Bioresource Technology 147 (2013) 338–344

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Properties comparison of biochars from corn straw with different pretreatment and sorption behaviour of atrazine

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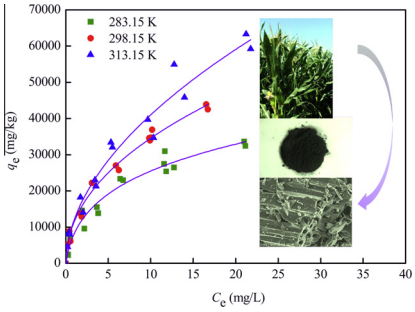
HIGHLIGHTS

- Two biochars were characterised via elemental analysis, BET-N2 and FTIR to illuminate the impact of different pretreatment on structure.
- The $NH_4H_2PO_4$ can improve the residue yield and specific surface area of biochar.
- Biochar with $NH_4H_2PO_4$ pretreatment has high efficiency of sorpotion behaviour of atrazine.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 June 2013
Received in revised form 4 August 2013
Accepted 6 August 2013
Available online 13 August 2013

Keywords:
Biochar
Agrochemicals
Sorption
Pyrolysis
Ammonium dihydrogen phosphate

ABSTRACT

Biochar has been recognised as an efficient pollution control material. In this study, biochars (CS450 and ADPCS450) were produced using corn straw with different pretreatment techniques (without and with ammonium dihydrogen phosphate (ADP)). The character of the two biochars was compared using elemental analysis, specific surface area (SSA) and Fourier transform infrared spectra (FTIR). ADPCS450 had a higher residue yield and a much larger specific surface area than CS450. The Freundlich, Langmuir and Redlich–Peterson models were used to interpret the sorption behaviour of atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), and the results fit the Redlich–Peterson equation best. The isothermal sorption parameters indicated that the sorption capacity of atrazine on ADPCS450 was much larger than the sorption capacity of atrazine on CS450. Atrazine sorption was also favoured in acidic solution and under higher temperature conditions.

1. Introduction

Agricultural chemicals are important sources of agricultural non-point source pollution. With rain erosion and irrigation processes, migration and transformation of contaminants occur in soil and water, resulting in the pollution of groundwater (Abate et al., 2004). Among the numerous agrochemicals in common use, atrazine (2-chloro-4-(ethylamino)-6-isopropylamino-s-triazine) is one of the most widely applied herbicides in many countries. Atrazine is used to control annual grasses and broadleaf weeds, primarily in corn. Atrazine and its metabolites are frequently detected in groundwater, rivers, lakes and soils (Zheng et al., 2010). Various methods have been developed for the removal of hazardous agricultural chemicals that migrate to the environment, including biological repair, photocatalytic degradation, sorption, etc. Sorption has been recognised as one of the most applicable technologies for contamination removal (Li et al., 2010).

In recent years, biochars have aroused much attention in environmental and agricultural applications as efficient and versatile environment-friendly materials. Biochar is the one of the main products of a biomass pyrolysis process conducted under low or limited oxygen conditions (Lehmann and Joseph, 2009). Various types of biomass, such as agricultural crop straw, wood, and animal manure, are used to produce biochars. With a porous structure and special physicochemical properties, biochar effectively sorbs

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http://dx.doi.org/10.1016/j.biortech.2013.08.042

organic pollutants from water and soil to reduce the risk of pesticides in groundwater contamination (Mullen et al., 2010). On a global scale, biochar has been promoted as a promising agent to prevent and remove contamination from water and soil. For instance, biochar produced from mixed sawdust burning was shown to affect the degradation characteristics of two common herbicides (atrazine and acetochlor) in soils used to grow corn (Spokas et al., 2009). More recently, cottonseed hull biochars have been reported to increase the sorption of triazine and organophosphorus pesticides (Uchimiya et al., 2012).

Properties of biochars are known to be significantly affected by pyrolysis conditions. Biochars obtained at lower temperatures by direct pyrolysis usually have a small surface area and poor sorption capacity. High temperatures are required at the sacrifice of the residual yield of biomass and energy consumption for pyrolysis. To reduce the production cost, some measures should be taken to optimise the production processes for biochars.

Biochar has structure and properties similar to activated carbon, but the surface area of activated carbon is much larger. Activation at high temperature is known to be a crucial process in the production of activated carbon. Chemical activation involves the impregnation of a precursor with catalysts such as $ZnCl_2$, KOH, H_3PO_4, $(NH_4)_2HPO_4$, or $NH_4H_2PO_4$ (Gao et al., 2011; Ioannidou and Zabaniotou, 2007; Sricharoenchaikul et al., 2008) and heating the precursor in an inert stream. For example, ammonium dihydrogen phosphate (ADP) as the catalyst for production of activated carbon, flame retardant in wood and agricultural fertiliser is an easily available and low cost material. Because of its activation, ADP develops the pore structure of a sorbent. Activated carbon fibres prepared from cotton stalks by chemical activation with ADP were efficient for the removal of *p*-nitroaniline (Li et al., 2010). ADP has also been used for the precursor pretreatment of carbon fibres (Dumanli and Windle, 2012). ADP is confirmed to accelerate the dehydration reaction in pyrolysis at low temperatures for its catalysis. ADP can also slow down the intensity of the thermal decomposition and prevent tar formation, so that ADP will enhance the residual yield of cellulose for its flame retardant and smoke suppression effect (Dobele et al., 2007; Dumanli and Windle, 2012).

Some catalysts promote the reaction of carbonisation at the pyrolysis stage in biomass, so biochars may obtain more superior properties at lower temperature. In previous research, catalysts in activated carbon production have been thoroughly discussed, but there are few studies focused on the impact of catalysts on the properties of biochars through biomass pyrolysis at low temperatures and the application of the high-efficiency biochars to agrochemical removal.

In this research, corn straw was chosen as the feedstock to produce biochars because the resource of corn straw is abundant in China. The output of corn straw is more than 0.2 billion tons per year (Chen et al., 2009). ADP was chosen as the catalyst for corn straw pretreatment. At the same pyrolytic temperature (450 °C), the biochar (ADPCS450) was derived from corn straw pretreated by ADP, and the conventional biochar (CS450) was pyrolysed directly from corn straw. The objective of the study was to compare the properties of biochars derived from corn straw with different pretreatments to the sorption behaviour of atrazine and to study the impact of ADP on the thermal decomposition of biomass and the properties of biochars. To study the sorption behaviour of biochars, atrazine was selected as the model agricultural chemical. The isothermal sorption mechanism of atrazine on both biochars was studied under different conditions. The results are valuable for the production of excellent biochars at a low cost and to provide direction for the application of biochars to agricultural waste management and water and soil amendment to reduce the risk of agrochemical pollution in the environment.

2. Methods

2.1. Chemicals and materials

Atrazine was supplied by Sigma–Aldrich (Shanghai) Trading Co., Ltd. (Shanghai, China) with a purity of 98.8%. Methanol, purchased from Shanghai ANPEL Scientific Instrument Co., Ltd. (Shanghai, China), was high performance liquid chromatography grade. ADP (analytical grade) was purchased from Xilong Chemical Co., Ltd. (Beijing, China). Deionised water (18 MΩ) used in the experiment was obtained from Millipore Simplicity 185 (Merck Millipore, US).

2.2. Preparation of biochars

Corn straw as biomass used in the study was collected from the suburbs of Beijing, China, cut into small pieces, and then washed with tap water to remove dust. After oven drying at 80 °C for 2 days, the corn straws were smashed into powder with a crusher and passed through a 2 mm sieve. The corn straw powder was dipped in 5% (*w*/*w*) ADP solution at a solid to solution ratio (g/mL) of 1:10 for 24 h, and then dried in an oven at 80 °C for 24 h. The corn straw powder without ADP (CS0) and with ADP (ADPCS0) was pyrolysed in a ceramic pot with a lid under O_2-limited conditions at 200 °C for 1 h, then subsequently at 450 °C for 4 h. The biochars (CS450 and ADPCS450) were milled to pass through a 0.2 mm sieve, then washed with HCl (0.1 mol/L) for 24 h to remove mineral substances. The biochars were washed with deionised distilled water until the aqueous phase pH was nearly neutral, then dried overnight at 80 °C for further use.

2.3. Characterisation of surface properties

Ash content was analysed according to the standard method outlined by the American Society for Testing and Materials (ASTM) D1762-84 (ASTM, 2007). Elemental (C, H and N) analyses were conducted using a Vario EI Elemental Analyzer (Elementar Company, Germany).

The surface physical properties of biochars were characterised by N_2 adsorption at 77 K using an ASAP-2020 surface area analyser (Micromeritics Instrument Corporation, US). The specific surface area (SSA) was calculated from the isotherm data using the Brunauer–Emmett–Teller (BET) equation, and the *t*-plot method was used to calculate the micropore volume (*t*-PMV). Total pore volume (TPV) and pore size distribution were calculated using the density functional theory approach (DFT) (Puziy et al., 2003).

The functional groups of the samples were detected using a Nexus 670 FTIR spectrophotometer (Thermo Nicolet Corporation, US), recording the spectrum region from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. The sample discs were prepared by mixing samples with KBr (spectroscopy grade) in an agate mortar.

2.4. Sorption experiments and models

The sorption experiments were conducted using a batch equilibration method according to previously reported research (Hao et al., 2013), and all sorption isotherms were obtained in duplicate. The effect of solution pH on atrazine sorption was investigated using batch experiments. The initial solution concentration was 5 mg/L. The solid and solution ratios (mg/mL) of CS450 and ADPCS450 were 1:2 and 1:8. The initial pH values of the solutions ranging from 2.0 to 9.0 were adjusted by HCl (0.1 mol/L) and NaOH (0.01 mol/L). The pH values were also recorded after the sorption experiment.

To evaluate the impact of the solution temperature on the isothermal sorption and compare the sorption capacities of atrazine