters (k_p, k_b, k_1) were estimated in each Run by using the least-square method. Simultaneous numerical solutions for differential equations 1 and 2 where used to fit curves in Fig. 2 obtained by using the calculated parameters. In the case of E2, deformation rate constant k_1 was defined as deformation rate to the unknown compounds except for E1 which was k_2. The calculated parameters with experimental conditions are shown in Table 2.

The maximum k_p was obtained in Run 1 when the experiment was carried out just after the sampling of sludge from wastewater treatment plant for values of E1, EE2, and BPA. These values were relatively higher than those in Run 2 to 8. In addition, k_1 value of EE2 was approximately double in Run 1 compared to Run 2 through Run 8. This result suggests that the laboratory acclimatization of activated sludge decreased biodegradability and capacity for adsorption of the target compounds.

k_p was in the order of E2 > EE2 > BPA > E1 in most of the experiments. This relationship was consistent with the order of LogK_{ow} values, for E2 of 4.01, for EE2 of 3.67, for BPA of 3.32, and for E1 of 3.13. The partition between water and sludge naturally correlated with K_{ow}, which is widely used for the prediction of fate of organic compounds. Biodegradation rates were in the order of E2 > E1 > BPA > EE2. It was proved that E2 and E1 which are natural estrogens originating from humans and livestock were more biodegradable than BPA and EE2 which are synthetic chemicals. The increase in biodegradation rates between Run 5 and Run 6, 7, 8 can be explained as the increase of water temperature. The concentration of substrates fed to the microorganisms in the reactor were increased from 200[mg/*l*] to 400[mg/*l*] in DOC during the experiments Run 3 through Run 5. The biodegradability of EDCs was stimulated by the increase in the feeding concentration in this period.

3.4 Comparison of treatment processes

In order to compare final effluent concentrations in different treatment processes, a numerical simulation was applied for two cases. The first is the typical conventional activated sludge process operated with MLSS of 1,000[mg/*l*] and HRT of 8[hr] while the other is the

Table 3
Comparison of treatment processes

		(i) Conventional AS		(ii) Membrane separation AS	
COND	MLSS [mg/*l*]	1,000		10,000	
	HRT [hr]	8		3	
	SRT [d]	4.8		83.3	
	R-SS(X_E) [mg/*l*]	10		0	
	Influent	Final effluent		Final effluent	
	C_{W0}	C_W (water)	$C_S X_E$ (R-SS)	C_W (water)	$C_S X_E$ (R-SS)
E2	100	7.9	0.02	2.2	0
E1	0	26.3	0.07	10.3	0
EE2	100	86.6	0.40	67.3	0
BPA	100	31.4	0.14	11.0	0

membrane separation activated sludge process operated with higher MLSS of 10,000[mg/*l*] and shorter HRT of 3[hr]. The results are shown in Table 3. Supposing residual suspended solid concentration (X_E) in final effluent was 10[mg/*l*], it was calculated that the contribution of residual SS ($C_S X_E$) to the effluent load were extremely smaller than that in water phase and almost all of E2, E1, EE2 and BPA in the final effluent were in water phase, as the amounts of these compounds adsorbed to the residual SS were vanishingly small. It was calculated that removal in the membrane separation process was higher than that in the conventional process. This high removal in the membrane separation process was due to higher MLSS operation of 10,000[mg/*l*] rather than to the complete solid-liquid separation by the membranes.

4. Conclusions

Biodegradation of 17β-estradiol (E2), estrone (E1), 17α-ethynilestradiol (EE2) and Bisphenol A (BPA) in activated sludge reactor was examined and two-phase fate model containing adsorption and desorption of target compounds between water phase and activated sludge phase and deformation kinetics in activated sludge phase was suggested. Model parameters were determined to assess the fate of the target compounds in water phase and sludge phase separately. In addition, the numerical simulations were introduced to evaluate the effectiveness of membrane separation activated sludge process. The conclusions were summarized as follows:

1) Water-sludge partition coefficient k_p has a close relationship with K_{ow}.
2) By calculating deformation rate constant k_1, it was proved that E2 and E1 which are natural estrogens originating from humans and livestock were more biodegradable than BPA and EE2 which are synthetic chemicals.
3) By calculating water-sludge partition coefficient k_p and deformation rate constant k_1, the differences of sludge property between acclimated sludge and sludge in a real wastewater treatment plant were found. It was also found that increase in DOC in the reactor stimulated the biodegradability of EDCs.
4) It is expected that the contribution of sludge extraction on the removal of the target compounds in membrane separation activated sludge process were negligible. The idea that long SRT operation may cause retention of special bacteria which can degrade chemicals efficiently was not supported by the experiments. The effect of membrane surface deposits which can act as a barrier for solute penetration was below 45%. The simulation shows that higher MLSS operation in membrane separation activated sludge promotes the migration of these pollutants from the liquid phase to the sludge phase, resulting in higher removal, although complete solid-liquid separation was not a dominant

factor of the advantage for membrane separation activated sludge process of the target compounds being relatively hydrophilic.

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