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Removal of Tetrabromobisphenol A by adsorption on pinecone-derived activated charcoals: Synchrotron FTIR, kinetics and surface functionality analyses

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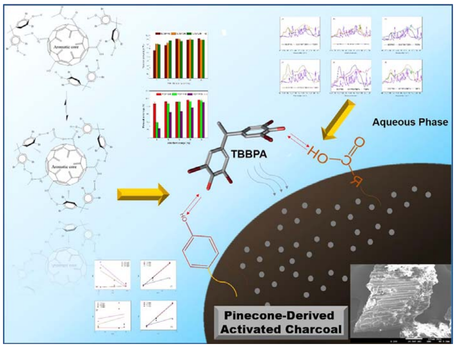
GRAPHICAL ABSTRACT



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ABSTRACT

This study explored the adsorption of Tetrabromobisphenol A (TBBPA) on pinecone-derived activated charcoal. The interactions between TBBPA and activated-charcoal surface, as well as the corresponding effects of functionality and adsorption capacities, were investigated through synchrotron FTIR, kinetics and surface functionality analyses. It was found that multiple acid functional groups and their interactive effects played important roles. The adsorption on activated charcoal from Yellow pinecone was favored by the surface with high polarity, low aromaticity, and low surface area. In comparison, adsorption on activated charcoal from Scot pinecone was favored by the surface with high aromaticity and high surface area. The adsorption capacity and removal efficiency were significantly dependent upon the contents of acid functional groups on charcoal surface. This study showed that the newly presented evidence of interactions between oxygen-containing functional groups and TBBPA will be helpful for exploring the treatment and transport of such a contaminant in the environment.

1. Introduction

Attention has been recently drawn to the environmental behaviors of Tetrabromobisphenol A (TBBPA), a widely used brominated flame retardant which accounts for 60% of total commercial market (Zhong et al., 2012). TBBPA is a relatively persistent organic pollutant which can be released into the environment through manufacturing, recycling, and disposal of various fabrics and materials. It poses a potential threat

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to the soil, water, atmosphere and living organisms (Peng et al., 2017). Exposure to TBBPA can induce a variety of adverse health effects including cytotoxicity, immunotoxicity and hepato-toxicity. TBBPA also has the potential to disrupt thyroid homeostasis and estrogen signaling (Nakajima et al., 2009). Moreover, the International Agency for Research on Cancer (IARC) listed this flame retardant into group 2A (probably carcinogenic to humans). Human exposure to TBBPA in the environment has become an important public issue (Abdallah, 2016). Therefore, efficient and environmental friendly technologies are desired for the removal of TBBPA from water.

Several approaches to remove TBBPA have been studied in the past decade, such as chemical oxidation, photocatalytic degradation, and membrane filtration (Luo et al., 2011). It was reported that Ni/nZVI bimetallic particles can be used as catalyst for the debromination of TBBPA (Li et al., 2016). Using graphene sheet as a support, synthesized the sol–gel method to the graphene-$BiFeO_3$ nanoscaled composite was also reported as a catalyst to degrade TBBPA (An et al., 2013). Adsorption is an effective method in pollution control and has been used in the removal of a wide variety of pollutant (An et al., 2011; An et al., 2017; Nguyen et al., 2015). It often features high efficiency and simple operation. Moreover, adsorption is a key process to influence transportation, degradation, and bioavailability of organic contaminants in the natural environment (An and Huang, 2015; An et al., 2016 a). Some adsorbents such as carbon nanotubes and graphene oxide have been used for the removal of TBBPA (Yu et al., 2015). Graphene nanosheets were reported as novel adsorbents in the adsorption of TBBPA due to π-π stacking interactions (Yu et al., 2015). Chemical sorption was found between TBBPA and magnetic ion exchange resin (Tang et al., 2014). Furthermore, π-π interaction and hydrogen bonds might be responsible for the adsorption of TBBPA on graphene oxide (Zhang et al., 2013). However, a number of critical issues regarding the characteristics and mechanisms for the adsorption of TBBPA are still unclear, which need further investigations.

There is also an increasing amount of interest in activated charcoal, which is a cost-effective adsorbent. Charcoals can be produced through the pyrolysis of natural biomass. Charcoal surfaces have a large number of exchangeable cations and surface adsorption sites. It contains various functional groups, especially oxygen containing ones. Its adsorption performance can be improved by suitable chemical activation. In previous studies, Wu et al. (2017) used modified bamboo charcoal in the removal of hexavalent chromium. Karaer and Kaya (2016) reported the adsorption of methylene blue on activated charcoal. Pingree et al. (2016) observed the high adsorption affinity to phenol using wildfire-produced charcoal from woody material. Pinecone biomass is widely available as a low-cost biomass from pine plantations, public parks and residential backyards. Pinecone charcoals have a well-developed porous carbon structure, which is favorable for the adsorption of contaminants (Das et al., 2015). Hydrophobic sites can form on the surface of activated pinecone charcoals, which may also favor the adsorption of other hydrophobic compounds (Li et al., 2014). Therefore, there is potential for using pinecone-derived activated charcoal as an effective adsorbent for the removal of TBBPA from aqueous solutions.

In general, some efforts have been made to investigate the adsorption of TBBPA on soil particles and modified adsorbents such as graphene nanotubes. However, there are few reports on the adsorption of TBBPA by activated charcoals. No comprehensive observation has been undertaken to understand the effects of surface area and surface-element composition, as well as the roles of surface functional groups in TBBPA adsorption. Based on the reasons mentioned above, this study seeks to explore the interactions between TBBPA and activated-charcoal surfaces, as well as the corresponding effects of functionality and adsorption capacities. In detail, (i) the change of surface functional groups on activated charcoals derived from different temperatures will be analyzed via synchrotron FTIR analysis; (ii) batch experiments will be conducted to investigate the distribution and kinetics for the adsorption of TBBPA on the surface of activated charcoals; (iii) surface behaviors and their interactions with TBBPA concentrations will be revealed by correlating the adsorption behavior of TBBPA with the surface composition of different activated charcoals. This study can provide a feasible adsorbent for the removal of TBBPA from aqueous solution. Kinetics and surface functionality features will be explored to better understand the process of TBBPA adsorption. Moreover, it is expected that the results can help to develop a sound treatment strategy for TBBPA and evaluate the mobility of TBBPA in the environment with charcoals produced from wildfire or other natural processes.

2. Materials and methods

2.1. Chemicals

TBBPA (4,40-isopropylidenebis(2,6-dibromophenol)) was purchased from Aldrich Chemical Co. (WI, USA) with a purity greater than 97%. Methanol (HPLC grade) was obtained from VWR Scientific (AB, Canada). The standard solution was prepared by dissolving TBBPA into methanol for a concentration of 200 mg/L. All other chemicals used were of reagent grade quality or higher. High-purity water used in all experiments was prepared by processing deionized water through a Milli-Q system.

2.2. Preparation of acid activated charcoals

Pinecone biomass was collected from Scots pines (*Pinus sylvestris* L.) and Yellow pines (*Pinus ponderosa*) from southern Saskatchewan, Canada. The procedure of preparing the acid activated charcoals was in accordance with standard method (Peng et al., 2016). Briefly, the collected pinecones were separated and washed with deionized water to remove impurities, and air-dried for 2 days before being oven-dried at 110 °C for 24 h. After drying, the biomass samples were grounded and passed through a 0.425 mm standard sieve. Fine pinecone powder was tightly packed into a ceramic pot and covered with aluminum foil. The powder was pyrolyzed for 4 h at varying temperatures (400, 500, 600 °C) in a muffle furnace in an oxygen-limited system to simulate temperatures of surface soil fire (Pingree et al., 2016). The heating rate was controlled at 5 °C/min. The obtained pinecone charcoals were cooled at room temperature and were washed with 1 M HCl for 6 h for activation to partially remove dissolvable organic matters and humic contents, centrifuged to remove supernatants, and washed with pure water to neutral pH. The samples were further oven-dried 24 h at 85 °C. The activated charcoals produced from Yellow pines were labeled as BCYPs, and those produced from Scots pines were labeled as BCSPs. The activated charcoals produced from Scots pines at 400, 500 and 600 °C were labeled as BCSP400, BCSP500 and BCSP600 respectively, and BCYP400, BCYP500 and BCYP600 for those produced from Yellow pines.

2.3. Characterization of charcoal adsorbents

Surface functional groups on the charcoal surfaces were analyzed using the synchrotron FTIR analysis method. The high-brilliant synchrotron radiation can help obtain results with adequate signal-to-noise ratio even with small apertures (Shen et al., 2017; Xin et al., 2017). Synchrotron FTIR analysis was carried out at the 01B1-01 (MidIR) beamline of the Canadian Light Source (Saskatoon, Canada). The Bruker Vertex 70v interferometer with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector was applied to analyze samples using synchrotron infrared light. To compensate for atmospheric and synchrotron ring current changes, background spectra was taken for each sample. Spectrum were measured with 512 co-added scans and the data was collected and analyzed using OPUS 7.2 software (Bruker, USA). Raw spectra were processed using 12-point smoothing and baseline correction. The elemental composition (C, H and N) of different activated charcoal samples were determined using an elemental