# Adsorption of chlorpyrifos on giant reed (*Arundo donax L.*)derivedbiochars

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Abstract. Adsorption of chlorpyrifos (CP) by giant reed(*Arundo donax L*.) derived biochars obtained at 300-600°C and their corresponding de-ashed biochars was investigated. With increasing pyrolysis temperature, the adsorption capacity( $Q_e$ ) of CP onto the biochars increased. The maximum values of  $Q_e$  of CP by the water-washed biochars (WBCs) and de-ashed biochars (BCFs) produced at 600°C were 4.8 mg/g and 8.9 mg/g, respectively. Pore-filling,  $\pi$ - $\pi$  electron donor-acceptor interaction hydrophobic interaction were the underlying mechanisms responsible for CP adsorption onto these biochars.

## Introduction

Organophosphorus pesticides(OPs) have been widely used to kill insects for obtaining healthy and high yields of crops. Over 500 various kinds of OPswere employedin agricultural production throughout the world[1]. Chlorpyrifos(CP) wasthe most widely used OPs with totalannual dosage of oversixty thousand tons used in the agricultural production around the world[6].Due to their insolubility, mobility and chemical stability, the residuals of OPsare frequently detected in soil, water, air and organic bodies[3],even vegetables and fruits,inducingserious environmental pollutionand harmful toanimals and human beings[4].Therefore, how to reduce Ops residuals in soil is an urgent task. Development offast and efficientmethodsare necessary to minimize residuals of OPs in diffrent conditions. A number of studies showed that biocharcould be a low-cost adsorbent to control OPs residuals.

Biochar(BC), asolid product fromheating biomass under limited oxygen supplied[7], has been used as an amendmenttoimprove soil quality, increase crop yields and sorbcontant minants water and soil[8, 9], because of its high surface area, abundant surface functional groups and mineral components. However, few data are available on the sorption behavior of CP by BC. In this study, the mechanisms responsible for CP adsorption by biochars were investigated.

## Materials and methods

Adsorbents. BC samples were produced fromgiant reed(*Arundo donax L.*) at 300-600°C as described by Zheng et al [10]. All BC samples were milled to pass a 120-mesh sieve. A portion of BC samples was washed by deinoized water four times to removal the excess minerals. The other portion of BC was rinsed with 1M HCl and 1M:1M HCl-HF solution four times, respectively. The deionized water-washed biochars (WBCs) and de-ashedbiochars (BCFs) were refferred to as WBCX and BCFX, respectively, where X represents heating treatment temperature (HTT). CP (purity >99%) wasobtained from Sigma-Aldrich Co.

**Sorption experiments.**CP stock solution (1g/L) were prepared in methanol solvent. The stock solution was diluted to0-1mg/L for CP, using a background solution containing0.01M CaCl<sub>2</sub> to maintain a constant ionic strength and 200mg/L NaN<sub>3</sub> to inhibit biological activity. The methanol content of the dilution was maintain below0.05% (v/v) to minimize the cosolvent effect. The sorption experiments were conducted in 15-mL glass vials with Teflon-lined screw caps.The pH of background solution was 6.5. All the vials were kept in dark and shaken for 24h for CPto reach sorption equilibrium.After centrifugation at 3000rpm for 10 min,theconcentrations were determined

by high-performance liquid chromatography (HPLC) with UV detection at 290nm.All samples were run in duplicate.

## **Results and discussion**

The scanning electronmicroscope (SEM) images of the WBCs and BCFs are shown in Fig. 1. The widely spatial arrangemet of particles on the surface of WBCs were more heterogenous than BCFs, resulting in the surface morphology of WBCs were largerly amorphous and uneven. It is reported that acid treatment could remove most of the minerals on BC [11]. The number of bright color particles on the surface of BCFs less thanthose of WBCs due to the acid treatment, it could be speculated that the particles were minerals. Therefore, BCFs had more smooth surface area compared with WBCs. With increasing HTT, the surface pore structure increased on the surface of the high-temperature BCbecause of more volatile matter released. However, minerals and tars could block the porosity on the surface of BC during pyrolysis process [12], acid-washed treatment could reduce these decomposition products.



Fig.1.SEM images of the biochars:(α)WBC300,(β)BCF300,(γ)WBC600,(δ)BCF600.WBC300 and WBC600 were water-washed biochars at heating temperature 300 °C and 600 °C; BCF300 and BCF 600 were de-ashed treatment biochars at heating temperature 300 °C and 600 °C.

The adsorption capacity  $(Q_e)$  of CP by WBCs and BCFs wereshown in Fig.2. At the same HTT, the  $Q_e$  values of CP by BCFs werehigher than those of WBCs. The  $Q_e$  values of the OPs for the BCFs was markedly higher than those of WBCs, indicating that the ash content in the biochars inhibited adsorption of CP by WBCs. The consistent results with previous study showed that the  $Q_e$  values of CP increased with the increasing HTT [5].



Fig.2.Adsorption capacity ofchlorpyrifos(CP)by the water-washed biochars (WBCs)and de-ashed treatment biochars (BCFs). The concentrations of CP was 1.0 mg/L.

The aromaticity and hydrophobicity of the BCs enhanced with increasing HTT due to the devotalization uring the pyrolysis process[13]. The logarithm of the1-octanol/water partition coefficient (log  $K_{ow}$ ) of CP is4.7, a low water solubility pesticide, thus CP could partition onto the hydrophobicity surface of biochars because of hydrophobic interaction. Therefore, BCFs contained more hydrophobic sites compared with WBCscould adsorbefficientlyCP via hydrophobic interaction(Fig.2). Pore-filling may be occurred for themoleculars of CP in themicropores biochars. The  $\pi$ - $\pi$ electron donor-acceptor interaction(EDA) interaction occured between the aromatic area of the biochars surface and the heteroaromatic ring in CP [14].

### Conclusions

The high-temperature biochars (e.g. WBC600, BCF600) possessed more pores compared with the low-temperature biochars (e.g. WBC300, BCF300), acid treatment increased thesmotheness of the BCFs due to the removal of the minerals BCs. The  $Q_e$  values of CP sorbed on these biochars increased with increasing HTT. In addition, the Qe values of WBCs werelower than those of BCFs, indicating that the minerals in WBCs inhibited the sorption of CP. These results could be helpful to promote application of plant-derived biochars in removal or immobilization of OPs inwater and soil.

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