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Soil Remediation by Biochar Derived from Agricultural Waste

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1. Introduction

Pesticides are increasingly used in agriculture to increase food production. However, accumulation and migration of pesticides in soil have been a matter of environmental concern [1-3]. Because many pesticides will migrate into ground and surface water with runoff and flow to food chain to cause human health risk by plant uptake [4, 5]. Therefore, pesticides migration control and removal have been focusing by scientists.

Biochar is the carbonaceous materials produced from oxygen–limited pyrolysis of biomass [6, 7]. Recently, biochar has become a hot spot because the application of biochar into farmland was advocated to provide approaches on sequestration of carbon and increase of soil fertility, as well as a low-cost adsorbent to remove different pollutants [8-10]. Variety of composition and structure of biochar is in terms of different stock and pyrolysis process[11]. Biochars show extraordinarily strong adsorption affinities for contaminants [12-14]. The adsorption of hydrophobic organic chemicals (HOCs) has been well documented [15-17]. The highly aromatic and porous structures in biochars, which favor both hydrophobic effect and specific interactions, have been suggested to contribute to the high adsorption coefficients. Hence, the application of biochars to soils can have a great impact on the fate of pesticides.

Besides, constructed wetland is an efficiency and ecological wastewater treatment technique which combined soil filtration, biodegradation and plants uptake. Constructed wetland contained filtration media, aquatic plants and bio-organisms, which was an ecological restoration for wastewater and contaminated soil.

The objective of this study was to investigate the effects of biochars on the fate of pesticides. In details, characteristics of biochars were analyzed and adsorption of the pesticides was revealed. In addition, biochar was applied as media in constructed wetland to identify purification effect of biochar in case study.

2. Method

Two kinds of biomass (maize straw and pig manure) were heated to two temperatures (350 ℃ and 700 ℃) to investigate the adsorption and catalytic hydrolysis of atrazine on the biochar, which were designed as MBC350, MBC700, PBC350, and PBC700, respectively.

Bulk elemental composition (C, H, and N) of the biochar samples was determined by an element analyzer. Ash content of samples was measured by the residual weight after heating the biochars at

750 ℃ for 6 h, and the O content was calculated by mass difference. Fourier transform infrared spectroscopy (FTIR) spectra of biochars were recorded between 4000 and 400 cm^{-1} wave numbers using an FTIR spectrometer.

Sorption isotherms for each biochar were determined at different initial solution concentrations. An aliquot of 50 mg of a sorbent was added in a 40 mL vial equipped with a Teflon–lined screw cap, followed by 40 mL of a background solution. The background solution contained 5 mM $CaCl_2$ to maintain a constant ionic strength and 200 mg/L $HgCl_2$ (pH 6.5) to inhibit aerobic biodegradation. Designated amounts of pesticide stock solutions were spiked into each vial. All the vials were left with minimal head space and sealed with Teflon film. The vials were put in a shaker operated at 150 rpm and 20 - 24 ℃ in the dark for 24 h to reach apparent equilibrium. Following equilibration, the vials were centrifuged at 3000 rpm for 20 min, and 2 mL of the supernatant was withdrawn and analyzed directly by high performance liquid chromatography (HPLC). The HPLC was equipped with a reverse phase column, XDB-C18 (Agilent Eclipse XDB-C18, 4.6 mm × 150 mm × 5 μm, 150 Å). Atrazine was determined with a variable wavelength UV detector at 223 nm. The mobile phase was methanol and water with an 85:15 (v/v) methanol-to-water ratio flowing at 0.5 mL/min. The adsorbed amount was calculated by the difference between initial and equilibrium concentrations in liquid phase.

A case study of biochar application was constructed in Xiamen City, China. A subsurface constructed wetland (SFCW) contained biochar as media to treat wastewater from an agritainment which was with average discharge of 10 m^3/d. Concentrations of COD was 284 mg/L, which was violated the wastewater discharge standard of the People's Republic of China (GB8978-2002) significantly. The subsurface constructed wetland was designed as 6 m (L)×3 m (W)×1.2 m (H) and contained 0.1 m height of clay, 0.2 m height of coarse gravel (grain size 50 mm), 0.5 m height of fine gravel (grain size 10-20 mm), 0.2 m height of sand (grand size 2 mm) and 0.2 m height soil-biochar (7:3,v/v). In addition, *Acorus calamus L.* and *Canna indica L.* were planted in the constructed wetland. COD of influent and effluent were tested to assess the effect of biochar.

3. Results

3.1 Composition and Characteristics of Biochar

Biochars derived from pig-manure contained high ash, however, biochars derived from straws had low ash contents. And the ash contents of biochar were increased with elevated temperature. Specific surface area and porosity of biochar were influence by feedstock and temperature. Porosity and specific surface area were increased at higher temperature. And specific surface area of biochar derived from straws was larger than that of biochar derived from pig-manure.

3.2 Isothermal Adsorption of Atrazine on Biochar

Adsorption isothermals of atrazine on biochars were fitted in Freundlich function and displayed nonlinear trends. The biochar derived from maize straw and pyrolyzed at 700 ℃ (MBC700) had the strongest adsorption affinity. The *Koc* of MBC700 was 104.50 L/kg at low solute concentration, and that was 103.10 L/kg at high solute concentration. Mechanism of adsorption of atrazine on biochars was combination of hydrophobic effect, pore-filling effect, inorganic moiety and specific effects. Contribution of inorganic moiety of PBC were negative in adsorption of atrazine. However, contribution of inorganic moiety of MBC pyrolyzed at 350 ℃ (MBC350) was negative in adsorption of atrazine, that of MBC pyrolyzed at 700 ℃ (MBC700) was positive. Atrazine could combine with O-functional groups and hydroxyl complexes on surface of biochars through H-bond effect. And atrazine could also combine with aromatic carbon of biochars through π-π electron donor and accepter effect.

3.3 Case Study

After 10 weeks, the COD concentrations of SFCW effluent ranged from 50 to 62 mg/L, with corresponding removal rates from 82% to 78%. SFCW reduced COD to meet the strict discharging requirement. Biochar could provide carbon source to microorganisms, release nutrition to plants, and adsorb organic pollutants, which played an important role in contaminants removal. During the operational period, the plant growth did not reach optimal status and there would be a potential for SFCW to approach higher removal capacity after a short time.

4. Innovation

This case study evaluated of novel biochar on the fate of pesticides. Biochar was composed of organic and inorganic moieties, which had specific effects on organic contaminants. Because biochar had huge specific surface area, porous structure, complex composition and chemical surface. Pig manure-derived biochar contain high ash contents, and show different interactions with pesticides compared to biochar from plant residues. The ash can combine with pesticides by specific interactions, however, accessible adsorption sites of organic moieties are masked by ash. As a result, the overall adsorption was decreased. In addition, biochar as filtration media could improve purification effect of wetland. This provide an innovative path for reuse of solid waste. On one hand, biochar derived from agricultural solid waste, which reduce the quantity of these waste. On the other hand, biochar applied in wetland could increase carbon sink in soil and mitigate emission of carbon dioxide from combustion of solid wastes.

5. Lessons Learned

Biochar derived from manure has more minerals than that derived from plant. In addition, aromatic, surface area and porosity of biochar increase with temperature elevated. These characteristics provided biochar with affinity on organic pollutants. Therefore, biochar could be as amendment in constructed wetland to improve contaminants removal. However, capacity of biochar was impacted by raw material and production condition. In addition, filtration media in wetland just one key for purification. Although biochar could improve effect of the wetland, capacity of plant could not be negative. Furthermore, duration of biochar should also be investigated in future.

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