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Adsorption of selected endocrine disrupting compounds and pharmaceuticals on activated biochars

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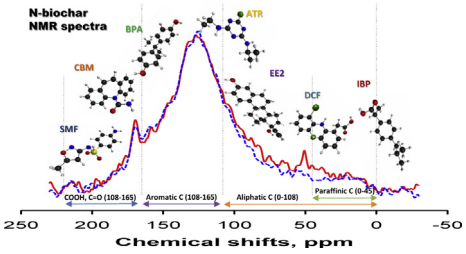
HIGHLIGHTS

- Biochars were prepared at different gas environments.
- The competitive adsorption among EDCs/PhACs were investigated.
- Aromaticity of adsorbent plays a significant role for EDCs/PhACs adsorption.

GRAPHICAL ABSTRACT



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ABSTRACT

Chemically activated biochar produced under oxygenated (O-biochar) and oxygen-free (N-biochar) conditions were characterized and the adsorption of endocrine disrupting compounds (EDCs): bisphenol A (BPA), atrazine (ATR), 17 α-ethinylestradiol (EE2), and pharmaceutical active compounds (PhACs); sulfamethoxazole (SMX), carbamazepine (CBM), diclofenac (DCF), ibuprofen (IBP) on both biochars and commercialized powdered activated carbon (PAC) were investigated. Characteristic analysis of adsorbents by solid-state nuclear magnetic resonance (NMR) was conducted to determine better understanding about the EDCs/PhACs adsorption. N-biochar consisted of higher polarity moieties with more alkyl (0–45 ppm), methoxyl (45–63 ppm), O-alkyl (63–108 ppm), and carboxyl carbon (165–187 ppm) content than other adsorbents, while aromaticity of O-biochar was higher than that of N-biochar. O-biochar was composed mostly of aromatic moieties, with low H/C and O/C ratios compared to the highly polarized N-biochar that contained diverse polar functional groups. The higher surface area and pore volume of N-biochar resulted in higher adsorption capacity toward EDCs/PhACs along with atomic-level molecular structural property than O-biochar and PAC. N-biochar had a highest adsorption capacity of

Abbreviations: ATR, atrazine; BET, Brunauer–Emmett–Teller; BPA, Bisphenol A; CBM, carbamazepine; DCF, diclofenac; DP/MAS, direct polarization/magic angle spinning; EDCs, endocrine disrupting compounds; EE2, 17α-ethinylestradiol; HCl, hydrochloric acid; IBP, ibuprofen; NaOH, sodium hydroxide; NMR, nuclear magnetic resonance; NOMs, natural organic matters; PAC, powdered activated carbon; PhACs, pharmaceutically active compounds; SMX, sulfamethoxazole.

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all chemicals, suggesting that N-biochar derived from loblolly pine chip is a promising sorbent for agricultural and environmental applications. The adsorption of pH-sensitive dissociable SMX, DCF, IBP, and BPA varied and the order of adsorption capacity was correlated with the hydrophobicity (K_{ow}) of adsorbates throughout the all adsorbents, whereas adsorption of non-ionizable CBM, ATR, and EE2 in varied pH allowed adsorbents to interact with hydrophobic property of adsorbates steadily throughout the study.

1. Introduction

Endocrine-disrupting compounds (EDCs) and pharmaceutically active compounds (PhACs) are trace-level organic contaminants that have been detected in aquatic environments such as surface waters, wastewater, runoff, and landfill leachates [1–3]. The widespread occurrence of these dissolved chemicals in water sources is of concern due to their adverse effects, such as mimicking or antagonizing natural hormones, hindering metabolic processes, occupying hormone receptors, and causing reproductive and development problems when consumed by humans and aquatic species [4,5].

A variety of EDCs exist, including pesticides, natural hormones, and industrial chemicals. Atrazine (ATR) is one of the most widely used herbicides and its continuous exposure into water causes its concentration to accumulate due to its poor degradability compared to other herbicides [6]. Recently, 17α-ethinylestradiol (EE2), an oral contraceptive, has been studied extensively due to its higher toxicity compared to other hormones such as estrone or 17β-estradiol [7]. Similarly, bisphenol A (BPA), a main monomer in epoxy resin and polycarbonate plastic, has been studied due to the ubiquitous use of plastic in everyday living. In addition, because of the increasing demand for PhACs, the level of exposure has increased, paradoxically causing a threat to health. Certain pharmaceuticals have been studied widely, such as non-steroidal anti-inflammatory drugs; diclofenac (DCF) and ibuprofen (IBP), as well as antibiotics (sulfamethoxazole; SMX) and anti-seizure medicine (carbamazepine; CBM). EDCs/PhACs are metabolized and adsorbed by organisms at low levels, resulting in exposure to the residues of these compounds as their origin molecular forms or their transformed products when they enter the aquatic environment [3,8]. Unfortunately, the treatment of EDCs/PhACs in wastewater and drinking water is inefficient [9,10] and consequently more effective technologies are required to achieve their removal from drinking water.

Adsorption with a high-binding adsorbent has been used to eliminate various contaminants in the aqueous phase [11]. The well-established manufacturing process and relatively low cost of activated carbon has led to it becoming a common adsorbent for water treatment due to its strong interaction with hydrophobic organic contaminants. However, the physical properties of activated carbon, including the irregular and closed pore structure with small micropore sizes (<2 nm), precludes the adsorption of large molecules, leading to a size-exclusion effect [12]. The improvement of this crucial role of pore size for the adsorption has been studied through physical and chemical activation of adsorbents [13,14].

With an advance of biorefinery in the near future, it is expected to have biochar available for precursors for value-added products. Biochar is the by-product of the pyrolytic processing of biomass to obtain biofuel such as controlled thermal process and gasification, and has a potential as a promising adsorbent for the elimination of micro-pollutants due to its superior properties including a highly condensed structure and surface density of functional groups, although its activated product provides a lower surface area and volume than commercialized activated carbon [15,16]. These properties are controlled by the pyrolysis conditions (residence time and temperature), activation, and type of feedstock; biochar pyrolyzed at a high temperature consists mainly of polyaromatic carbons and has a higher microporosity, which enhances the adsorption of organic compounds, while higher proportions of aliphatic carbons and functional groups are typical of biochars pyrolyzed at a low temperature [16,17]. A separate study has shown that chemically activated biochar resulted in higher porous structure, surface area, and lower ash content than commercialized activated carbon [18]. Since most of organic forms such as any kind of plants, domestic and industrial wastes, sewage sludge, and animal manures have used as a source in pyrolysis, their composition of elements and ratio of inorganic compounds in biomass varies the both product yield and quality of bio-oil and biochar [19]. The overall objective of this study was to characterize activated biochars produced in a laboratory, where biochars were prepared at different gas environments using conventional analytical methods as well as advanced solid-state nuclear magnetic resonance (NMR) techniques and how these properties determine the competitive adsorption characteristics and mechanisms of EDCs/PhACs. Commercialized powdered activated carbon (PAC) was also examined as a comparison. Seven EDCs/PhACs commonly occurring in the aquatic environment were selected as adsorbates and the effects of their hydrophobicity and molecular size on adsorption capacity were also investigated. The competitive adsorption among EDCs/PhACs were investigated in terms of characteristic difference both adsorbents and adsorbates. Furthermore, adsorption inhibition by natural organic matters (NOMs), described by humic acid, in this study was determined for better understanding in real wastewater condition.

2. Materials and methods

2.1. Target adsorbates

Three EDCs (BPA, ATR, and EE2) and four PhACs (SMX, CBM, DCF, and IBP) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Although the seven compounds have similar molecular weights (206–296 g/mol), their pK_a values and octanol–water partition coefficients (K_{ow}) cover broad ranges. Detailed physicochemical properties are provided in Supporting Information (Table S1).

2.2. Adsorbents

The N- and O-biochar samples were produced through the thermal treatment of torrefied loblolly pine chips (15 mm × 6 mm) containing bark at 300 °C for 15 min in a laboratory-scale batch tube-furnace (OTF-1200X, MTI Corporation, Richmond, CA, USA), under pure nitrogen (N-biochar) and 7% oxygen + 93% nitrogen atmospheres (O-biochar). Due to the limitation of the loadable amount of samples in the tube furnace, N-/O-biochars were generated with several batches. After each batch, the weight loss from the thermal treatment was measured, and then the samples with a difference of ±3% in weight loss were collected for further experiments. The yields for N-/O-biochar were 42.3% and 64.2%, respectively. 3 g of each pyrolyzed biochar was activated with 40 mL of 4 M NaOH for 2 h and dried overnight at 105 °C. The NaOH-impregnated biochar samples were then heated at 800 °C for 2 h under a nitrogen gas flow (2 L/min) and cooled down (10 °C/min)