



Sorption and desorption of pentachlorophenol to black carbon of three different origins

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ABSTRACT

Rice straw charcoal, soot and fly ash (collectively termed “black carbon” or BC), which were found to widely exist in the environment and exhibit strong sorption of many organic compounds, were prepared for this study, and recorded as RC, SC, and FC, respectively. The characterization, sorption isotherm, and the effect of pH (from 3.0 to 9.0) on sorption capacity of each BC were investigated. It is demonstrated that RC possessed the largest surface area (234.9 m²/g), the highest porosity (0.4392 mL/g), and the largest amount of functional groups (2.995 mmol/g) of all. All the Freundlich, Langmuir and Dual-mode model can fit the sorption data of each BC well. The pH value could apparently affect the sorption capacity of pentachlorophenol (PCP) to BCs, which reached maximum value at pH 4.0. Furthermore, in order to validate the effect of pH on desorption capacity, we designed sorption–desorption cycle experiments at pH 9.0 and then pH 7.0, and found that the effect of pH on irreversible sorption and hysteresis effects were significant. As pH value decreasing from 9.0 to 7.0, the irreversible sorption capacities for RC, FC, and SC increased, and the desorption hysteresis index (*H*) values of PCP increased approximately 3 times for each BC.

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1. Introduction

There is an accumulating body of evidence that suggests black carbon (BC), generated from incomplete combustion of biomass and fossil fuels, could act as supersorbent for contaminants in soils or sediments [1–5]. Pure BCs could adsorb up to 10–1000 times stronger than other types of organic carbon (OC) [6,7]. BCs have demonstrated high and nonlinear sorption of organic compounds [6], and were responsible for more than half of the total sorption in the nanogram per liter range [8]. As sorption is one of the key factors regulating the bioavailability and the toxicity of organic contaminants in soils or sediments, a better understanding of the sorption behavior and mechanisms of organic pollutants to BC is crucial to assess the ecological risks of these chemicals.

Many studies have been conducted about the sorption of hydrophobic organic compounds (HOCs) by BC from a single source, such as crop-ash, fly ash, or soot [9–11]. It is widely agreed that the properties and the sorption behavior of BC will vary, depending on the type of the raw materials, as well as the combustion conditions [12]. Jonker and Koelmans [13] investigated the sorption of PAHs and PCBs on several BCs, they found that fly ash and coal soot always had the lowest sorption values whereas activated carbon

was shown to have the highest sorption for all compounds measured, and differences as large as 4 log units were often observed between these two extremes. Nguyen and Ball [14] investigated the sorption of HOCs employing four kinds of soot (i.e., hexane soot, ozonated hexane soot, diesel soot SRM 2975, and diesel soot SRM 1650b) with various properties, and found that samples with higher O/C ratio or higher content of extractable antigenic organic chemicals showed less sorption. However, studies which compared the sorption behavior among different kinds of BC, or related sorption with intrinsic properties of different BC particles, are still scarce.

Pentachlorophenol (PCP) has been used as an industrial antiseptic and biocide for many decades since the 1960s. Due to its proven carcinogenicity, toxicity, and ubiquity, PCP has been designated as a “priority toxic pollutant” by the United States Environmental Protection Agency (EPA) [15]. In China, PCP was produced and used extensively from 1960s until 2000, and generated a large amount of residues in the environment even now [11]. Duan et al. [16] have shown that the concentrations of PCP were 3.61–2010 ng/L in river water and seawater in China. On the other hand, previous studies about the sorption on BC mainly focused on only several classes of chemicals, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), chlorobenzene, or some pesticides, but the sorption of PCP by BC has received relatively little attention. Moreover, there is little information about the effect of pH on the sorption of PCP by different kind of BC, or the PCP sorption hysteresis by different BC.

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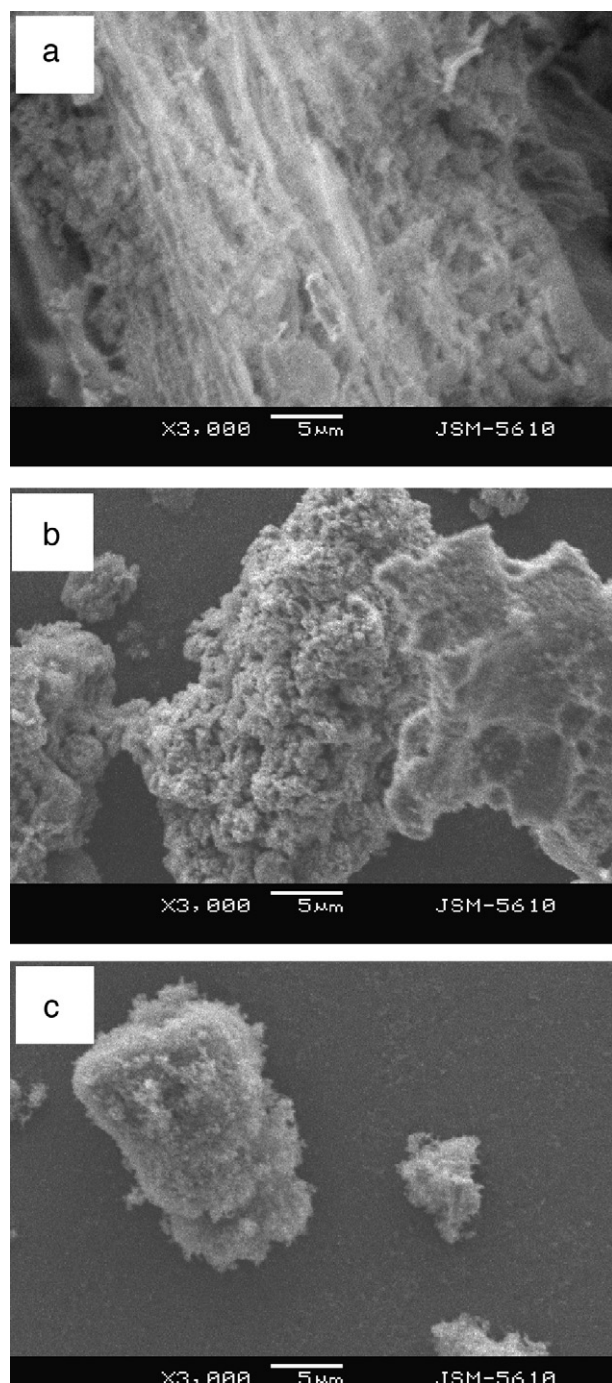


Fig. 1. Scanning electron microscopy images of black carbons with a magnification of $\times 3000$: (a) RC; (b) FC; and (c) SC.

In this study, rice straw charcoal, fly ash, and soot were selected as representatives of BC particles with different characteristics. Based on the information about surface properties among different BCs, sorption properties and effect of pH on the sorption capacity of PCP to each BC were studied. Moreover, cycles of sorption–desorption tests at pH 9.0 and then pH 7.0 were conducted to investigate irreversible sorption of PCP to BCs influenced by pH.

2. Experimental

2.1. Chemicals and materials

PCP, with a purity of $>98\%$, was purchased from Sigma–Aldrich (China). It is a highly chlorinated HOC and a weak acid with a pK_a of 4.75, and its aqueous solubility (S_w) at 25°C usually ranges from 25 to $30\ \mu\text{g}/\text{mL}$ [9].

Rice straw charcoal, fly ash, and soot, were used as precursors of BC. Dry rice straw was cut into small pieces ($<20\ \text{mm}$) and oven-dried at 105°C . The rice straw was placed in a ceramic pot, covered with a fitting lid, and pyrolyzed under the oxygen-limited conditions for 3 h at 600°C [1]. The fly ash produced during the combustion of coal (at 1400°C) was collected on electrostatic filters of Hangzhou thermoelectric plant, Zhejiang province, China. Soot was purchased from Degussa Company, Germany. These samples were treated to get purified BC using a similar method from some previous papers [1,10,12] with slight modifications. Briefly, each BC sample (10 g) was treated in 200 mL of 2 M HCl for 24 h at 25°C and centrifuged at 4800 rpm for 20 min to remove the supernatants, and this procedure was then repeated four times. Subsequently, the same procedure was performed except that 1 M:1 M HCl–HF solution was used instead of 2 M HCl. The treated samples were then thoroughly washed with distilled water five times to remove residual acids, Si, and soluble salts. The treated rice straw charcoal, fly ash, and soot were oven-dried overnight at 105°C , and recorded as RC, FC, and SC, respectively.

2.2. Characteristics of RC, FC, and SC

The elemental composition (C, H, N) of the treated RC, FC, and SC were determined by an Element Analyzer (EA 1110, USA). The surface area and pore volume of BC samples were measured by a 100CX surface area analyzer (Coulter Omnisorp, USA). The BET (Brunauer–Emmerr–Teller) equation was used to calculate the surface area of BCs and the total pore volume (i.e., sum of micro- and mesopore volume) was defined as the volume of nitrogen adsorbed at the $P/P_0=0.981$ [17]. The structure and morphology of each BC sample were examined using a scanning electron microscopy (SEM, JSM-5610LV, Jeol, Japan) at ambient temperature and 10.0 kV.

The surface acidity and basicity were determined using the Boehm's titration method [1,11]. Each BC (0.500 g) was accurately weighed and reacted with 25 mL of 0.1 M Na_2CO_3 , NaHCO_3 , NaOH, NaOC_2H_5 or HCl solution in 50-mL conical flasks for 48 h. The back-titration was carried out using 0.1 M HCl or NaOH solution to neutralize the excess acid or base. Surface acidity and basicity were calculated on the basis of the assumption that NaHCO_3 neutralizes carboxyl groups only, Na_2CO_3 neutralizes carboxyl and lactonic groups, NaOH neutralizes carboxyl, lactonic and phenolic groups, NaOC_2H_5 neutralizes carboxyl, lactonic, phenolic and quinonyl groups, and HCl neutralizes all basic groups. Furthermore, in order to validate the presence of surface functional group, the FTIR (Fourier transform infrared spectroscopy) spectra of BC samples were recorded using a Nicolet Impact 410 FTIR spectrometer (Nicolet Instrument Corporation) with $4\ \text{cm}^{-1}$ resolution and 64 scans between wavenumbers of 400 and $4000\ \text{cm}^{-1}$.

2.3. Sorption experiments

In this study, PCP was dissolved in methanol to form a 250 mg/L stock solution. Before use, the stock solution was diluted into a set of concentrations ranging from 0.1 to 20 mg/L with an electrolyte matrix containing 1 mM CaCl_2 , 1 mM MgCl_2 , and 0.5 mM $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, with $200\ \mu\text{g}/\text{mL}$ NaN_3 , which was added to inhibit aerobic biodegradation [18]. All sorption experiments were con-

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