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ORIGINAL ARTICLES

Performance Evaluation for Endosulfan Removal by Carbon-based Adsorbents

Heesoo Eun[1]*, Geunhyoung Choi[2†], Dal-Soon Choi[2], Su-Myeong Hong[2]

[1]*Research Center for Advanced Analysis, National Agriculture and Food Research Organization (NARO), 3-1-3 Kannondai, Tsukuba, Japan*

[2]*National Academy of Agricultural Science, Rural Development Administration (RDA), 166, Nongsaengmyeong-ro, Iseo-myeon, Wanju-gun, Jeollabuk-do 55365, Republic of Korea*

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Abstract The widespread use of endosulfan in agriculture has increased public concern regarding their residual presence in food and ecosystems. In this study, the removal efficiency of α- and β-endosulfan was evaluated with organic and inorganic adsorbents. The results indicate that carbon-based adsorbents (CBAs) are more effective for α- and β-endosulfan removal than non-CBAs (inorganic adsorbents). The removal efficiencies of α- and β-endosulfan in the solutions by powdered activated carbon (PAC) were 100%, by granular activated carbon (GAC) were 97%, by oak charcoal (OC) were 82% and 74%, and by rice husk charcoal (RHC) were 64% and 60%, respectively. Removal efficiencies of CBAs depend on their specific surface area and average pore size. In non-CBAs, silica and alumina exhibited poor removal efficiency for endosulfan; in contrast, Florisil and zeolite showed effective adsorption, especially for β-endosulfan. In the 9-day soil column leaching test in the CBAs-free and the PAC-, OC-, and RHC-added columns, α-endosulfan decreased in the leachate by 87%, 82%, and 63% and β-endosulfan decreased by 85%, 74%, and 60%, respectively. These differences in endosulfan removal performance were supported by scanning electronic microscopy results. Our results suggest that CBAs can be tentatively utilized for endosulfan removal from contaminated agricultural environment.

Key words carbon-based adsorbents(CBAs), α-endosulfan, β-endosulfan

Introduction

On January 1, 2019, Korea's Ministry of Food and Drug Safety adopted a pesticide Positive List System (PLS) to regulate agricultural chemical residues in food and food products (FAIRS, 2018). Thus, much focus is being placed on ensuring food safety. However, residues of a previously used pesticide, viz. endosulfan, are found around the world, causing various problems (Rolón et al., 2017; Odukkathil and Vasudevan, 2016; Sutherland et al., 2004). It is a widely used agricultural pesticide as a broad-spectrum insecticide worldwide on cotton, tea, sugarcane, vegetables, and fruit crops (Choi et al., 2018; EPA, 2010), despite its life-threatening toxic effects (Menezes et al., 2017). In 2011, the fifth meeting of the Conference of the Parties (COP5) to the Stockholm Convention on Persistent Organic Pollutants (POPs) listed technical endosulfan and its isomers (COP.5, 2011). POPs uptake by plants resulting in food contamination continues to be a problem, even where their application was discontinued decades ago, because of their persistence in the environment (Norstrom, 2002). Thus, the widespread use of endosulfan in agriculture has increased public concern regarding the presence of their residues in food and ecosystems.

In Korea also the problem of endosulfan residue had been occurring frequently. (Kim et al., 2020; Park et al., 2004). Furthermore, there are serious concerns that residual pesticides will persist in succeeding crops. This is a serious problem for farmland where pesticides that have a long persistence, such as endosulfan, are used. Various crops are

†Co-first author: This author contributed equally to this work.
E-mail: tendergreen@korea.kr

*Corresponding author
E-mail: eun@affrc.go.jp

generally cultivated seasonally in fields and greenhouses; therefore, there is a high possibility that pesticides that have not been used will remain. This is the current issue surrounding residual crops after pesticides use. Post-crop residue of pesticides is the unintentional uptake of residual pesticides on subsequent crops cultivated on the farmland after harvesting; the pesticides previously used remain in the soil, and the succeeding crops are contaminated (Bruce-Vanderpuije et al., 2021; Oh et al., 2020). There is a concern that the residual standard value of the Food Sanitation Law, especially the uniform standard, will be exceeded.

Numerous studies have been conducted on the removal of residual pesticides from soil and water using the physical properties of adsorption and aggregation, such as biochar, activated carbon, and zeolite (Varjani et al., 2019; Suo et al., 2019; Yonli et al., 2012). In particular, carbon-based adsorbents (CBAs) have a strong attraction for organic chemicals. For instance, granular activated carbon (GAC) has been used in industrial and municipal wastewater treatment and in various industrial processes (Hung et al., 2005). Biochar and charcoal are also often used for pesticides removal (Bae et al., 2019; Taha et al., 2014). Recently, char and activated carbon have been used to remove endosulfan in vegetables and soil (Choi et al., 2018). In our previous work, the efficiency of the removal of endosulfan and its metabolite was evaluated with organic and inorganic adsorbents (Choi et al., 2013). The result showed that activated carbon adsorbents are remarkably more effective for POPs removal in contaminated soils than non-activated carbon adsorbents. Moreover, activated carbon adsorbents were useful for POPs removal in water/soil systems (Eun et al., 2011). Therefore, the aim of this study was to investigate the removal efficiencies of various adsorbents for endosulfan in the water–soil system.

Materials and Methods

Chemicals & absorbents

All chemicals used were of analytical grade, used as received without any further purification, and obtained from Sigma-Aldrich (USA), Wako (Japan), and Merck (USA). Laboratory water was used from a Milli-Q system water purification (Millipore, USA) and hexane-washed water for analysis. The stock solution of endosulfan (α and β-endosulfan: Sigma-Aldrich, USA) was prepared in acetone (1,000 μg/mL) and used for calibration after dilution on appropriate concentration. Endosulfan standard solutions were prepared to 100 mL of distilled water, permeated for 0.5, 2, 12 h, left for 24 h, and 50 mL of the filtered supernatant was partitioned with dichloromethane and concentrated, then reconverted to 1 mL of *n*-hexane for quantification. For the treatment of a commercial grade zeolite, Florisil, silica, alumina, rice husk charcoal (RHC; Daewon GSI, Korea), oak charcoal (OC; Hongcheon chamsoot, Korea), 12-20 and 20-40 mesh granular activated carbon (GAC), and powdered activated carbon (PAC; Sincol, Tokyo, Japan) were used as adsorbents (Eun et al., 2011).

Removal efficiency of various adsorbents

In the batch reaction, an aqueous solution (100 mL) containing dissolved α-endosulfan and β-endosulfan (5 mg/L) was mixed with the adsorbent (0.5 g) in a bottle, kept on a shaker for 1 h, and kept at room temperature (25ºC) for 1 d. An initial screening study was conducted to examine the performance of all adsorbents at a fixed total endosulfan concentration. After completing the reaction, suspensions were centrifuged (10 min, 3600 rpm), filtered (0.45 μm syringe filter) to achieve solid-liquid separation, and extracted with dichloromethane. The extracted solution was filled up to 1 mL with n-hexane.

Soil column leaching test

The granulated soil was composed of 65% volcanic soil, 35% humus, and contained 200 mgL^{-1} nitrogen, 2500 mgL^{-1} phosphorus, 200 mgL^{-1} potassium, and 200 mgL^{-1} magnesium. The total carbon (TC) was 3.45%, EC was 1.0 mS/cm, pH 5.8-6.5, and particle diameter 0.5-3.0 mm, respectively. Soil column leaching studies were conducted according to OECD guidelines for the testing of chemicals (Test No. 312) with modification. Soil columns were packed with a granulated soil in glass columns of 5 cm (i.d.) × 60 cm (length) (Fig. 1). The granulated soil was sieved through 2 mm and 1 mm sieves. The glass column was filled with clean sand washed with pure water to 5 cm and granulated soil sieved with the 2 mm sieve to 30 cm for the control sample. The columns were covered with glass fiber filter to prevent surface disturbance. For comparison with the CBAs, CBAs were not added to the soil column in the control sample. Three separate glass columns were filled with soils mixed with 0.1 %wt OC, RHC, and PAC, respectively. The soil columns were saturated with 0.01 M $CaCl_2$ solution before pesticide application. And commercial formulation of

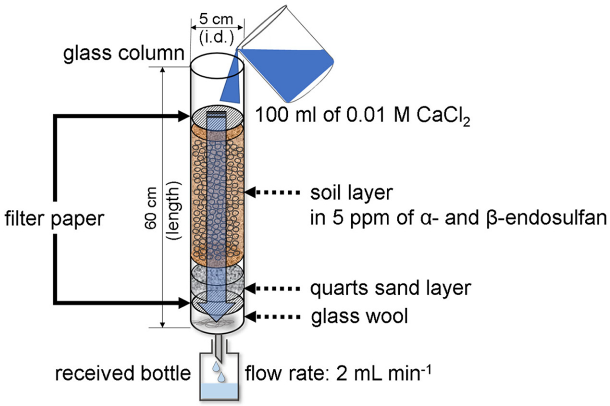

Fig. 1. Diagram of soil column leaching experiment.

endosulfan (Thiolix Dustable powder, 3% a.i.) was extracted with dichloromethane and resolved in methanol and used as 100 μg spiking solution for soil column.

Next, 1 mL of solution was spiked to the top of columns and remained in contact with soil for 24 h. Then, 100 mL of 0.01 M $CaCl_2$ solution was irrigated with a dropping funnel at a flow rate of 2 mL min^{-1}. After 24 h, the procedure was repeated, and leachates were collected daily in a glass flask that was kept away from light. For the 9-day soil column leaching test, the leachates were extracted with dichloromethane. The extracted solution was filled up to 1 mL with n-hexane.

Analysis

α-endosulfan and β-endosulfan were analyzed using EPA method 8081A. An Agilent 7890A gas chromatograph equipped with an electron-capture detector (GC/ECD) and automatic split-splitless injector was used. A non-polar DB-5 fused silica capillary column (30 m, 0.25 mm I.D., 0.25 μm film thickness) supplied by J&W Scientific (USA) was employed, using helium as the carrier gas at 1 mL min^{-1}. The column temperature was programmed from 100ºC to 160ºC at 15ºC min^{-1}, followed by 160ºC to 270ºC at 5ºC min^{-1} and maintained for 5 min. The injector port was maintained at 225ºC and the detector temperature was 300ºC. A 2 μL volume was injected. External standard methodology was used to assess the instrumental calibration. Instrument performance was evaluated in terms of linearity, LOD (α-endosulfan: 2 ng/mL, β-endosulfan: 0.5 ng/mL), and precision.

The UV-Vis spectra were acquired on aqueous Toluidine blue (TB) solutions using the high-performance Shimadzu UV-3150 spectrophotometer, operating with a resolution of ± 2 nm and a photometric accuracy of ± 0.005 AU. The temperature was maintained with a variation of ± 1°C, and the pH was ~7. The TB dye formed a meta chromic state and absorption bands appear at 550 nm and at 650 nm.

The specific surface area (N2-BET surface area) of all samples was determined using Autosorb-1, Quantachrome instruments (USA). Nitrogen adsorption isotherms were obtained at liquid nitrogen temperature. Prior to the determination of the adsorption isotherm, the sample was degassed at 120ºC.

The bases of the samples were subjected to platinum sputter coating and high-resolution scanning electronic microscopy (SEM; JEOL JSM-5610 LV, Tokyo, Japan) images were obtained in high vacuum mode at 20 kV.

Results and Discussion

Removal efficiency of various adsorbents

In this study, the residue of endosulfan sulfate, which is a main metabolite of endosulfan, was not examined because the test was carried out in a short term. Fig. 2 shows the removal efficiency by various adsorbents of 50 ng/g α-endosulfan and β-endosulfan from aqueous solution. Among them, the removal efficiency of carbon-based adsorbents (CBAs, organic adsorbents) was higher than noncarbon-based adsorbents (inorganic adsorbents). The removal efficiencies of α and β-endosulfan in the solutions by PAC were both 100%, by GAC were both 97%, by OC were 82 and 74%, respectively, and by RHC were 64 and 60%, respectively. The order of removal performance of endosulfan was PAC > GAC > OC > RH. CBAs are the most widespread technology used to manage sorption of water and soil contaminated by toxic organic chemical substances. PAC had the highest specific surface area (1052 m^2 g^{-1}) (Table 1), and the average pore size was 10.5 Å. PAC was the best performing because it is a fine powder which contains many cavities with a large number of reaction sites on which organic chemical substances can be adsorbed. The adsorption may occur via their surface area and the incorporation of α and β-endosulfan inside the pore cavity, providing a hydrophobic exterior. Activated carbons (ACs) have a high absorptivity to toxic organic chemical substances (Mohammad et al., 2020). The partitioning of organic chemicals between the solid and solution phase into the active matrix due to the sorption process depends on the physico-chemical characteristics of the surface. The removal

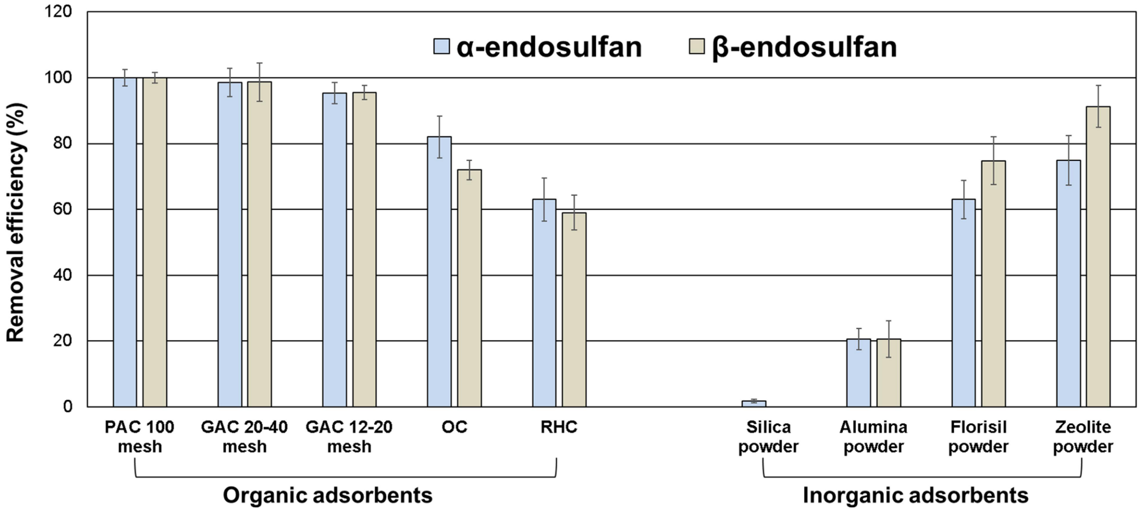

Fig. 2. Comparison of the removal efficiency of α and β-endosulfan by organic and inorganic adsorbents (PAC: powdered activated carbon, 12-20 and 20-40 mesh GAC: granular activated carbon, OC: oak charcoal, RHC: rice husk charcoal).

Table 1. Specific surface area of carbon-based adsorbent materials analyzed using the BET technique

Adsorbent materials	BET surface area (m^2g^{-1})	Average pore size
Rice husk charcoal	8	6.11 μm
Oak charcoal	190	35.90 nm
Granular activated carbon	815	4.01 Å
Powdered activated carbon	1052	10.50 Å

efficiency of CBAs increased over time and maintained a steady level, which was also observed in previous studies (Choi et al., 2013; Eun et al., 2011). There was a strong tendency toward decreased endosulfan concentrations in water with PAC and GAC treatment.

However, AC and GAC have some limitations when used as agricultural materials First, these materials are costly and require substantial investment by farmers. Further, because AC and GAC are fine powders, they are similar to dust and are difficult to apply. Conversely, OC is cheaper than AC and GAC, and it is relatively easy to handle as an agricultural material. In addition, RHC has the advantage that it can be naturally produced by effectively utilizing rice husks, which has become a source of substantial agricultural waste. As a soil conditioner, RHC can reduce the financial burden on farmers. Therefore, it was shown that OC and RHC are promising agricultural materials, although they are less effective than PAC and GAC on endosulfan. Silica, alumina, Florisil, and zeolite are typically used as inorganic materials in pesticide purification experiments. Bapat et al. (Bapat et al., 2016) and Stadler et al. (Stadler et al., 2010) reported that silica and alumina are effective pesticide absorbents. However, in their studies, silica and alumina showed poor removal efficiency for endosulfan. The adsorption mechanism depends on differences in polarity between the different feed components. The more polar a molecule, the more strongly it will be adsorbed by a polar stationary phase, and vice versa. This is because silica and alumina are polar stationary phase. Interestingly, however, Florisil and zeolite adsorbents exhibited effective adsorption capacity for endosulfan, especially for β-endosulfan. Yonli et al. also reported that zeolite is an effective material for the adsorptive removal of endosulfan from water (Yonli et al., 2012). Because of these unique properties, zeolites can be shape and size selective in catalytic molecular rearrangements, which may be caused by its water-solubility. The water-solubilities of α-endosulfan and β-endosulfan are 0.32 and 033 mg/L, respectively.

Consequently, among the various adsorbents, the removal efficiencies of CBAs are higher than those of non-CBAs. CBAs can purify a solution of endosulfan by adsorbing 60-100%.

Dye decolorization

One of the most common adsorbing tests of organic chemicals is the dye decolorization test, which has been systematically evaluated in CBAs. The dye test is simple and rapid, and is usually conducted by monitoring the dye absorbance at a specific wavelength as a function of reaction time (Azari et al., 2020; Li et al., 2020). Based on the removal efficiency results of CBAs (Fig. 2), the dye

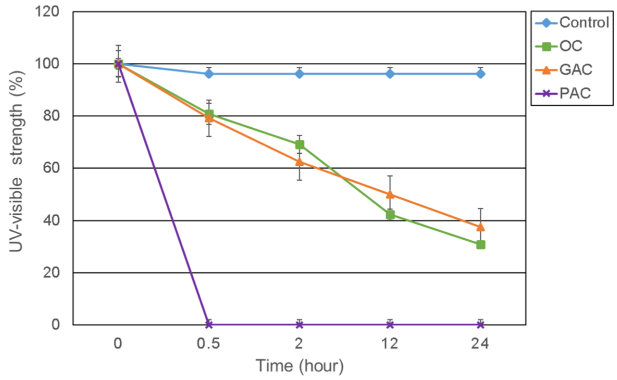

Fig. 3. Comparison of dye toluidine blue (TB) decolonization for carbon adsorbents (PAC: powdered activated carbon, GAC: granular activated carbon, OC: oak charcoal).

adsorption performance was compared for the top three materials that showed effective adsorption performance. Fig. 3 shows the comparison of dye toluidine blue (TB) decolorization for CBAs. In this study, the organic dye was absorbed in water without stirring. PAC adsorbed TB in water in 30 min and maintained its decolorization ability thereafter. Interestingly, GAC and OC showed similar reaction tendencies to TB. As shown in Table 1, although GAC should be more advantageous for the adsorption performance of organic substances than OC in terms of specific surface area and average pore size, the decoloni-zation ability of TB dye is almost the same. In general, GAC is the adsorbent material the most widely used for purifying public water systems. However, some organic species cannot be removed completely using GAC.

Scanning electronic microscopy (SEM) micrographs of CBAs

Fig. 4 shows the surface morphologies of the three types of CBAs (RHC, OC, and PAC). The images with a spatial resolution of 50 show that the particles of RHC and OC are bigger than those of PAC. The images of carbon adsorbents with spatial resolutions of 5,000 and 10,000 show that only PAC maintained particle integrity; RHC and OC showed widely smooth surface conditions. The results clearly supported the soil column leaching test. Specifically, this indicates that the hydrophobic exteriors of RHC and OC mainly adsorbed α and β-endosulfan in leached solutions. In contrast, PAC uses its pore cavities and its hydrophobic exterior to achieve high adsorptive capacity. The removal efficiency of organic chemical substances depends on the specific surface area and average pore size of the adsorbent. As a result, PAC (activated carbons) shows higher removal efficiency than non-activated carbons (RHC and OC).

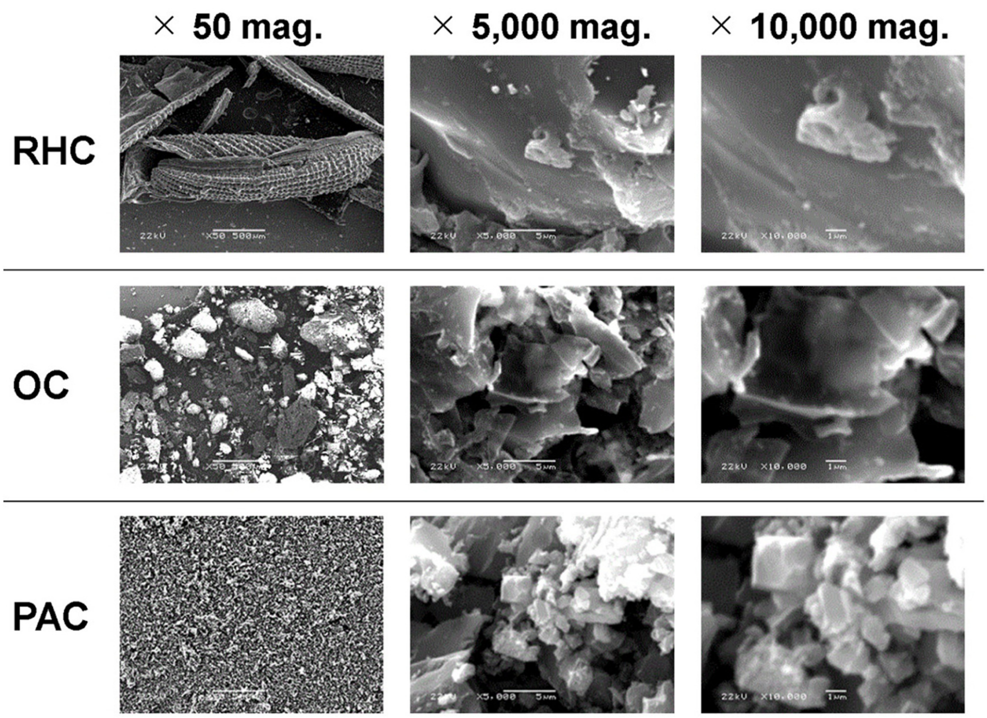

Fig. 4. Scanning electronic microscopy (SEM) micrographs of carbon-based adsorbents (CBAs) (RHC: rice husk charcoal, OC: oak charcoal, PAC: powdered activated carbon).

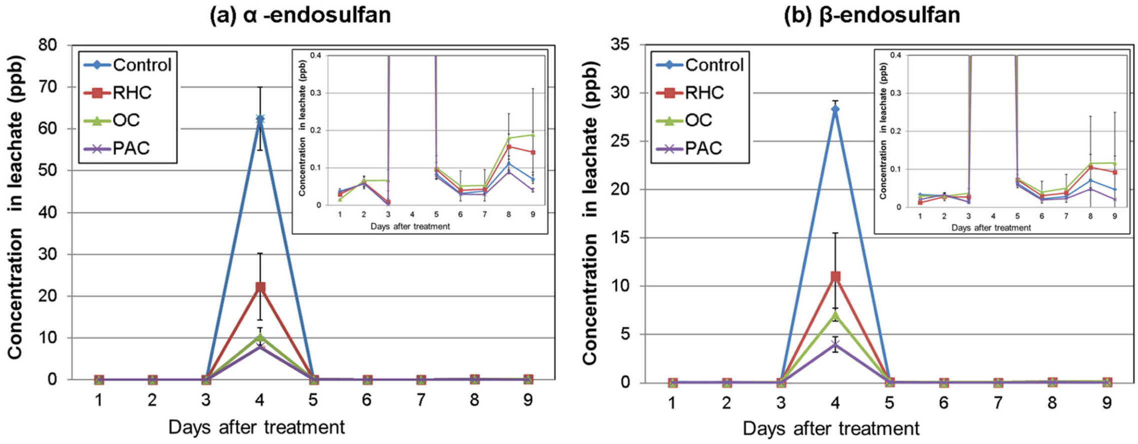

Fig. 5. Elution comparison of α (a) and β-endosulfan (b) in the leaching test of carbon-based materials mixed soil column. The magnified inset illustrates differences in concentration except for day 4 (PAC: powdered activated carbon, OC: oak charcoal, RHC: rice husk charcoal).

Soil column leaching test

The reaction tendencies of GAC and OC were similar, thus, the adsorption efficiencies of endosulfan by PAC, OC, and RHC were investigated using the soil column leaching test (Fig. 5). The soil column was eluted with 100 mL of 0.01 M $CaCl_2$ aqueous solution for 9 days (Fig. 1). Leaching phenomena differed according to CBA type. As the total carbon (TC) of the tested soil was 3.45%, adsorption of α and β-endosulfan was observed in the control. The results show a maximum leaching amount of endosulfan on day 4 (the total eluate 400 mL). Subsequently, all the column maintained the adsorption performance by CBAs. α and β-endosulfan leaching in the soil column. When the results of CBAs-free column and PAC-, OC-, and RHC-added columns were compared, it was observed that α-endosulfan decreased in the leachate by 87%, 82%, and 63% and β-endosulfan decreased by 85%, 74%, and 60%, respectively. This may occur as a result of the adsorption and desorption interactions owing to the physico-chemical properties of the CBAs absorbent. In other words, it will depend on their specific surface area and the size of the average pore (Table 1). These differences in the endosulfan removal performance were also supported by SEM results (Fig. 4).

However, though the concentrations of α- and β-endosulfan decreased in the column of CBAs mixed with the soil, a small amount of endosulfan leached into the lower layer due to the continuous water-like mobile phase. It is suggested that even if CBAs are applied to the agricultural field, some endosulfan may leach into the groundwater depending on the time and mobile phase. Therefore, it is suggested that the use of CBAs is effective for the purpose of temporarily preventing endosulfan absorption and subsequent transfer to agricultural products, but it probably cannot prevent long-term leachate to the ground water.

Conclusions

Carbon-based adsorbents (CBAs) have been used to remove organic pollutants from contaminated sources. The removal efficiencies of endosulfan by CBAs were substantially more effective than those of non-CBAs in the study. The removal efficiency of organic chemical substances depends on the specific surface area and the average pore size of the carbon adsorbent. Interestingly, the non- CBAs Florisil and zeolite showed effective adsorption capacity of endosulfan. In the soil column leaching test of PAC, OC, and RHC, the adsorption performance was maintained. However, although CBAs are mixed with the soil, endosulfan may leach into the groundwater. This study suggests that CBAs can be tentatively utilized as a suitable material for endosulfan removal in contaminated agricultural environment and may assist in ensuring the safety of agricultural products.

Author Information and Contributions

Heesoo Eun, Research Center for Advanced Analysis, National Agriculture and Food Research

Organization (NARO), Principal researcher, https://orcid.org/0000-0003-4334-5917

Geun Hyoung Choi, National Academy of Agricultural Science (NAAS) of the Rural Development Administration (RDA). Agricultural researcher, http://orcid.org/0000-0003-1991-1544

Dal-Soon Choi, National Academy of Agricultural Science (NAAS) of the Rural Development Administration (RDA), Senior agricultural researcher, https://orcid.org/0000-0001-7106-5918

Su-Myeong Hong, National Academy of Agricultural Science (NAAS) of the Rural Development Administration (RDA), Senior agricultural researcher, https://orcid.org/0000-0003-2035-5039

Experimental work: H. E., and G. C., drafting and writing of the manuscript: H. E. and G. C., reviewing of the manuscript: H. E., G. C., D. C., and S. H.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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