

Treatment of TNT and Parathion Using Constructed Wetland Microcosms

Jong-Kyu Choi, Se-Kyung Kim, Se-Hee Oh, Eun-Sook Lee, Kyung-Duk Zoh^{1*}

¹ *Department of Environmental Health, Graduate School of Public Health,
Seoul National University, Seoul, 110-799 Korea*

Abstract

This study was carried out to investigate the removal of TNT (2,4,6-trinitrotoluene) and parathion in the batch and the continuous constructed wetland microcosms consisting of marsh and pond. The batch system study showed that TNT was almost reduced in the marsh and pond system within 20 days and parathion was within 8 days. The major reductive metabolites of TNT includes 2,4-diamino-6-nitrotoluene (24DANT) > 2,6-diamino-4-nitrotoluene (26DANT) > 4-diamino-2,6-nitrotoluene (4ADNT) > 2-diamino-4,6-nitrotoluene (2ADNT), and the concentrations of these metabolites were decreased during further operation. The generation rates of 4-nitrophenol, the major metabolite of parathion, were 82% and 15% in the bottom of marsh and pond system, respectively. In the continuous system study, although TNT/parathion degradation pattern was similar to the batch's, marsh-pond system showed the most stable TNT/ parathion removal among various continuous reactor combinations.

Introduction

Wastewaters discharged from the munitions production facilities contain high explosives and were often dumped into unlined pits and disposed in lagoons during the early manufacturing period. These improper disposal practices led to the contamination of the environment and until now, it is often found in the soil, groundwater, and surface waters of the sites where they were manufactured. Among these, TNT (2,4,6-trinitrotoluene) is the most common explosive compound. The toxicity of TNT and its reductive metabolites has led to the concern about its fate in the environment and potential for human exposure. TNT

is found to be toxic to algae and chronic exposure to it of human causes harmful health effects.

Parathion is organophosphorous pesticide in the great amount use. Because of its very high acute toxicity, parathion is classified to toxicity class I by U.S.EPA and included in the Restricted Use Pesticide (RUP). Although parathion is degraded rapidly in nature and has low persistence, its metabolites (paraoxon, p-benzoquinone, and 4-nitrophenol) present very high toxicity. It is the representative non-point pollutant and so, it has limitation to use the existing wastewater treatment system for removal of parathion.

Constructed wetlands have been successfully used to clean up municipal, industrial and agricultural non-point pollutants, storm-water runoff, and many other types of polluted wastewaters. The objective of this study is to investigate the feasibility of constructed wetland in treating TNT/parathion-contaminated water. We observed the removal of TNT/parathion and the production of their metabolites using the batch and continuous constructed wetland microcosms consisting of marsh and pond.

Materials and Methods

Marsh (D:35cm, H:50cm) and pond microcosms (D:35cm, H:60cm) were made of the acrylic plastic chambers. Marsh was planted with reeds (density of 1 ports /0.1m²), ubiquitous and most reproductive wetland plant in Korea, on the sand-gravel bed. The substratum zone consisted of three different types of media: gravel (10kg, size 40-60µ m) at the bottom, small size gravel (15kg, size 10-20µm) in the middle and sand (15kg, 2-4µm) on the top. Each experiment were performed with the addition of 10mg/L TNT and 2mg/L parathion separately, maintaining natural level of nutrients. Flow rate in continuous systems was maintained at 400mL/h and hydraulic retention time for marsh and pond was 2.6 day and 5.2 day, respectively. TNT, parathion and their metabolites were determined using HPLC (Dionex) with Supelcosil C-18 column⁴). Detection wavelength was 254nm for TNT, 215nm for TNT metabolites, 277nm for parathion, and 314nm for 4-nitrophenol. Total nitrogen and phosphorous compounds was measured using *Standard Method*.

Results and Discussion

TNT/parathion removal and the production of their metabolites in the batch system are shown in the Fig. 1 and Fig 2, respectively. The result indicates that more than 90% of TNT was degraded after 20 days in the water phase and the total amount of its metabolites produced was up to 25% of initial mole concentration of TNT. The major reductive metabolites of TNT were 2,4-diamino-6-nitrotoluene (2,4-DANT) > 2,6-diamino-4-nitrotoluene (2,6-DANT) > 4-diamino-2,6-nitrotoluene (4-ADNT) > 2-diamino-4,6-nitrotoluene (2-ADNT).

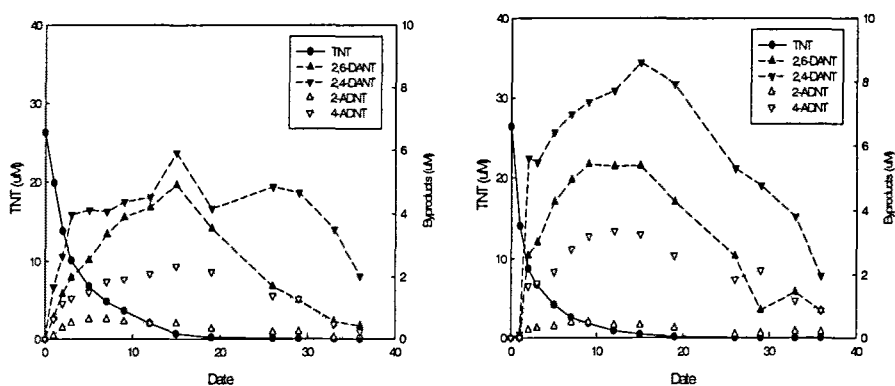


Fig. 1. TNT removal and the production of its metabolites in the batch system (left: marsh, right: pond)

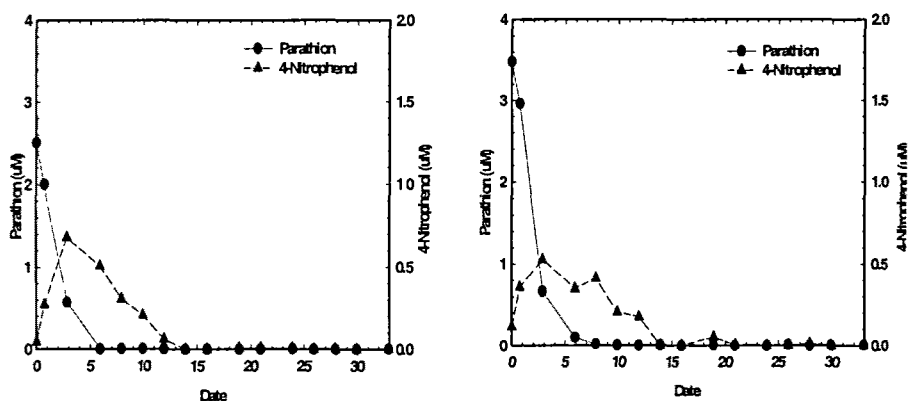


Fig 2. Parathion removal and the production of 4-nitrophenol in the batch system (left: marsh, right: pond)

More than 99.9% of parathion was degraded after 8 days and the generation rates of 4-nitrophenol were 82% and 15% in the bottom of marsh and pond system, respectively

The results of continuous system study using various microcosm combinations (marsh-pond, pond-marsh, marsh-marsh, and pond-pond,) were shown in table 1.

TNT and parathion were effectively removed from the water phase in every combination after three weeks and one week, respectively. Comparing continuous systems, total metabolites production rate of TNT was about 20% in marsh-marsh and pond-pond system. However, more metabolites were produced in the marsh-pond and pond-marsh system. Also major byproducts in marsh-marsh and pond-pond system were aminonitrotoluene type metabolites, while diaminonitrotoluene type metabolites were dominant in the marsh-pond and pond-marsh system. These results indicate that marsh-pond or pond-marsh system is more stable and complete for the removal of TNT and its metabolites. The reason is that marsh-pond and pond-marsh systems have both aerobic and anaerobic conditions. About parathion,

both marsh-pond and pond-marsh system showed similar results.

In further study, the effect of TNT sorption into the soil and the TNT mineralization extent are to be investigated with the mesocosm scale study.

Table 1. Summary of removal efficiency of TNT and parathion in the continuous systems of various combinations

Reactor type	Target material	Average Removal efficiency (%)	By product (%)	Major byproduct
Marsh-Pond	TNT	88.5	43.5	DANT
	Parathion	95.36	18%	.
Pond-Marsh	TNT	95.8	35.8	DANT
	Parathion	98.70	27%	.
Marsh	TNT	85.6	25.6	ADNT
Pond	TNT	92	19.2	ADNT

References

- Spaulding, R.F. and Fulton, J.W. : Groundwater Munition Residues and Nitrate near Grand Island, Nebraska, U.S.A, *J. Contaminant Hydrol.*, 29, 139–153,1988.
- Bhadra, R., et al. : Characterization of Oxidation Products of TNT Metabolism in

Aquatic Phytoremediation Systems of *Myriophyllum aquaticum*. *Environ. Sci. Technol.*, **33**, 3354-3361,1999.

Yinon, J. : Toxicity and Metabolism of Explosives. CRC Press, Boca Raton, Fla., pp. 81-122,1990.

Kadlec, R.H. and Knight, R.L. : Treatment Wetlands. Lewis Publishers, CRC Press, pp. 181–280,1996.