PERFORMANCE EVALUATION OF CARBON ADSORBENTS FOR THE REMOVAL OF ENDOSULFAN FROM CONTAMINATED SOILS

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Introduction

In 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[1]. 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 its major metabolite is endosulfan sulfate. It acts as a contact poison to a wide variety of insects and mites. Chiefly, it is widely used as a broad spectrum insecticide worldwide on cotton, tea, sugarcane, vegetables, and fruit crops (U.S. EPA, 2002)[2]. 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[3-5]. 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 ecosystem. Although these cyclodiene compounds are persistent in many agricultural land areas until now, there are no exact solutions on how to properly reduce if not eliminate them.

Charcoal and granular activated carbon (GAC) have been used to remove organic organic pollutants and toxins from public water supplies. Especially, GAC has been used in industrial and municipal wastewater treatment and in various industrial process applications. In our previous work, the efficiency of the removal of endosulfan and its metabolite was evaluated with organic and inorganic adsorbents[6]. The result showed that activated carbon adsorbents were remarkably effective for the endosulfan contaminated soils than non-activated carbon adsorbents. Moreover, activated carbon adsorbents were very useful for endosulfan and its metabolites removal in water/soil system[7]. The aim of this study is to investigate the removal efficiencies of different carbon adsorbents for freely dissolved endosulfan in the soil/water system.

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 (RHC) and powdered activated carbon (PAC) were used as adsorbents[6].

Soil column leaching test; 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 packed with a granulated soil in glass columns of 5 cm (i.d.) x 60 cm (length). 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 OC, RHC and PAC for 0.1 % by weight were filled in three glass columns each. The soil columns were saturated with 0.01M $CaCl_2$ solution before pesticide application. A commercial formulation of endosulfan (Thiolix Dustable powder, 3% a.i.) was extracted with dichloromethane and was evaporated/concentrated. 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 $CaCl_2$ solution was irrigated with dropping funnel and flow rate was 2mL/min. After 24 h, the procedure was repeated and leachates were collected every day in a glass flask that was kept 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 dichloromethane. The extracted solution was filled up to 1ml with hexane.

The analysis of α-endosulfan, β-endosulfan, and endosulfan sulfate is based on EPA method 8081A. The specific surface area (N2-BET surface area) of all samples was determined by using an Autosorb-1, Quantachrome instruments. A JEOL JSM-5610LV scanning electronic microscopy was used to take the micrographs of the samples.

Results and discussion

Fig. 1 shows the comparison of dye toluidine blue decolonization for carbon adsorbents. The organic dye was absorbed in water without stirring. The decolonization ability of powdered activated carbon (PAC) is very faster and higher level than that of charcoal and granular activated carbon (GAC). It indicates that PAC exhibited good adsorption ability for organic chemical substances in water than charcoal and GAC. From the obtained result (Table 1), although the surface area of GAC is bigger than that of charcoal, the decolonization ability of dye toluidine blue is almost the same. In general, GAC is the most widely used adsorbent materials for cleaning up public water systems. However, some organic species cannot be removed completely with the use of GAC. This result suggests that PAC is a more powerful adsorbent material for the removal of organic species in water than GAC.

Table 1. Surface area of carbon adsorbent materials

Adsorbent materials	Surface area
Charcoal (under 35mesh)	50 m^2/g
GAC (Granular Activated Carbon)	815 m^2/g
PAC (Powdered activated carbon)	1052 m^2/g

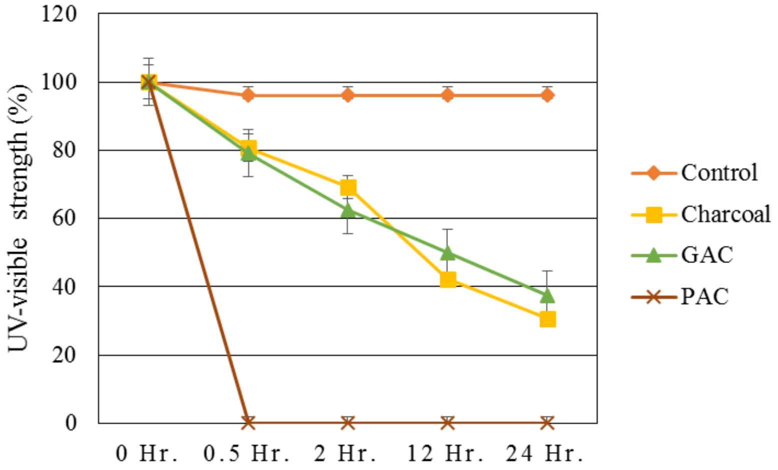


Fig. 1. Comparison of dye toluidine blue decolonization for carbon adsorbents

In the previous study[6], among the adsorbents, florisil and the three different types of alumina showed poor removal efficiency for endosulfan and its metabolites. This is because florisil and alumina are polar stationary phase. Conversely, zeolite adsorbent showed good adsorption capacity to adsorb endosulfan and its metabolites. With its unique properties, zeolites are able to shape and size selectively sort molecules in catalytic molecular rearrangements. Yonli *et al.* [7] exhibited the ability of adsorptive removal of α-endosulfan from water by hydrophobic zeolites. There was a linear relation between the adsorption capacities of α-endosulfan and the hydrophobicity (HI) of the samples. By determining the values of HI for a type of zeolite, it was possible to deduce the uptake of α-endosulfan.

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%. It is because that the more non-polar a molecule is, the more it will be adsorbed strongly by a non-polar stationary phase. The removal efficiency of ACs increased with time and maintained a steady level. This steady level was also observed in earlier studies [8, 9].

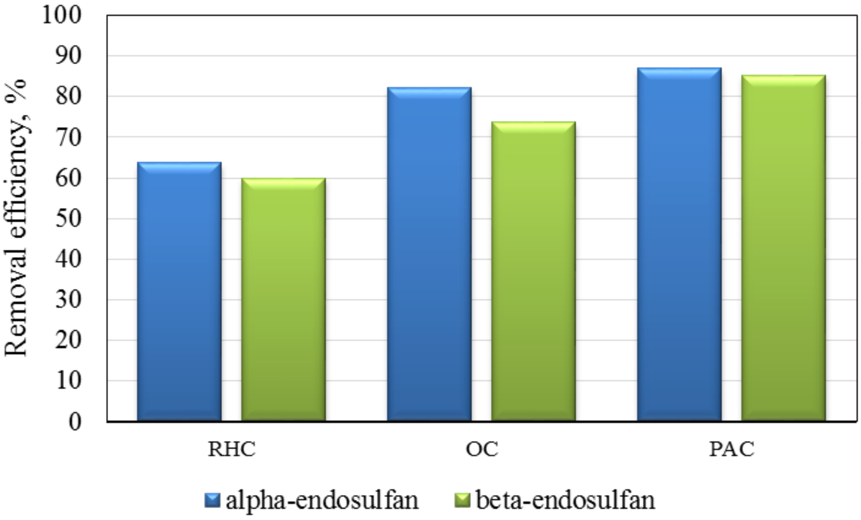


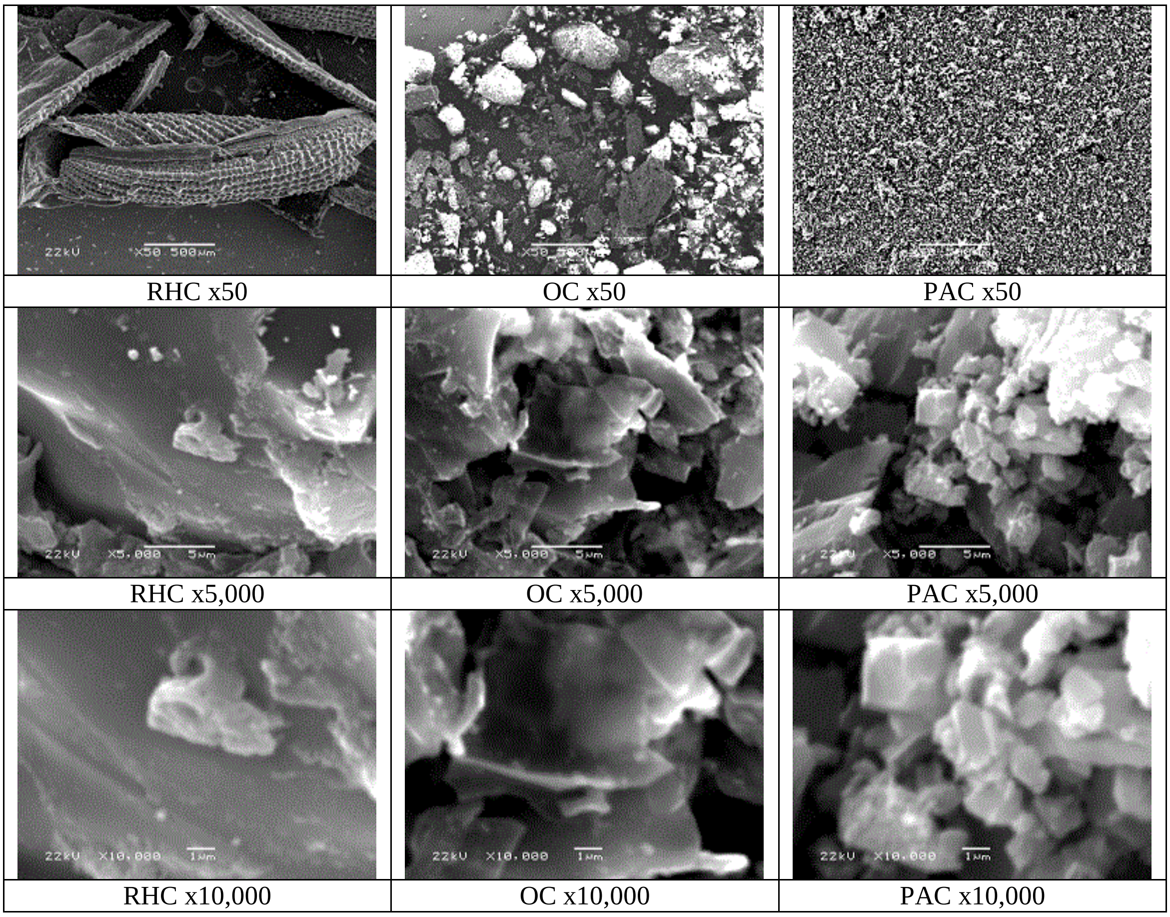
Fig. 2. Comparison of the removal efficiency for α and β-endosulfan by carbon adsorbents

Among the carbon adsorbent materials, oak charcoal (OC), rice husk charcoal (RHC) and powder activated carbon (PAC) were selected for soil amendment experiment from endosulfan added soil. The removal efficiency for endosulfan was investigated using soil column leaching test. The soil column was eluted with 100ml of 0.01M $CaCl_2$ aqueous solution for 9 days[10]. During 9 days, endosulfan sulfate was not determined from all leached solutions. The maximum amount of α and β-endosulfan was day 4 (the total eluate 400mL). After then, the concentration of α and β-endosulfan was decreased in leached solutions.

Fig. 2 shows the removal efficiency for α and β-endosulfan in the three types of carbon adsorbents mixed with the soil during 9 days. The removal efficiency for α and β-endosulfan in leached solutions by PAC was 87 % and 85 %, by OC was 82 % and 74 %, by RHC was 64 % and 60 %, respectively. The order of removal efficiency for α and β-endosulfan was PAC > OC > RHC. The mechanism may be through the incorporation of α and β-endosulfan inside the pore cavity, providing a hydrophobic exterior.

Fig. 3 shows the surface morphologies of the three types of carbon adsorbents. It is clear that the 50 times images of the particle of RHC and OC are bigger than that of PAC. In the 5,000 and 10,000 times image of carbon adsorbents, only PAC showed the remaining of their particles. RHC and OC showed widely smooth surface conditions. It indicates that the hydrophobic exteriors of RHC and OC mainly adsorbed α and β-endosulfan in leached solutions. On the other hand, PAC exhibiting its high adsorptive capacity, uses its pore cavities and its hydrophobic exterior. As a result, PAC shows higher removal efficiency than RH and OC (non-activated carbons). 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.

However, even if PAC has the highest specific surface area (962 m^2 g−1) than that of OC (190 m^2 g−1) and RHC (8 m^2 g−1), the obtained result showed that the removal efficiency was not remarkably different in leached solutions. The removal efficiency of PAC was decreased compare with water treatment experiments[6]. Therefore, it can be concluded that the adsorbent's specific surface area is not only a key factor for endosulfan removal in contaminated soils. Mishra and Patel[11] investigated the removal efficiency of endosulfan from water by two low cost adsorbents viz. sal wood charcoal and sand along with activated charcoal. The efficiency of sal wood charcoal is moderately high with 87%. Hence, non-activated carbon adsorbents, OC and RHC, which were less expensive adsorbents compared that of PAC, can be tentatively proposed as a suitable adsorbents for endosulfan removal in contaminated soils.



RHC x50 | OC x50 | PAC x50

RHC x5,000 | OC x5,000 | PAC x5,000

RHC x10,000 | OC x10,000 | PAC x10,000

Fig.3 SEM micrographs of carbon adsorbents.
(RHC: rice husk charcoal, OC: oak charcoal, PAC: powder activated carbon)

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