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Extracellular polymeric substances (EPS) modulate adsorption isotherms between biochar and 2,2′,4,4′-tetrabromodiphenyl ether

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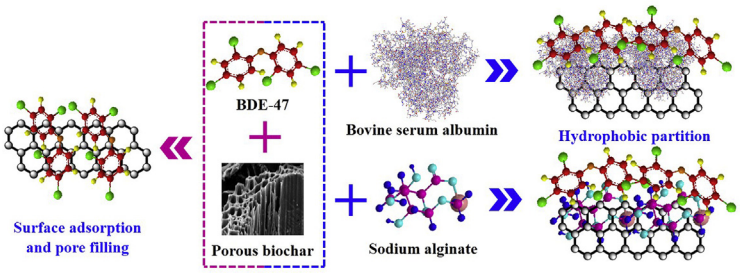
HIGHLIGHTS

- Bovine serum albumin (BSA) at 5 mg L^{-1} increased BDE-47 ($c_e = 1$ S_w) adsorption.
- Sodium alginate (SA-80 mg L^{-1}) had a positive effect on BDE-47 ($c_e = 1$ S_w) sorption.
- BSA at 80 mg L^{-1} decreased the adsorption capacities of BDE-47 on biochars.
- BDE-47 adsorption on biochar was dominated by surface adsorption.
- Hydrophobic partition dominated the adsorption with the existence of BSA (or SA).

GRAPHICAL ABSTRACT



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ABSTRACT

Extracellular polymeric substances (EPS), chars and persistent organic pollutants (POPs) frequently coexist in the environment. However, a knowledge gap exists regarding their interactions. Therefore, we applied 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) as a model POP to investigate the influence of bovine serum albumin (BSA) and sodium alginate (SA) - representing protein and polysaccharide components of EPS - on POP adsorption to biochars. Surface activities of tested biochars were characterised using nuclear magnetic resonance, X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. The adsorption capacities of BDE-47 on biochars were significantly improved by both EPS analogues: BSA at concentrations of only 5 mg L^{-1} and SA at 80 mg L^{-1} at $c_e = 1$ S_w BDE-47 concentration. However, 80 mg L^{-1} BSA decreased the BDE-47 adsorption capacities on biochars at the tested BDE-47 concentrations. Chemisorption and pore filling mechanisms appeared to dominate the adsorption process of BDE-47 on maize straw and wheat straw biochars. After adding BSA (or SA), a hydrophobic partition effect was found to best explain the adsorption process and linearity of adsorption was enhanced. These results progress our understanding of bioavailability and migration of POPs: especially relevant to the water industry and biochar/EPS facilitated removal of these contaminants.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs), are a group of brominated flame retardants (BFRs) having 209 congeners. As additive components, PBDEs are blended with many polymers for a range of products and thus manifold routes exist for transfer to the environment, including the aquatic environment (Alaeea et al., 2003). In addition to characteristics of persistence and high toxicity (Wu et al., 2017), these persistent organic pollutants (POPs), also bioaccumulate (Leonetti et al., 2016). Existing research shows that among a variety of PBDEs, 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) demonstrates the highest bioconcentration factor and biota-sediment accumulation factor in bivalves from aquaculture areas (Gu et al., 2017). As fishery products, fish and bivalves contribute significantly to human PBDE exposure (Schecter et al., 2004). Elevated levels of PBDEs in human tissue is suspected to cause several negative health impacts including endocrine disruption and developmental/reproductive problems (Harley et al., 2010). Given the almost global of adoption of PBDEs as a flame retardants, and their mobility in household dust and the atmosphere (Jones-Otazo et al., 2005), it is vital we understand how these compounds can be efficiently adsorbed and immobilised, or otherwise decrease their bioavailability.

To control the further transport of PBDEs, adsorption is the most useful and simple approach. The nature (and cost) of the employed adsorbent is also crucial to the practicality of this approach. Biochars have been widely developed as low-cost and value-added solid adsorbents for inorganic and organic contaminants due to their great capacity to sequester contaminants and control pollutant-migration. Biochars are produced by anoxic heating of carbon-rich biomass (Shi et al., 2014; Sima et al., 2017). Generally, the chemical compositions and surface characteristics of biochars are determined by the original biomass type and pyrolysis temperature. Typically, pyrolysis temperature has a more pronounced effect than feedstock type in determining biochar surface properties such as O-containing functional groups and surface area (Ahmad et al., 2013; Han et al., 2017; Sun et al., 2012) while other work has suggested the biochar feedstock plays a more important role in determining surface properties such as cation exchange capacity and hydrophobicity (Shen et al., 2017). Therefore, in different adsorption systems, the roles of biomass sources and pyrolysis temperatures are expected to be different. Until now, research on adsorption of BDE-47 to corn-straw biochars has only focused on the effect of different pyrolysis temperatures and carbonization time (Xin et al., 2013; Yan et al., 2016). However, there is currently no published research on biologically-augmented sorption of PBDEs to biochars.

In addition to the adsorption of pollutants onto man-made (or naturally occurring) active surfaces of biochars, the transport of pollutants in water can be modified by adsorption onto solid materials such as natural biofilms (Guo et al., 2014). Natural biofilms are heterogeneous solid materials that develop on the surfaces of almost all solid matrices in aquatic environments. Biofilms are typically formed of several co-existing species of microorganism, bound together by the extracellular polymeric substances (EPS) they exude (Writer et al., 2011). In general, EPS have been identified as the most important components responsible for adsorbing organic pollutants onto natural biofilms (Dong et al., 2017). EPS are a heterogeneous mixture of biopolymers and are mainly composed of proteins and polysaccharides, with other macromolecules such as nucleic acids, lipids and humic-like substances present as minor constituents (Liang et al., 2017). One study showed that the introduction of bovine serum albumin (BSA) as a protein analogue could hinder ibuprofen adsorption onto biochar (Lin et al., 2017). Subsequent research demonstrated that BSA also restricted the adsorption of sulfamethazine (SMT) onto high temperature biochar (600 °C), while it enhanced SMT-adsorption onto low temperature biochar (300 °C) (Jia et al., 2018). However, the polysaccharide, sodium alginate (SA) had no effect on SMT adsorption to biochar (Jia et al., 2018). Thus current knowledge is focused on the influence of EPS on the sorption behavior of ionised organic compounds to biochar, whereas little is known about the roles of EPS on the adsorption behavior of hydrophobic organic contaminants to biochar.

Therefore, the objective of the present study was to investigate the effect of EPS on PBDE adsorption to biochars, and describe sorption mechanisms using biochars produced at different temperatures and from contrasting biomass types. Maize and wheat straw were chosen as the biochar feedstocks since these materials contribute the largest fraction of total output of agricultural residues (Chen et al., 2009). BDE-47, a low brominated congener of PBDE, was selected as a model compound of PBDE due to the high concentrations detected in natural environmental samples (McGrath et al., 2016). Owing to the complex compositions of EPS, BSA and SA were both used to represent protein and polysaccharide components of EPS, respectively. We studied their influence on the adsorption behavior of BDE-47 through a combination of batch experiments, characterisation with nuclear magnetic resonance, X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy.

2. Materials and methods

2.1. Chemicals

The standard BDE-47 solid (98.5% purity) was purchased from Chem Service incorporated company (West Chester, Pennsylvania, USA). The BSA (purity >98%) and SA (90% purity) were purchased from Aladdin industrial corporation (Shanghai, China). The structures of BDE-47, BSA and SA can be found in the supplementary information of our previous study (Liu et al., 2017). N-hexane and methanol of chromatographic purity were bought from Tedia company (Fairfield, USA). All other chemicals and solvents were of analytical grade. Ultrapure water (Millipore, 18 MΩ cm) was used throughout the experiments. The BDE-47 stock solution of methanol (1000 mg L^{-1}) was stored at −20 °C. The stock solutions of BSA and SA (1000 mg L^{-1}) were stored at 4 °C.

2.2. Preparation and characterisation of biochars

Maize straw and wheat straw were used to prepare biochars under oxygen-limited conditions as previously reported (Jia et al., 2013). After washing with deionized water and oven-drying for 12 h at 80 °C, the maize- and wheat-straw were then transferred to the biochar reactor. For smooth pyrolysis, avoiding abnormalities related to spontaneous release of gasses in the biochar reactor, we adopted a stepwise heating program. The starting temperature was set to 200 °C, and was then elevated stepwise to 250, 300, 400, and 500 °C. The temperature was held at each step for 1.5 h, except for the final step, where heating was stopped once no further smoke was produced from pyrolysis. Two contrasting products from each feedstock were prepared, with final pyrolysis temperatures of 300 °C and 500 °C, respectively. After cooling to room temperature, the biochar samples were crushed and passed through a 100 mesh sieve (149 μm). Biochars produced from maize straw at 300 °C and 500 °C were labeled as MBC300 and MBC500, respectively. Those produced at 300 °C and 500 °C from wheat straw were separately labeled as WBC300 and WBC500.

The elemental analyses were performed with a CHN analyser (Vario MICRO, Germany elementar, Germany). The specific surface