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Removal of Endocrine-Disrupting Chemicals by Phytoremediation

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ABSTRACT: Phytoremediation refers to a set of technologies that use plants to degrade or contain contaminants. The objectives of this study are to investigate the possibility of the treatment of endocrine disrupting chemicals (EDCs) by phytoremediation and to evaluate the removal performance. Two types of laboratory-scale experiments were conducted. First, batch experiments were conducted using a vessel containing plant and EDCs solution. Second, continuous experiments were carried out with a hydraulic residence time (HRT) of 5 hours. Plants used were submerged plants, emerged plants, and floating plants. EDCs were 2,4-Dichlorophenol (DCP), 4-t-Octylphenol (OP), Pentacholorophenol (PCP), Nonylphenol (NP), and Bisphenol-A (BPA). The initial and feed concentration of all EDCs was 10 μg/L. Experimental results showed phenolic compounds except PCP could be removed by every plant. Removal of EDCs was possible in very low concentration observed. Removal rates of EDCs were in the range from 0.1 to 1.0 μg/g-biomass/day in batch and continuous experiments.

INTRODUCTION

Phytoremediation is an emerging technology which uses plants and their associated rhizospheric microorganisms to remove, degrade, or contain chemical contaminants (Chappell, 1997). Mechanisms are divided into phytoextraction, phytovolatilization, rhizo-filtration, phytostabilization, rhizodegradation, phytodegradation, hydraulic control, vegetative cover, and riparian corridors (U.S. EPA, 2000).

Phytoextraction is the uptake and translocation of contaminants from groundwater into plant tissue as the plant takes in water and micronutrients from soil through its root system (U.S. EPA, 2005). One or more mechanisms may occur at once when contaminants or EDCs are removed by plants. Phytoextraction may be important in this study from the point of view of the removal rate. It relates plant uptake from contaminated sites. Plant uptake of a chemical was quantified by its octanol-water coefficient (Kow) (Briggs et al., 1982). Direct uptake of organics by plants is a surprisingly efficient removal mechanism for moderately hydrophobic organic chemicals with log Kow between 1 and 3.5 (Schnoor, 1997).

Phytostabilization is the immobilization of a contaminant through absorption and accumulation by roots or precipitation within the root zone of plants (U.S. EPA, 2001). This mechanism is typically applied to hydrophobic organics such as pentachlorophenol (Schnoor, 1997).

Earlier studies showed that phytoremediation is superior to conventional technology especially in terms of cost-performance and environmental burdens. Moreover, plants can be used to treat most classes of contaminants, including petroleum hydrocarbons, chlorinated solvents, pesticides, metals, radionuclides, explosives, and excess nutrients.

(Chappell, 1997). Recent researches have focused on removal of heavy metals or chlorinated organic compounds in soils or groundwater. Some report suggested that applying phytoremediation to persistent chemicals such as pentachlorophenol (Mills et al., 2005), atrazine (Singh et al., 2004), and polychlorinated biphenyl (Chekol et al., 2004) was also effective. It is said that alkylphenols are degraded by microorganisms or plants. For example, oxidation of BPA by tomato enzyme (Xuan et al.,2002), oxidation of BPA, NP, and OP by Armoracia rusticana peroxidase (Sakuyama et al., 2003). In fact, degradation of BPA by Nasturtium Officinale and Phragmites australis was reported (Morita et al., 2004). Additionally, aquatic plants such as Vallisneria acsiatica var. biwaensis, Egena densa, Cabomba caroliniana, Limnophila sessiliflora and Ceratophyllum demersum removed Nonylphenol in the range from 50% to 90% for initial concentration of 11.0 mg/L and HRT of 24 hours (Suzuki and Saitou, 2002).

Sufficient information has not been available because most former studies on EDCs focused on one specific substance and the initial concentrations were almost over several mg/L. Different types of EDCs are existing as a mixture and their concentrations were several µg/L. This study was conducted to investigate the possibility of the treatment of trace EDCs by phytoremediation and to evaluate the removal performance.

MATERIALS AND METHODS

In this study, two types of laboratory-scale experiments were conducted. First, batch experiments were conducted to investigate the possibility of phytoremediation of EDCs as well as the removal performance. Second, continuous experiments were conducted to verify the stability of removal performance.

Experimental device is shown in Figure 1. A small container with plant, EDCs, and nutrients solution was prepared and the time-course changes of EDCs was measured. One container without plant (blank) was also prepared and used as a reference.

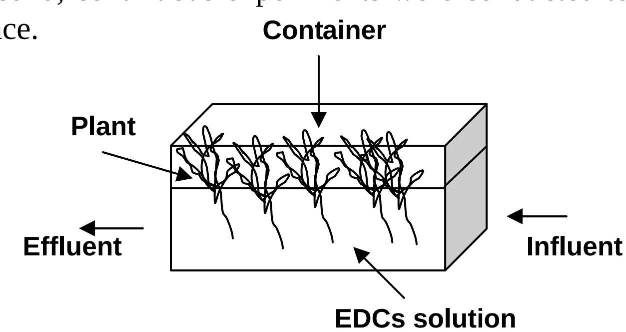

FIGURE1. Experimental device outline.

Batch experiments with a period of 12 hours (batch 1) and 10 days (batch 2) were conducted to measure time-course changes in concentration of EDCs. In each experiments, EDCs were measured at 1,2,3,5,7,12 hours in batch 1 and at 1,2,3,5,7,10 days in batch 2. Continuous experiments were conducted for about 40 days, where measurements were made once or twice a week.

The EDCs were divided into two groups (C1 and C2). The C1 group consists of phenolic compounds; 2,4-Dichlorophenol (DCP), 4-t-Octylphenol (OP), Pentacholorophenol (PCP), Nonylphenol (NP), Bisphenol-A (BPA). The C2 group consists of Diethyl phthalate (DEP), Diethylhexyl adipate (DEHA), Diethylhexyl phthalate (DEHP), and Benzophenone (BP). The property of EDCs may be divided into two groups, Group1 and 2. Group1 (G1) is that log Kow is around 3 and G2 is that log Kow is over 5. Initial concentration of EDCs was all 10 µg/l. Plants used in this study were seven species;

Limnobium Laevigatum (LL), *Fantinalis Antipyretica* (FA), *Nasturtium Officinale* (NO), *Ricciocarpos natans* (RC), *Riccia fluitans* (RF), *Hydrilla verticillata* (HV), and *Potamogeton oxyphyllus* (PO). They were divided into three types. LL, RC, and RF were floating plants. FA, HV, and PO were submerged plants. NO was emerged plant. These plants were used, because (1) they are widely distribution in nature and (2) they are relatively vigorous. Experimental conditions are shown in Table 1.

TABLE 1. Experimental conditions.

Type	Batch 1	Batch 2	Continuous
Plants	LL, FA, NO, blank	RC, RF, HV, PO, blank	FA, NO, blank
EDCs	C1, C2, BP	C1	C1, C2, BP
Other substance	nutrients salt	nutrients salt	nutrients salt,
Light Condition		2500lux, 14-10h	
Water Volume	200 ml	4 L	200 ml
Water Temperature	18 degree	16 degree	18 degree
Flow Rate			40 ml/h
Period	12 hours	43 days	10 days

In analysis, EDCs were extracted from liquid samples by organic solvent with shaking. Then, the sample was dehydrated by sulfuric acid and left for over 12 hours. Thereafter the sample was concentrated and measured by GC/MS.

RESULTS AND DISCUSSION

The Batch Results. The time course of EDCs by NO is shown in Figure 2. Removal performance was different in each EDC. However, there was a tendency that after quick decrease at initial phase, EDCs decreased gradually. PCP was not removed during 12 hours.

Results in batch 1 showed that EDCs except PCP were removed by plants and EDCs in C2 were hardly removed. But, the results in batch 2 suggested that PCP could be removed for longer time. The removal performances by plants were evaluated by the following removal rate:

$$\text{Removal rate [µg/g-biomass/day]} = ([EDCs]_b - [EDCs]_p) *V/ W/ T$$

where,

$[EDCs]_b$ = the concentration of EDCs in blank [µg/L]

$[EDCs]_p$ = the concentration of EDCs in plant [µg/L]

V = water volume [L]

W = biomass weight [g]

T = time [day]

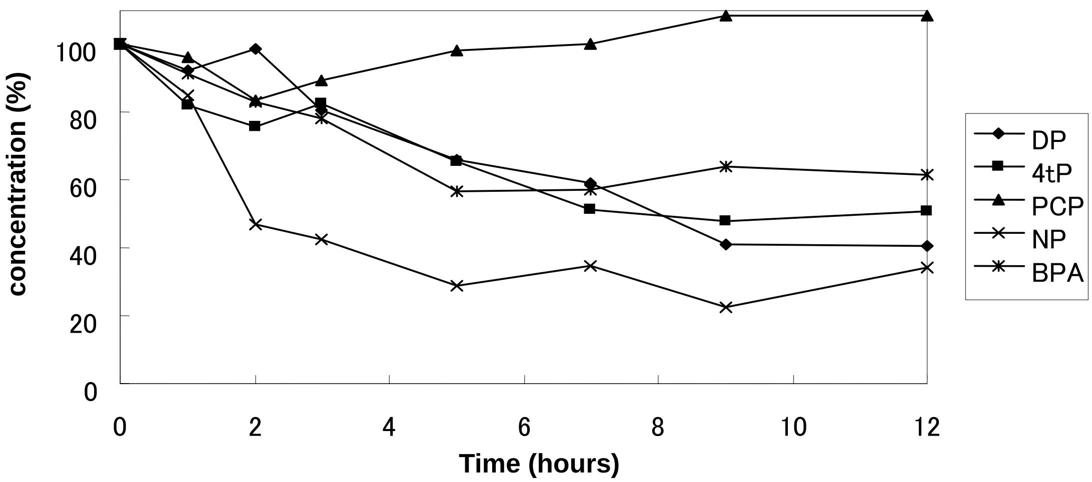

FIGURE 2. The time course of EDCs by NO.

Removal rates in batch experiments are shown in Table 2. The rates were in the range from 0.1 µg/g-biomass/day to 1.0 µg/g-biomass/day. That of PCP was least in C1 groups and was less than 0.2 µg/g-biomass /day. This may be because PCP is used as a pesticide. In this study, PCP concentration was close to blank concentration within an experimental period of 12 hours. However, it tended to reduce with purification time. So these results suggested PCP could be removed by plants with longer time. A former study showed atrazine and simazine used as pesticide were removed by planted soil. Within 80 days, both were reduced by half (Singh et al., 2004). It was also shown that removal of these pesticides by plants was more effective with longer experimental period.

TABLE 2. Removal rate by each plant in batch experiments.

Plants (µg/g-biomass/day)	LL	FA	NO	RC	RF	HV	PO
OP	0.3	0.4	0.4	0.1	0.5	0.0	0.1
PCP	0.0	0.0	0.1	0.0	0.0	0.0	0.1
BPA	0.6	0.5	0.4	0.3	1.0	0.0	0.3
NP	0.5	0.9	0.1	0.9	1.6	1.0	4.4
DCP	0.4	0.9	0.6	0.1	0.5	0.1	0.3

LL = *Limnobium Laevigatum*, FA = *Fantinalis Antipyretica*, NO = *Nasturtium, Officinale*,
RC = *Ricciocarpos natans*, RF = *Riccia fluitans*, HV = *Hydrilla verticillata*, and PO = *Potamogeton oxyphyllus*

The Continuous Results. The continuous experiments were carried out to verify the stability of removal performance by plants. The results are shown in Figure 3 and were similar to the batch results. In continuous experiments, C1 except PCP could be removed. The EDCs except PCP could be stably removed by plants at very low concentration during the experimental period of 40 days.

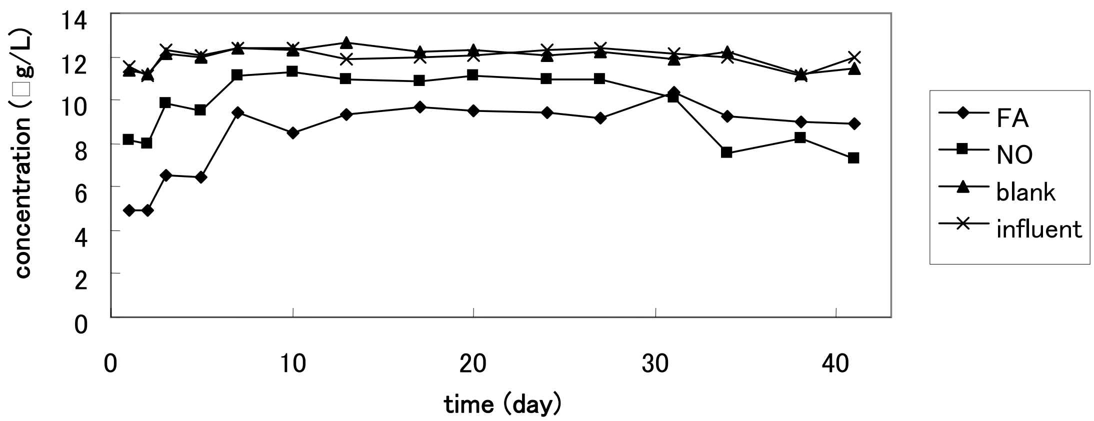

FIGURE. 3. The time course of BPA

Removal rates in continuous experiments are shown in Table 3. The rates were in the range from 0.3 µg/g-biomass/day to 0.9 µg/g-biomass/day. PCP was not efficiently removed and its removal rate was less 0.1 µg/g-biomass/day.

TABLE 3. Removal rate by each plant in continuous experiments.

Plant (µg/g-biomass/day)	FA	NO
OP	0.3	0.7
PCP	0.1	0.0
BPA	0.3	0.6
NP	n.d.	n.d.
DCP	0.6	0.9

The Relationship between Removal Rate and Water-Octanol Coefficient (Kow). Plant uptake of a chemical was quantified by its octanol-water coefficient (Kow) (Briggs et al., 1982). Direct uptake of organics by plants is an efficient removal mechanism from sites contaminated at a shallow depth with moderately hydrophobic organic chemicals with log Kow between 1 and 3.5 (Schnoor, 1997). In general, moderately hydrophobic organic compounds (with log Kow between 0.5 and 3.0) are most readily taken up by and translocated within plants (U.S. EPA, 2000). In this study, EDCs was classified into 2 groups. Group1 is OP and PCP whose Kow are higher (over 5) and Group2 is BPA, NP, and DCP whose Kow are lower (about 3). Water-octanol coefficient of C1 is listed in Table 4 (IPCS, 2005). Table 2 showed that the removal rate in Group1 was lower than Group2 in most of the plants. Removal rate tended to increase with a decrease in Kow. This result may indicate that plants did not remove EDCs only by adsorption. Further studies will be needed to analyze the mechanism and to evaluate the removal performance more accurately.

TABLE 4. Water-octanol coefficient (Kow) of C1.

	Log Kow
OP	5.28
PCP	5.01
BPA	3.32
NP	3.28
DCP	3.06

CONCLUSION

In this study, two types of laboratory-scale experiments on phytoremediation were conducted to treat EDCs. Experimental results demonstrated that removal of phenolic EDCs except PCP by plants could be possible in batch and continuous modes at very low concentration about 10 μg/L. Removal rates were in the range from 0.1 to 1.0 μg/g-biomass/day.

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