SUPPRESSION OF ENDOSULFAN UPTAKE IN ORIENTAL RADISH BY CHARCOAL AND ACTIVATED CARBON AMENDMENT IN SOIL

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Introduction

Endosulfan is organochlorine insecticide and was listed on persistent organic pollutants at Stockholm convention in 2009. In Korea it was prohibited from crop application in 2004 and abandoned in 2011. But its half-life in soil ranges from 19 days to150 days and remains in field nowadays. And it was translocated to the crop and frequently detected in agricultural products. So this study was conducted for prevent the uptake of endosulfan to crop form the soil residue. We used the activated carbon and powdered oak charcoal which has been shown to be effective in adsorption and sequestration of organic contaminants.

Materials and methods

Adsorbents

Powdered activated carbon was from Sincol (Tokyo, Japan) and three charcoals (powdered oak charcoal, granulated oak charcoal, rice husk charcoal) were purchased in Korea. These three charcoals are sold as agro-materials for soil amendment. And organic material rich soil was from Jeju Island and had more organic materials (40.1 g kg^{-1}) than average OM contents of upland soil in Korea (2).

Plant growth experiment

Oriental radish (*Raphanus sativus var. sativus*) was used as the test plant in this experiment. Seeds were sowed in plastic pot (20 cm in diameter and 14 cm in height) as a closed system allowing no leaching of water or the pesticide. The fresh soil used in this experiment was collected from the surface soil layer (0-20 cm) in an organic farming field of National Academy of Agricultural Science in Suwon. Each pot was filled with 2 kg (dry weight) of the adsorbent-free soil or adsorbent-amended soils. Then 1.4g of dust formulation containing 3% endosulfan was mixed with soil of each pot, resulting in a spiked concentration of 21 mg kg^{-1} of endosulfan. The six treatments used in this experiment were control (0% adsorbent), four amendments with powdered activated carbon, powdered oak charcoal, granulated oak charcoal under 2 mm particle size and rice husk charcoal (1%) and organic material rich soil (1%). Each treatment was carried ou in five replicates. The pots were irrigated and stayed for 1 month. Oriental radish seeds were sowed in each pots and growed for 4 months in green house. The plants were watered every day.

At the end of the experiment, the plants were cut as roots and leaves and weighed to obtain the fresh weights. Radish roots were gently washed with tap water to remove the soil particle on the rood surface and air-dried at room temperature for 2 h. The radish roots and leaves were chopped and stored in the refrigerator until the residue analysis. After the plants were removed from the soil, soils were collected and air-dried in the shadow at room temperature for 48 h.

Endosulfan Residue analysis

To determine the residue of α-endosulfan, β- endosulfan and endosulfan sulfate in soils and plants, we followed the analysis method of Park *et al.*(1) with modification. Briefly each samples (25 g of soils and plants) were extracted with 100 mL of acetone and filtered. The extracts were concentrated and re-extracted with dichloromethane. After concentration of dichloromethane, extracts were dissolved with hexane and cleaned up with florisil (60~100 mesh) which had been activated in 130℃ for over 18 h. The eluates of samples were concentrated and dissolved with hexane and used for instrumental analysis with GC-ECD. An Agilent 5890 gas chromatograph with μ-ECD (Santa Clara, CA, USA) equipped with Rtx-5 (Restek, Bellefonte, PA, USA) was used for analysis of endosulfan in soils and radish samples. Instrumental conditions are discribed below in Table 1.

Table 1. GC operating conditions for the analysis of endosulfan in soils and radishes

Instruments	GC-ECD Agilent 6890 with 7683 auto-sampler
Injection	1 μL splitless mode, 230℃
Column	Rtx-5, 30m × 0.25mm, film thickness 0.25μm
Carrier gas	N_2 (0.8 mL min^{-1}), total flow N_2 (60 ml min^{-1})
Oven temperature	Initial 150℃ (held for 2 min) Raised to 260℃ at 10℃ min^{-1} (held for 5 min) Raised to 280℃ at 5℃ min^{-1} (held for 7 min)
Detector temperature	300℃

Results and discussion

Present findings and impact of your research. Please embed your tables and figures in the text[3].

The biomass of fresh weights of Oriental radish of adsorbent amended soil was slightly enhanced. Fresh weight of radish harvested from powdered activated carbon and powdered oak charcoal treatment was 452.9 and 474.1 g pot^{-1}. They showed slightly higher yield but they had no significant difference. Several papers had reported yield increase effect of charcoal or biochar amendment (3, 4). But the container used in this experiment did not have sufficient height and soil volume for Oriental radish growth. So it cannot be sure that there was no yield increase effect of adsorbent treatment.

Table 2. Average fresh weight of Oriental radish harvested from six treatments (g pot^{-1}).

	Radish root	Radish leaf	Sum
Control	182.7	231.9	414.6
Powdered Activated Carbon	267.2	185.7	452.9
Powdered Oak Charcoal	291.2	182.9	474.1
Granulated Oak Charcoal	276.4	149.1	425.6
Rice Husk Charcoal	238.0	185.2	423.2
Organic Material Rich Soil	259.7	178.3	438.0

After 4 months of growth in the adsorbent amended soils, the residues of endosulfan were determined in the soils, radish roots and radish leaves separately. The concentrations of endosulfan in all samples are described in Table 3. The concentration of endosulfan (total) in control soil was 8.64 mg kg^{-1} and in powdered activated carbon amended soil showed highest value of 12.16 mg kg^{-1}. And lowest concentration was showed in powdered oak charcoal amended soil because of low concentration of endosulfan sulfate. Activated carbon and biochars are known to good adsorbent for most of organic contaminants and lead to the increase of half-life of pesticide (5). In this result, powdered oak charcoal amendment to soil leaded to decrease of endosulfan sulfate. It needs to further study of adsorbent characteristics. The other adsorbents and soil showed similar results of control soil and Saito *et al.*(6). The residue of endosulfan in radish root and leaf was significantly decreased with powdered activated carbon and powdered oak charcoal amended soil. But granulated oak charcoal, rice husk charcoal and organic material rich soil did not affect to the uptake of endosulfan in plant.

Table 3. Concentration of endosulfan in soil, radish root, radish leaf

		Control	Powdered Activated Carbon	Powdered Oak Charcoal	Granulated Oak Charcoal	Rice husk Charcoal	Organic Material Rich Soil
Concentration in Soil (mg kg^{-1})	α-endosulfan	3.56	5.94	3.24	3.99	3.39	3.05
	β- endosulfan	3.37	4.73	2.17	3.87	3.35	3.19
	endosulfan sulfate	1.71	1.49	0.56	2.42	1.91	2.31
	Endosulfan (Total)	**8.64**	**12.16**	**5.97**	**10.28**	**8.65**	**8.55**
Concentration in Radish Root (mg kg^{-1})	α-endosulfan	0.0209	0.0049	0.0010	0.0207	0.0120	0.0083
	β- endosulfan	0.0261	0.0075	0.0012	0.0283	0.0141	0.0121
	endosulfan sulfate	0.1650	0.0574	0.0098	0.2457	0.1236	0.1296
	Endosulfan (Total)	**0.2120**	**0.0698**	**0.0120**	**0.2946**	**0.1497**	**0.1501**
Concentration in Radish Leaf (mg kg^{-1})	α-endosulfan	0.0014	0.0012	0.0006	0.0016	0.0012	0.0009
	β- endosulfan	0.0015	0.0016	0.0006	0.0014	0.0018	0.0011
	endosulfan sulfate	0.0308	0.0232	0.0035	0.0430	0.0308	0.0603
	Endosulfan (Total)	**0.0337**	**0.0260**	**0.0047**	**0.0460**	**0.0338**	**0.0623**

Root concentration factor (RCF) was calculated by dividing the endosulfan (total) concentration of radish root by the concentration of soil at the harvest. The RCFs of endosulfan are discribed in Table 4. For the plants of untreated soil, the RCF was 0.025 as total endosulfan and it was mainly due to the endosulfan sulfate. For the plants grown in the soils amended with powderd activated carbon and powdered oak charcoal, the RCF values were 0.006 and 0.002. With rice husk charcoal and organic materila rich soil amendement, the corresponding RCF values were 0.017 and 0.018. The RCF value of granulated oak charcoal was 0.029.

Table 4. Comparison of the root concentration factor

	α-Endosulfan	*β-Endosulfan*	*Endosulfan sulfate*	*Total Endosulfan*
Control	0.0059	0.0078	0.0965	0.025
Powdered Activated Carbon	0.0008	0.0016	0.0385	0.006
Powdered Oak Charcoal	0.0003	0.0006	0.0176	0.002
Granulated Oak Charcoal	0.0052	0.0073	0.1015	0.029
Rice Husk Charcoal	0.0035	0.0042	0.0646	0.017
Organic Material Rich Soil	0.0027	0.0038	0.0561	0.018

This study showed that powdered activated carbon and powdered oak charcoal amendment in a soil could reduce the uptake of pesticide to plant grown in highly contaminated soil. Powdered activated carbon and powdered oak charcoal is likely to be more effective than rice husk charcoal and granulated oak charcoal, mainly due to its higher surface area and greater absorption capacity. But reduction mechanism might be different. However, in some kind of adsorbent like granulated oak charcoal can increase the uptake of contaminants. Soil amendment with absorbent or biochar for carbon sequestration purposes and soil improvement can be applied as remediation technique to minimize pesticide residue in agricultural products from highly contaminated soils. And the adsorbent would be carefully chose.

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