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Sorption behavior of Cr(VI) on pineapple-peel-derived biochar and the influence of coexisting pyrene

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ABSTRACT

The influence of pyrolytic temperatures and of the properties of pineapple-peel-derived biochar (PABC) on Cr(VI) sorption behavior with and without pyrene was investigated. The structural characteristics of PABC were analyzed by scanning electron microscopy (SEM), and the surface groups of PABC were analyzed before and after Cr(VI) sorption, using Fourier transform infrared spectroscopy (FTIR). The results indicate that the characteristics of PABC depend on the pyrolytic temperature, and the adsorption isotherms fit well with the Freundlich equation. The greatest sorption capacity, 7.44 mg g^{-1}, occurred with PABC pyrolyzed at 750 °C for 2 h. In addition, the slow sorption kinetics fit well with second-order reaction kinetics. When pyrene coexisted in the solution, the adsorption of Cr(VI) was inhibited because of the inner complex between the hydroxyl groups on PABC and pyrene flushbonading the H bond with Cr(VI). There were no significant changes in the functional groups of the biochar surface between the two sides of the adsorption equilibrium, which demonstrates the slight contribution of organic matter in chromium adsorption. PABC has the potential to remove Cr(VI), but the presence of pyrene can inhibit Cr(VI) adsorption.

1. Introduction

Chromium appears in nature mainly in trivalent and hexavalent forms (Mohan and Pittman Jr., 2006; Pan et al., 2014; Yu and Gu, 2008). The wide use of chromium in industry is its main anthropogenic source (Tytlak et al., 2015; Yu et al., 2007). Chromium contamination in surface water, soil, or groundwater has been detected at and around a wide variety of industrial sites. Chromium contaminants have led to adverse effects on the cell membranes of living organisms and affect human health by eventually passing through the food chain.

The trivalent and hexavalent states of chromium have different properties such as bioavailability, mobility, and toxicity. Cr(VI) is more dangerous to public health and to the ecosystem than Cr(III) because of its higher toxicity, mutagenicity, carcinogenicity, teratogenicity, and mobility (Yu et al., 2008). Unlike Cr(VI), Cr(III) has a low solubility and tends to stick to soil particles in normal conditions (Hsu et al., 2009). Hexavalent chromium compounds are approximately 1000 times more mutagenic and toxic than trivalent chromium compounds (Polti et al., 2014).

Many techniques are used to reduce the Cr(VI) concentration in the environment (Cheung and Gu, 2003, 2005, 2007), such as sedimentation, chemical precipitation, membrane separation, ion exchange, ultrafiltration, and adsorption. The bioavailability, reactivity, and mobility of contaminants are well controlled by adsorption (Zheng et al., 2013; Qian et al., 2015). Therefore, it is necessary to prepare a low-cost adsorbent with a high adsorption capacity (Deveci and Kar, 2013; Tzeng et al., 2015). Carbon-rich biochar is pyrolyzed from various biomass feedstocks (Ahmad et al., 2012). Its application as an alternative adsorbent in recent years has attracted attention because it can remove different kinds of contaminants, including nutrients, heavy metals, and pharmaceuticals, from aqueous solutions (Inyang et al., 2012; Zhou et al., 2013). Many studies show that heavy metals can be immobilized by biochar and that the properties and structure of biochar play important roles in this process (Qian et al., 2015; Sun et al., 2014; Inyang et al., 2012). The performance of biochar is based on

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characteristics such as pore size, specific surface area, surface functional groups, and pH, which depend on the pyrolysis temperature (Wang et al., 2013). In addition, the immobilization of heavy metals may be affected by the coexistence of other elements (Qian et al., 2015).

Much research has studied the effects of various types of biochar on the immobilization of a variety of heavy metals. Biochar made from the oily seeds of *Pistacia terebinthus* L., natural zeolite biochar, and blends of raw material with alumina biochar were used as low-cost adsorbents for the removal of chromium ions (Deveci and Kar, 2013). The adsorption characteristics of As(III)/As(V) ions and the effects of coexisting Cr(VI) on arsenic adsorption on coal-based activated carbon were studied (Gong et al., 2015). The incorporation of rice straw biochar into soil significantly increased the adsorption of Pb(II) by the soil (Jiang et al., 2012). Bamboo, sugarcane bagasse, hickory wood, and peanut hull were used to produce biochar. Almost all of these chitosan-modified biochars showed enhanced removal of three metals (Pb^{2+}, Cu^{2+}, and Cd^{2+}) compared to the unmodified biochars (Zhou et al., 2013). In addition, the adsorption of organic compounds by biochar has gained attention (Ahmad et al., 2014; Isah et al., 2015; Mohammed et al., 2015; Zheng et al., 2013). Previous research is useful for producing designer biochar that can reduce the toxicity of a specific heavy metal or the bioavailability of organic contaminants.

Above all, there are large numbers of published data involving heavy metal adsorption or organics adsorption solely. In fact, most wastewater often contains both heavy metals and organic pollutants, and therefore, it is necessary to investigate the influence of coexisting of organic pollutant on heavy metals adsorption. Pyrene was studied as a representative because it is among the commonly found hydrophobic organic contaminants (HOCs) in contaminated sites in the environment. In addition, its sorption has been widely characterized in previous studies (Zielinska and Oleszczuk, 2015; Chen et al., 2008; Zhang et al., 2014). Pineapple waste biomass was chosen as the raw material to produce biochar (pineapple-peel-derived biochar = PABC). Previous literature has reported on the characterization of biochar from pineapple for dye removal (Mahamad et al., 2015) and for improving pyrene bioremediation (Wang et al., 2015). However, little data is available on the effects of organic compounds on heavy metal sorption by biochar (Zhang et al., 2015).

The aim of this study was (1) to examine the effects of pyrolytic temperatures on the resulting biochar's physicochemical properties and on Cr(VI) sorption to PABC and (2) to investigate the influence of pyrene coexisting in aqueous solution with the biochar on Cr(VI) sorption. This work will provide an understanding of Cr(VI) adsorption on PABC and provide a reference for Cr(VI) removal by biochar in wastewater or Cr(VI) immobilization in soils amended with biochar.

2. Materials and methods

2.1. Characterization and preparation of PABC

Biochars were produced at various pyrolysis temperatures using pineapple peel. Pineapple peel was obtained from a fruit store at the campus of Wenzhou University, Wenzhou, China. Samples were washed several times with tap water, air-dried for one day, and oven-dried overnight at 70–80 °C. They were then easily ground and passed through a 100-mesh sieve (Chen et al., 2008). The powdered pineapple peel tightly filled a ceramic pot with a fitted lid to ensure oxygen-poor conditions. It was heated at various temperatures (350 °C, 500 °C, and 750 °C) in a muffle oven for 2 h with a heating rate of 5 °C min^{-1}. The charred solids were allowed to cool to room temperature and then immersed in 0.1 M HCl solution overnight. Pumping filtration and repeated washing with distilled water was necessary to obtain a neutral filtrate prior to oven-drying the residue overnight at 50–60 °C. After cooling, the solids were passed through a 100-mesh sieve to gain the final biochar samples. The PABC samples were named B350, B500, and B700. The numbers represent the pyrolysis temperatures (Tytlak et al., 2015; Qian et al., 2015).

The surface area of the biochar was determined using an accelerated surface area and porosimetry system (ASAP, 2020 HD88, Micromeritics Instrument Corp., Norcross, GA, United States) with nitrogen adsorption at 77 K, and using the Brunauer-Emmett-Teller (BET) model, while micropore volume was determined from *t*-plot analysis. Fourier transform infrared spectroscopy (FTIR) was used to characterize the surface functional groups on the PABC. The spectra of samples were determined from wave numbers of 400–4000 cm^{-1} by the KBr method on a FTIR spectrometer (TRENSOR 27, Bruker Optics Inc., Germany), from the average of 64 scans at 4.0 cm^{-1} resolution. Surface structure was measured using a scanning electron microscope (JSM-6700F, JEOL Ltd., Japan).

2.2. Batch sorption experiment

$K_2Cr_2O_7$ powder (guaranteed reagent, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was dissolved in 0.1 mol L^{-1} $CaCl_2$ as a background electrolyte to prepare the stock solution of Cr(VI) (500 mg L^{-1}). The adsorption experiment was conducted in 50 mL Erlenmeyer flasks. The initial hexavalent chromium concentration in the solution ranged from 10 to 100 mg L^{-1}. Then, 0.2 g biochar and 20 mL Cr(VI) solution with an initial pH of 4 were mixed into the flasks. All the flasks were sealed with silicon caps and then shaken at 120 rpm in a reciprocating shaker for 24 h to reach equilibrium, based on a preliminary study. After 24 h, a 0.45 μm Millipore filter was used to filter the solution. Finally, the standard colorimetric method with 1, 5-diphenylcarbazide was used to determine the hexavalent chromium concentration in the filtrate. In addition to the adsorption isotherm and kinetics, the influence of pH and of coexisting pyrene was investigated in several series of similar batch experiments, using the PABC pyrolyzed at 500 °C for 2 h.

2.3. Quality control and data analysis

The experiments were performed in triplicate at each temperature, including appropriate blanks and benchmarks. NaN_3 was added into the Cr(VI) solution containing pyrene to avoid microbial degradation. The adsorption of Cr(VI) was calculated using the loss from the initial solution after equilibrium, with respect to the values in the controls. We used a first-order kinetics equation and a second-order kinetics equation to investigate the kinetics of Cr(VI) adsorption onto PABC. The experimental data were fitted to Freundlich and Langmuir models.

3. Results and discussion

3.1. Biochar characterization

Table 1 shows the main characterization of PABC. The pyrolytic temperature significantly affected biochar production, with the yield dropping from 33.6% to 23.6% as temperature increased from 350 °C to 750 °C. This result supports a previous report that biochar yield significantly decreased from 72.5% at 300 °C to 52.9% at 700 °C (Khanmohammadi et al., 2015) and a report that biochar yield dropped from 77% to 23% as temperature increased from 250 °C to 600 °C (Ding et al., 2014). Another relevant study is Claoston et al. (2014).