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Sorptive removal of selected emerging contaminants using biochar in aqueous solution

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ABSTRACT

The adsorption of sunscreen compounds (benzophene [BZP] and benzotriazole [BZT]) and widely known endocrine-disrupting compounds (bisphenol A [BPA] and 17 β-estradiol [E2]) was investigated using commercially available powdered activated carbon (PAC) and activated biochar produced in the laboratory. The removal efficiency by biochar was approximately 5–30% higher than that by PAC depending on experimental conditions, presumably due to the higher surface area and pore volume of biochar. The removal of compounds followed the order E2 > BZP > BPA > BZT: K_f $(\mu g/g)/(mg/L)^{1/n}$, Freundlich affinity coefficients, were as follows – 19.7, 19.7, 6.57, and 4.56 for PAC, and 30.2, 28.4, 9.22, and 6.79 for biochar. An increase in pH from 3.5 to 10.5 decreased the adsorption of BZP, BZT, BPZ, and E2 by 11.5, 11.4, 10.7, and 4.7% by biochar, respectively. Overall, biochar had a higher adsorption capacity for all chemicals tested compared with PAC.

Introduction

Numerous emerging micropollutants, such as endocrine-disrupting compounds, pharmaceuticals, and personal care products, have been detected at trace concentrations (<1 μg/L) in various surface and ground waters and wastewaters globally, some of which have been connected with ecological influences, even at these very low concentrations [1–8]. Reports have raised significant concerns on micropollutants in public health assessments and environmental risks with both regulatory agencies and the public [9–12]. Many emerging organic micropollutants are more polar than 'conventional' contaminants (e.g., polycyclic aromatic hydrocarbons and pesticides) and may have numerous acidic and/or basic functional groups [13].

These emerging micropollutants cannot be removed completely during wastewater or water treatment [1,14–22,8]. In particular, during water treatment, previous studies have reported that coagulation processes typically remove only insignificant percentages of micropollutants in aqueous solutions [23,24]. However, numerous pesticides, pharmaceuticals, and estrogenic compounds can be removed significantly using activated carbon [23–28]. The removal degree of activated carbon is governed by the physicochemical properties (shape, size, charge, and hydrophobicity) of the solute and the sorbent (surface area, pore size distribution, surface charge, oxygen content) [29]. The main removal mechanisms for most organic compounds in activated carbon adsorption systems are hydrophobic interactions. Due to hydrophobic attractions, activated carbon significantly removes most non-polar organic compounds (i.e., those compounds with log K_{OW} > 2) [13].

It is anticipated that biochar will be available for value-added products due to advances in biorefineries in the near future [30]. Biochar is obtained as a byproduct of the pyrolytic processing of biomass when biofuel is produced during controlled thermal processes and gasification [31]. Additionally, biochar shows potential as a promising adsorbent for the removal of micropollutants due to its better properties, including its surface density of functional groups and highly condensed structure, while the

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activated product provides a smaller surface area and volume than commercially activated carbon [32]. These properties vary depending on the type of feedstock, pyrolysis conditions (residence time and temperature), and activation. In particular, while higher proportions of aliphatic carbons and functional groups are typical of biochars pyrolyzed at low temperatures, biochar pyrolyzed at higher temperatures contains mainly polyaromatic carbons and has a higher microporosity, which enhances organic compound adsorption [31,33]. In one study, chemically activated biochar resulted in a relatively larger surface area, porous structure, and lower ash content than commercially available activated carbon [34]. Many organic forms, including plants, sewage sludge, domestic and industrial wastes, and animal manures, are used as material sources for pyrolysis. The composition of elements and the ratio of inorganic components in biomass varies and affects both the product yield and quality of bio-oil and biochar [35].

An efficient treatment strategy for micropollutants has been considered using cost-effective adsorption, particularly with biochar in an aqueous environment [30,36–38]. A recent study reported the effect of temperature on sulfamethoxazole removal using a biochar pyrolyzed at 600 °C [39]. A separate study discovered distinct adsorption abilities of demineralized pine wood biochar for sulfamethoxazole and sulfapyridine [37]. In that study, their adsorption was reduced in the presence of humic acid or a cation (Cu^{2+}). However, there has been little research effort devoted to biochar prepared under different pyrolysis conditions and the inversely proportional relationship between biochar and bio-oil production. Also, most previous studies on biochar have not compared its performance with commercially available activated carbon and cover only a few compounds under limited water quality conditions.

Thus, the objective of this study was to determine the removal of four micropollutants: sunscreen compounds (benzophene [BZP] and benzotriazole [BZT]) and widely known endocrine-disrupting compounds (bisphenol A [BPA] and 17 β-estradiol [E2]), each having different physicochemical properties, by biochar under various water quality conditions (pH, background ions, ionic strength, and natural organic matter [NOM]). Activated biochar produced in the laboratory was also characterized using conventional analytical methods as well as advanced solid-state nuclear magnetic resonance (NMR) techniques to address how these properties determine the mechanism(s) and micropollutant adsorption characteristics.

Material and methods

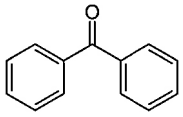
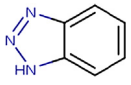
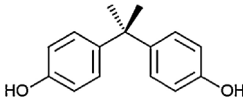
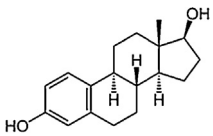
Reagents and selected micropollutants

All standards and chemicals were at least reagent grade and/or of the highest purity available commercially. For adsorption experiments, four micropollutants were selected as target compounds. Table 1 summarizes the target EDC/PPCP compounds that were studied by spiking the compounds into various synthetic waters. In selecting the target compounds, two issues were considered: (i) their occurrence in source waters and (ii) the physicochemical properties of the particular compound. All target compounds were obtained from Sigma–Aldrich (St. Louis, MO, USA). Concentrated spiking solutions of the target compounds were prepared at high concentrations (approximately 500–1000 mg/L) in methanol to minimize the volume of solvents introduced into the experiments. BZP, BPA, and E2 had low water solubilities and thus could not be spiked as neat standards. A small volume of each spiking solution (<5 mL) was injected into a 5-L flask containing a target synthetic water.

Adsorbents

Biochar samples were produced with torrefied loblolly pine chips (15 mm × 6 mm) containing bark through thermal treatment at 300 °C for 15 min in a laboratory-scale batch tube-furnace (OTF-1200X, MTI Corp., Richmond, CA, USA) under pure nitrogen. A thorough description of the production method has been published previously [30]. The yield of biochar was 42.3%. Biochar samples of 3 g were soaked with 40 mL of a 4 moles/L NaOH solution and incubated with shaking (15-min intervals) for 2 h at room temperature. NaOH-impregnated samples were filtered (Buchner filter funnel) to remove excess NaOH solution and dried overnight (105 °C oven). The NaOH-impregnated biochar samples were then heated at 800 °C for 2 h under a nitrogen gas flow (2 L/min) and cooled (10 °C/min). The dried samples were rinsed with 0.1 mole/L HCl followed by deionized water until they reached neutral pH, dried at 105 °C, milled, and passed through a 74-μm sieve. Additionally, a commercially available powdered activated

Table 1
Properties of target micropollutants used in this study.

Compound [ID] (use)	Structure	MW (g/mol)	Log D_{ow}[a]			Log K_{ow}	pK_a[a]
			pH 3.5	pH 7.0	pH 10.5		
Benzophenone [BZP] (sunscreen)		182.2	3.43	3.43	3.43	3.43	−7.5
Benzotriazole [BZT] (sunscreen)		119.1	1.30	1.27	−1.01	1.30	8.2
Bisphenol A [BPA] (plasticizer)		228.1	3.44	3.44	2.64	3.44	9.6 −10.2
17β-Estradiol [E2] (hormone)		273.2	3.75	3.75	3.55	3.75	10.3

[a] Chemicalize.org by ChemAxon (http://www.chemicalize.org).