



Sorption of naphthalene and its hydroxyl substitutes onto biochars in single-solute and bi-solute systems with propranolol as the co-solute



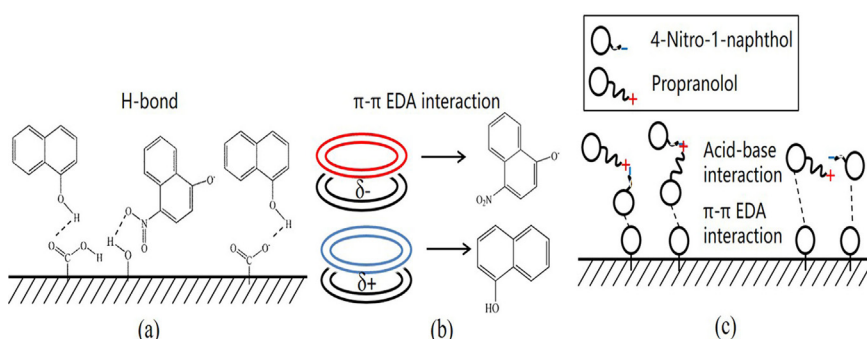
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HIGHLIGHTS

- –OH and –NO₂ enhanced naphthalene substituents sorption on low-temperature biochar.
- Hydrophobicity and molecular volume determined the sorption on high-temperature biochar.
- The ion-pair reaction increased the sorption of anionic 4-nitro-1-naphthol.
- pH changed sorption mechanisms in both single-solute and bi-solute systems.

GRAPHICAL ABSTRACT



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ABSTRACT

The sorption of naphthalene and its hydroxyl-substituted compounds onto two biochars that were produced at different temperatures was studied. The influences of propranolol as a co-solute and solution pH on the sorption were investigated. The sorption capacities of 1-naphthol and 4-nitro-1-naphthol on the biochar with a pyrolytic temperature of 200 °C (BC200) were greater compared to naphthalene. This occurred because the substitution of hydroxyl- and nitro-groups on the aromatic ring enhanced surface adsorption, e.g. hydrogen bond and π - π electron donor-acceptor interaction, while the hydroxyl in 1-naphthalenemethanol did not show the promoting effect. The sorption on the biochar with a pyrolytic temperature of 700 °C (BC700) followed a different sequence of 4-nitro-1-naphthol < 1-naphthalenemethanol < 1-naphthol < naphthalene, which was determined by the hydrophobicity and molecular volume of the sorbates, indicating the dominance of hydrophobic partition and pore-filling in the adsorption on BC700. The co-existence of propranolol promoted the surface hydrophobicity of BC200, which led to an enhancement in the sorption of naphthalene and 1-naphthalenemethanol. Propranolol prohibited the sorption of 1-naphthol by competing for the mutual available surface adsorption sites. The ion-pair reaction between anionic 4-nitro-1-naphthol and cationic propranolol increased the sorption of 4-nitro-1-naphthol. On BC700, propranolol generally prohibited the sorption of the tested sorbates mainly due to competition and pore-blocking. The influence of pH was complicated in both single-solute and bi-solute systems. It simultaneously affected the surface charge of biochars and the form of the tested compounds, which led to the shifting of sorption mechanisms. The finding will shed light on the suitable application of biochar technology.

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1. Introduction

Biochar is acquired by pyrolyzing biomass residues under oxygen-limited conditions [1]. Recent studies showed that biochar samples show great sorption capacity for different kinds of heavy metals and organic pollutants [2–4]. Moreover, in four or five cycles of the sorption-desorption process, the sorption capacity of biochar remained >70% [4–6]. Hence, the high-efficiency and low-cost, together with the reusability make biochar emerge as a promising sorbent [7]. To guide the screening of a good biochar sorbent for a specific type of contaminants, increasing studies have been conducted to explore the sorption mechanisms of various organic pollutants onto biochars [8–10]. In summary, the main driving force for biochar sorption is the partition of hydrophobic organic chemicals from the incompatible water environment to the hydrophobic organic moiety of biochar [11,12]. Moreover, the entrapment of chemical molecules into the rigid aromatic structure and micropores with similar size (2–3 times) to the chemical molecular size exerts an important role, especially for biochars obtained at a high pyrolyzing temperature, due to the great content of crystal aromatic ring sheets and micropores [12,13]. These features make biochar a good sorbent for non-polar compounds, such as polycyclic aromatic hydrocarbon (PAHs) and polychlorinated biphenyl (PCBs) [11,14,15]. On the other hand, sorption can also occur via polar interactions, e.g., van der Waals force and hydrogen bonds, between the residue polar groups on the biochar surface and chemicals with polar functional groups [3]. This is one of the main sorption mechanisms for the sorption of polar pesticides onto biochar [3,16]. As for aromatic compounds, surface adsorption can be strengthened via electron transfer between aromatic rings if one is rich and the other is deficient in electron density, i.e., π - π electron donor-acceptor (EDA) interaction [8,17]. Besides, biochars are usually negatively charged, and ionizable organic compounds (IOCs) have extra electrostatic interaction with a cationic sorbate having a strengthened sorption and an anionic sorbate having a reduced sorption [4,18]. Hence, the sorption mechanisms change greatly with the structure of biochars and the properties of sorbates, which increases the challenge in screening a suitable biochar sorbent and needs a specialized study on a specific kind of contaminants.

Compared to the large amount of literature on non-polar organic pollutants and pesticides, studies on the sorption of industrial polar organic pollutants and IOCs onto biochars are lacking. Phenols and alcohols are common environmental pollutants and widely detected in the wastewater from plastics, dyes, pharmaceuticals, rubber, pesticides and other industries [19,20]. Exposures to these kinds of pollutants cause adverse effects on human health, including carcinogenic, teratogenic and endocrine disrupting effects [21]. Because of the high water solubility due to the substitution of the hydroxyl group, these chemicals tend to exist in water phase [22], making their removal by sorbents a big challenge. On the other hand, the substitution of polar groups, like hydroxyl, may strengthen the surface polar interactions, such as hydrogen bond and π - π EDA interactions, which favor the sorption. Studies on other carbonaceous sorbents have confirmed this. Yu et al. [23] found extremely stronger sorption of aniline and naphthylamine than benzene on reduced graphene oxide due to π - π EDA interactions. Similarly, Chen et al. [24] reported that π - π EDA interactions increased the sorption of amino-/hydroxyl- aromatics on carbon nanotubes compared to non-polar aromatics. However, no study has investigated the effect of hydroxyl-substitution on the sorption mechanisms of aromatics pollutants onto biochars.

As for IOCs, they can exist either as ionic form or as molecular form, depending on environmental conditions, mainly on pH. At the same time, the surface charge of biochar depends on the protonation and deprotonation reactions of surface oxygen-containing

groups, mainly —OH and —COOH, which is also a function of solution pH [25]. Hence, both the existing form of IOCs and the surface charge of the sorbent change with pH [23,24] and pH can have great impacts on the sorption of IOCs or polar organic compounds compared to non-polar organic compounds [26–29]. Recently, one study checked the pH influence on methylene blue's sorption on carbon nanotube-biochar nanocomposites [30] and found that the sorption of methylene blue (pK_a : 3.8) on biochars increased with increasing pH at pH < 7, above which, there was no significant pH dependence. The authors ascribed this to the increased electrostatic attraction between the positively charged methylene blue and negative biochar and π - π EDA interactions with increasing pH at pH < 7 [30]. However, studies on the pH impact on the sorption of IOCs onto biochars are still scarce.

Pollutants do not exist alone in wastewaters and different types of compounds may co-exist [31]. The co-existing compounds may compete for the mutually available sorption sites, leading to an antagonism effect in sorption. This was well documented on biochar and other geosorbents [14,32]. The other well studied bi-solute sorption is on surfactants as co-solute. Surfactants can form micelle and micelle-like structures both in solution (usually anionic surfactants) and on the surface of sorbents (usually cationic surfactants) [32,33]. The former enhances the dissolution of hydrophobic organic pollutants and hence inhibits the sorption, whereas the latter may promote apparent sorption by combining pollutant molecules in the micelle-like structure. Polar organic and IOCs have both a hydrophilic part and a hydrophobic part, which, above a proper concentration, may form micelles that behave like surfactants [14]. In summary, the sorption of non-polar organic pollutants, polar organic pollutants and IOCs onto biochar may occur through different processes and on different sorption domains; hence, their mutual effects in bi-solute sorption are far from competition and requires further study [34,35].

Hence, we investigated the sorption of naphthalene and three hydroxyl-substituted naphthalene substitutes, i.e., 1-naphthol, 4-nitro-1-naphthol and 1-naphthalenemethanol, onto two biochars. We used biochars derived from corn straw at pyrolytic temperatures of 200 °C (BC200) and 700 °C (BC700) to obtain a comparison between the two biochars. Cellulose, hemicellulose and lignin are the three main components of corn straw. Cellulose and hemicellulose decompose at 200–400 °C, and lignin decompose at 200–700 °C [36]. Therefore, the two biochars were completely different in their structures. The influence of substitution of chemicals on sorption mechanisms was discussed. In addition, the sorption was measured under different pH values to elucidate its influence on the sorption of the target sorbates with different forms. Pharmaceuticals and personal care products (PPCPs), as emerging compounds with high production and diverse groups, are frequently detected in aquatic environments [37]. Most PPCPs have a polar structure and are ionized and they may alter the sorption of co-existing compounds with similar sorption mechanisms. Therefore, we chose propranolol, which is a β -blocker and exists mainly in cationic form under neutral pH, as a model compound and studied the impacts of the co-existence of propranolol on the sorption of the above target compounds under different molar ratios of the two solutes and different pHs. The following hypotheses were examined: (1) Whether hydroxyl functional groups affect polar organic pollutants sorption onto biochars at different pyrolyzing temperatures, and (2) Whether the co-existence of cationic organic pollutants have different effects on the sorption behavior of naphthalene and its hydroxyl substitutes. This study helped us to obtain a comprehensive understanding of the sorption mechanisms of naphthalene and its hydroxyl-substituted compounds under different environmental conditions on biochar and provide a scientific basis for screening a suitable biochar sorbent.

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