EVALUATION OF ADSORBENTS FOR THE REMOVAL OF ENDOSULFAN FROM CONTAMINATED SOILS

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Introduction

Contamination of the environment from a variety of sources has become an increasingly serious problem in recent years. Persistent organic pollutants (POPs), such as dioxins, PCBs, and organochlorine pesticides, are persistent, bioaccumualtive and toxic environmental contaminants. POPs have been of great concern due to their occurrence in high concentrations even in remote ecosystems, despite bans on production and usage. [1, 2] In May 2011, the fifth meeting of the Conference of the Parties (COP5) to the Stockholm Convention on POPs decided to list technical endosulfan and its isomers in Annex A with exemptions for specified crop-pest complexes [3]. Endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9, 9a-hexahydro-6, 9-methano-2,3,4-benzo(e)dioxathiepin-3-oxide) is a chlorinated hydrocarbon insecticide and acaricide of the cyclodiene subgroup. Technical endosulfan is a 7:3 mixture of stereoisomers i.e. α and β-endosulfan and major metabolite is endosulfan sulfate. It acts as a contact poison to a wide variety of insects and mites.

Especially, it is widely used as a broad spectrum insecticide worldwide on cotton, tea, sugarcane, vegetables, and fruit crops (U.S. EPA, 2002)[4]. Organochlorine pesticide (OCP) uptake resulting in food and feed contamination continues to be a problem even where applications were discontinued decades ago because of their persistence in the environment[5,6]. Thus, the widespread use of endosulfan and its metabolites in agriculture has increased the public concern on the presence of their residues in foods and environment.

Our current work aims to investigate the removal efficiencies of different adsorbents for freely dissolved endosulfan in the soil solution, resulting in enhancement of their removal efficiency.

Materials and methods

Adsorbents ;For the treatment of a commercial grade zeolite, florisil, silica, alumina, oak charcoal (OC), granular activated carbon (GAC) , rice husk charcoal (RH) and powdered activated carbon (PAC) were used as adsorbents. Laboratory water was used with a Milli-Q system water purification (Millipore, USA) and hexane-washed water for analysis.

Soil column leaching; The granulated soil is composed of 65% of volcanic soil, 35% of humus, and contained 200 mgL^{-1} nitrogen, 2500 mgL^{-1} phosphorus, 200 mgL^{-1} potassium, and 200 mgL^{-1} magnesium.Soil column leaching studies were done as OECD guidelines for the testing of chemicals (Test No. 312) with modification. Soil columns were pack with a granulated soil (Nippi Engei-Baido-1gou; Nihon Hiryo Co., Tokyo, Japan) in glass columns of 5 cm (i.d.) x 60 cm (length). Bottom of columns were plugged with little amount of glass wool. A granulated soil was sieved and selected between 2mm and 1mm sieve. Clean sand washed with pure water was filled up to 5 cm and a granulated soil sieved with 2 mm sieve up to 30 cm for control sample. Top of columns were covered with glass fiber filter to prevent the disturbance of surface. The pore volume of column was measured by the volume difference of water between poured and drained. Soils mixed with activated carbon, rice husk charcoal, oak charcoal and organic matter rich soil for 0.1 % and organic matter rich soil for 1% by weight were filled in three glass columns each.And soil columns were saturated with 0.01M CaCl2 solution before pesticide application. A commercial formulation of endosulfan (Thiolix Dustable powder, 3% a.i.) was extracted with dichloromethane and concentrated. Then it was dissolved with methanol. Its concentration was determined with GC/MS. 1 mL of solution was spiked to the top of columns and remained in contact with soil for 24 h. Then 100ml of 0.01M CaCl2 solution was irrigated with dropping funnel and flow rate was 2mL/min. After 24 h the procedure was repeated and leachates were collected for everyday in glass flask prevented from the light.

In a typical batch reaction, an aqueous solution (100 ml) containing dissolved α-endosulfan, β-endosulfan, and endosulfan sulfate (5 ppm) was mixed with the adsorbent (0.5 g) in a bottle, kept on a shaker for 1 hour and stood 1 day at room temperature. An initial screening study was conducted to examine 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 dichlormethan. The extracted solution was filled up to 1ml with hexane.

The analysis of α-endosulfan, β-endosulfan, and endosulfan sulfate based on EPA method 8081A. A 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 (30m, 0.25 mm I.D.) and 0.25 m film thickness supplied by J&W Scientific, was employed, with helium as carrier gas at 1 ml /min. The column temperature was programmed at 100 ºC to 160 ºC at 15 ºC /min, followed by 160 ºC to 270 ºC at 5 ºC /min, held 5 min. The injector port was maintained at 225 ºC and the detector temperature was 300 ºC. A 2 μl volume was injected. The specific surface area (N2-BET surface area) of all samples was determined by using a Autosorb-1, Quantachrome instruments. Nitrogen adsorption isotherms were obtained at liquid nitrogen temperature. Prior to the determination of the adsorption isotherm, the sample was outgassed at 120 ºC.

A JEOL JSM-5610LV scanning electronic microscopy was used to take the micrographs of the samples.

Results and discussion

Fig. 1 shows the efficiencies of adsorbents in the removal of α-endosulfan, β-endosulfan, and endosulfan sulfate from aqueous solution. The removal efficiency of activated carbons (ACs) is at a higher level than that of non-ACs. ACs can purify a solution of endosulfan and its metabolites, by adsorbing 95% to 100%. The silica sorbent also exhibited good adsorption abilities for α-endosulfan andβ-endosulfan, but endosulfan sulfate is not strongly adsorbed. It may be caused by their water-solubility. The water-solubility of α-endosulfan, β-endosulfan and endosulfan sulfate is 0.32, 033 and 0.48 mg/L, respectively.

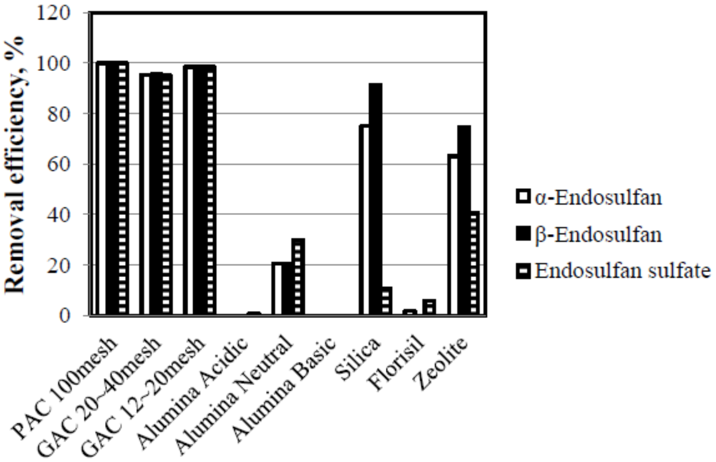


Fig.1 Comparison of removal efficiencies for endosulfan and its metabolites.

The florisil and the three different types of alumina show poor removal efficiency for endosulfan and its metabolites. The adsorption mechanism depends upon 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. Similarly, the more non-polar a molecule, the more strongly it will be adsorbed by non-polar stationary phase. This is because florisil and alumina are polar stationary phase. Zeolite adsorbent shows good adsorption capacity to adsorb endosulfan and its metabolites. Because of these unique properties, zeolites are able to be shape and size selective in catalytic molecular rearrangements.

ACs are the most widespread technology used to deal with sorption of water and soil contaminated by toxic organic chemical substances. ACs have a high adsorptivity to toxic organic chemical substances. The partitioning of organic chemicals between the solid and solution phase into the active matrix due to sorption process, depends on the physico-chemical characteristics of the surface.

The removal efficiency of ACs increased with time and maintained a steady level. This steady level was also observed in earlier studies [7, 8]. There was a strong tendency towards decreased endosulfan concentrations in water with ACs treatment.

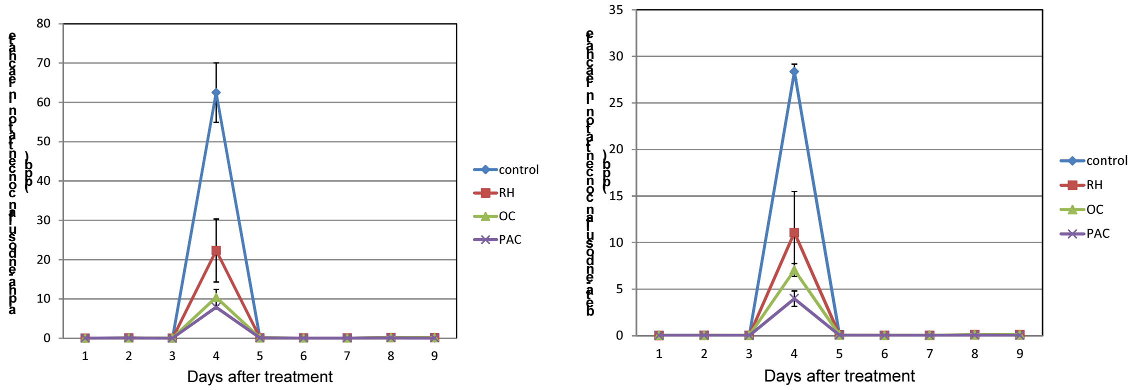
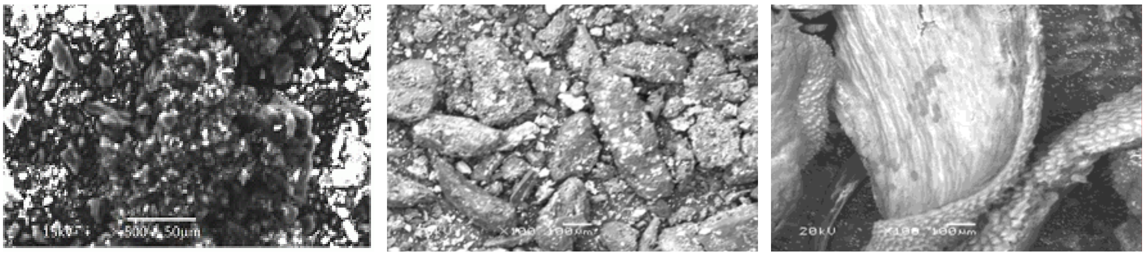


Fig.2 Elution comparison of endosulfan in the leaching test of carbon-based material mixed soil column （Left: α-endosulfan, right: β-endosulfan）

Among the carbon adsorbents, it was investigated the adsorption efficiency for endosulfan using soil column leaching test. The soil column was eluted with 100ml of 0.01M $CaCl_2$ aqueous solution for 9 days. The results show a maximum amount of endosulfan for day 4 (the total eluate 400mL). The concentration of α -endosulfan and β-endosulfan were decreased in the column of carbon adsorbents mixed with the soil. The order of adsorption performance of endosulfan is powder activated carbon (PAC) > Oak (OC) > rice husk charcoal (RH). In particular, powdered activated carbon (PAC) treatment was remarkably effective. PAC was 962 m^2 g^{-1} of the specific surface area and the average pore size was 10.5 Å. Fig. 3 shows the surface morphologies of the carbon adsorbents. The expected mechanism may be through the incorporation of α-endosulfan and β-endosulfan inside the pore cavity, providing a hydrophobic exterior, which enables the sorption of endosulfan sulfate. As a result, PAC shows much higher removal efficiency than RH and OC (non-activated carbon). It is well known that the removal efficiency of organic chemical substances depend on the specific surface area of the adsorbent. Thus, PAC indicates much higher adsorption efficiency for endosulfan than non-activated carbon.



powder activated carbon (PAC) (b) Oak (OC) (c) rice husk charcoal (RH)

Fig.3 SEM micrographs of powdered activated carbon (PAC).

From the above results, ACs (PAC) can be tentatively proposed as a suitable method for endosulfan and its metabolites removal in contaminated agricultural soils. Therefore, PAC is very useful for endosulfan and its metabolites removal in water/soil, and that may provide a useful means to protect agricultural products safety.The conclusions section should come at the end of the article.

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Acknowledgements

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