Chemical Engineering Journal 264 (2015) 1–9

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Competitive adsorption of selected non-steroidal anti-inflammatory drugs on activated biochars: Experimental and molecular modeling study

Chanil Jung [a], Linkel K. Boateng [a], Joseph R.V. Flora [a], Jeill Oh [b], Marcus C. Braswell [a], Ahjeong Son [c], Yeomin Yoon [a,*]

[a] Department of Civil and Environmental Engineering, University of South Carolina, Columbia, SC 29208, USA
[b] Department of Civil and Environmental Engineering, Chung-Ang University, 84 Heukseok-ro, Dongjak-gu, Seoul 156-756, South Korea
[c] Department of Environmental Science and Engineering, Ewha Womans University, 52 Ewhayeodae-gil, Seodaemun-gu, Seoul 120-750, South Korea

HIGHLIGHTS

- Biochars prepared in the lab were used to remove NSAIDs.
- Competitive adsorption among NSAIDs was investigated.
- Aromaticity of adsorbent plays a significant role for NSAIDs adsorption.
- Interaction energies between the NSAIDs and the biochar were calculated.

ARTICLE INFO

Article history:
Received 10 October 2014
Received in revised form 14 November 2014
Accepted 15 November 2014
Available online 22 November 2014

Keywords:
Adsorption
Binding energy
Biochar
Diclofenac
Naproxen
Ibuprofen

ABSTRACT

The adsorption of targeted non-steroidal anti-inflammatory drugs: diclofenac (DCF), naproxen (NPX), and ibuprofen (IBP) by two types of activated biochar (N-/O-biochar) was studied in single- and multi-solute adsorption experiments in conjunction with molecular modeling subsequently interpreting the binding energy. The carbonaceous structure of the biochars was elucidated via nuclear magnetic resonance and the intensity of the interactions between the solute and adsorbent was also determined. Using fractions of the carbonaceous functional group on the adsorbent for the single-solute adsorption, the overall binding energies were determined to be in the order of DCF > NPX > IBP (−21.8 > −17.5 > −14.1 kcal/mol for N-biochar and −21.2 > −17.3 > −14.2 kcal/mol for O-biochar), while the maximum adsorption capacities of DCF, NPX, and IBP for N-biochar and O-biochar were 372, 290, 311 mg/g and 214, 228, 286 mg/g, respectively. A strong interaction between the DCF and the adsorbent resulted in the occupation of effective adsorption sites as compared to other solutes, while blocking the pores in which smaller sized NPX and IBP that may have been adsorbed. A weaker adsorption of IBP was observed in the presence of adsorption competitors. More specifically, the presence of adsorption competitors caused lower binding energy due to a combination of lower binding energy, polarity, and π-energy with the adsorbent and electrostatic repulsion from the cosolutes that occupied adsorption sites.

1. Introduction

Biochar is a byproduct from the pyrolytic processing of biomass. Its presence significantly improves not only mechanical features of industrial materials, but also chemical properties of soil [1]. It is also plays a critical role in environmental remediation of soil and water by acting as an adsorbent for micropollutants [2]. These potentialities are controlled by feedstock source and pyrolytic profiles (time, temperature, and carrier gas). The carbon and ash content are governed by the feedstock (livestock manure > plant > wood) [3] and the condensed aromatic carbon (400–700 °C) as well as the fraction of functional groups (250–400 °C) are governed by the pyrolysis temperature [4].

Non-steroidal anti-inflammatory drugs (NSAIDs) are often prescribed for the treatment of headaches, arthritis, ankylosing, spondylitis, sports injuries, and menstrual cramps. In fact, they are one of the most prescribed pharmaceuticals. Unfortunately, NSAIDs

* Corresponding author. Tel.: +1 (803)777 8952; fax: +1 (803)777 0670.
E-mail address: yoony@cec.sc.edu (Y. Yoon).

http://dx.doi.org/10.1016/j.cej.2014.11.076
1385-8947/

often pass through the patients' digestive system and eventually made their way to water systems via incomplete treatment of human waste. NSAIDs have been detected in trace to considerable levels in the environment [5], and they are known to cause significant renal, degenerative, and necrotic changes on vertebrates [6]. Therefore it is critical to study and understand their fates in order to develop effective treatment and mitigation strategies [7].

Adsorption has been considered as an efficient treatment strategy for organic contaminants in aqueous environment. For instance, Altmann et al. [8] reported the selective and competitive adsorption among carbamazepine, diclofenac, and sulfamethoxazole onto limited surface area of powdered activated carbon, and Sotelo et al. [9] introduced the reduced adsorption ability in the cocktailed solutions of caffeine and diclofenac onto granular activated carbon compared to their single adsorption system, resulting in the reduced adsorption capacity of 29.1% and 32.1%, respectively. The use of carbon nanotubes and activated carbons in this strategy has garnered significant attention due to their high-binding energy and inducement of hydrophobic interaction [10]. Unfortunately, these approaches are insufficient to reveal the adsorption mechanism due to their diversity and intricateness. Therefore, it is required to investigate the additional adsorption mechanisms toward physicochemical properties of both adsorbent and adsorbate. Consideration of the accessibility of the adsorptive sites and pore size of adsorbent in order to minimize the size-exclusion effect and desorption is able to ensure the adsorption mechanism influenced and crucial role in competitive adsorption by characteristics of adsorbent [11].

It is hypothesized that the adsorption of NSAIDs onto activated biochar is related to the binding of NSAIDs onto the surface of the adsorbent at the molecular level. Therefore molecular level simulation of the adsorption process can potentially provide valuable mechanistic insight into the adsorption strength differences between different NSAIDs and various char surface functional groups. Various computational techniques have been employed to study the physisorption of different chemicals onto graphene [12], single-walled carbon nanotubes, and multi-walled carbon nanotubes [13]. However, molecular level studies involving adsorption of chemicals onto biochar has not been explored. This is probably due to the difficulty in generating the exact molecular structure of the char. Previous work by our research group reported the interaction energy associated with the adsorption of atrazine onto hydrochar [14]. In that study, it was found that atrazine was more strongly adsorbed to surfaces without weakly associated alkyl groups.

Xie et al. [15] discovered distinct adsorption ability of demineralized pine wood biochar for sulfamethoxazole and sulfapyridine and reduced adsorption behavior in the presence of humic acid or cation (Cu^{2+}), while Li et al. [16] showed the effect of temperature in sulfamethoxazole adsorption onto the biochar pyrolized at 600 °C. However, there has been less research effort devoted to the biochar under slow and fast pyrolysis produce due to the reverse-proportional relationship between bio-oil production and biochar. Therefore, in this study, the adsorption of three NSAIDs; diclofenac (DCF), naproxen (NPX), and ibuprofen (IBP), onto fast pyrolyzed biochar at 300 °C was investigated to demonstrate the feasibility of simultaneous fulfilment of the effective adsorbent with the bio-oil yield. Physicochemical properties of less carbonized biochars due to low pyrolytic temperature were complemented by chemical activation that increased the surface areas and pore volumes. More specifically we used dispersion-corrected density functional theory in single or competitive adsorptive conditions under consideration of conformation and chemical properties of both solute and adsorbent. Interaction energies between the NSAIDs and the biochar were also calculated to characterize the strength of adsorption and the effect of the various surface functional groups on the adsorption capacity of the char. In addition, each adsorption capacity for both N-biochar and O-biochar was pronounced under single and competitive adsorption systems to evaluate adsorption ability for NSAIDs removal. Throughout the adsorption evaluation, possible adsorption mechanisms were described with molecular modeling.

2. Materials and methods

2.1. Materials

Biochars produced by pyrolyzing torrefied loblolly pine chip (15 × 6 mm) at 300 °C for 15 min were classified as either N-biochar or O-biochar in terms of pyrolysis with pure nitrogen or 7% oxygen with 93% nitrogen gas, respectively. Both biochars were activated by NaOH to increase the surface area and pore volume of the biochars. The detailed pyrolysis and activation procedures are described in the Supplementary information. Biochars were milled and passed through a 200-mesh (74-μm) sieve, and then stored with ultrapure water (2000 mg/L) for 24 h as a stock solution to hydrate prior to use; the designed dosages of biochar were confirmed by measuring control samples. Three NSAIDs (DCF, NPX, and IBP) and acetonitrile were purchased from Sigma–Aldrich (St. Louis, MO, USA). Their detailed physicochemical properties are provided in the Supporting information (Table S2). A 10 mM stock solution for each NSAID was prepared with acetonitrile solution (anhydrous, 99.8%). The solution was diluted to a target NSAID concentration with ultrapure water after pre-evaporating a known amount of NSAID to minimize any cosolvent effect. Ultrapure water produced by a Milli-Q water filtration system (Millipore, Billeriac, MA, USA) was used for the preparation of all solutions.

2.2. Adsorption experiments

A 20 μM of each pharmaceutical solution was added to 40-mL glass vials equipped with a polytetrafluoroethylene-lined screw cap, and then six known volumes (0.1–0.8 mL) of biochar stock suspension, prepared by adding 200 mg of adsorbent to 100 mL of DI water (2 g/L) and mixing over a magnetic stirrer at 500 rpm, were spiked for the production of a single-solute adsorption isotherm. The pH of the aqueous phase was adjusted to 7 with 1.0 M HCl and NaOH prior to the addition of the adsorbent. Following solute and adsorbent addition, the vials were shaken for 7 d under ambient conditions to achieve equilibrium. After equilibrium, each sample was filtered by 0.22 μm Durapore membrane filters (PVDF) to prevent an adsorption of adsorbates on the filters and concentrations of NSAIDs were analyzed using an Agilent 1200 series high-performance liquid chromatograph (Agilent technologies, Santa Clara, CA, USA). To produce competitive isotherms, bi- and tri-solute adsorption experiments were also performed, and the adsorption method was identical to that used to produce the single-solute isotherm, except for the addition of two or three solutes in the vials. All adsorption experiments were conducted in duplicate or triplicate.

2.3. Characterization of adsorbents

Elemental analysis of the adsorbent was performed on a Perkin-Elmer 2400 Series II CHNS/O Elemental analyzer (PerkinElmer, Waltham, MA, USA). The ash content was determined by heating the biochars to 750 °C and the oxygen content was calculated by subtracting the ash, and carbon, hydrogen and nitrogen contents from the total mass of the samples. Surface and pore characteristics were examined by gas adsorption using a Gemini VII 2390p surface