Chemical Engineering Journal 265 (2015) 219–227

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Sorptive removal of salicylic acid and ibuprofen from aqueous solutions using pine wood fast pyrolysis biochar

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HIGHLIGHTS

- Pinewood biochar was used to remove two pharmaceutical compounds.
- Both carboxylic acid adsorbates have pH-dependent equilibria between their acid and carboxylate anion forms.
- Adsorption was not limited to the small surface area.
- Sorption followed pseudo-second order kinetics with regression of coefficients of 0.98 or greater.

ARTICLE INFO

Article history:
Received 3 September 2014
Received in revised form 1 December 2014
Accepted 2 December 2014
Available online 9 December 2014

Keywords:
Ibuprofen
Salicylic acid
Biochar
Adsorption
Solution pH

ABSTRACT

Pine wood biochar, prepared at 698 K with a residence time of 20–30 s in an auger-fed reactor, was used as a 3-dimensional adsorbent to remove salicylic acid and ibuprofen from aqueous solutions. This biochar was characterized by FT-IR spectroscopy, scanning electron microscopy, transmission electron microscopy, surface area determination, and zero point charge measurements. Batch sorption studies were carried out at pH values from 2 to 10, adsorbate concentrations from 25 to 100 mg/L and temperatures from 298 to 318 K. The adsorption of both adsorbates was highest at low pH values, dropped as pH increased and then exhibited a second increase related to the p*K*a of these carboxylic acid adsorbates. This was followed by a further drop at high pH. Conjugate acid/base equilibria of the adsorbates and the phenolic hydroxyl and carboxylic acid biochar sites versus pH dominated the mechanism. Sorption followed pseudo-second order kinetics. Sorption was evaluated from 298 to 318 K using the Freundlich, Langmuir, Redlich–Peterson, Toth, Sips, and Radke–Prausnitz adsorption isotherm models. Langmuir adsorption capacities for both salicylic acid and ibuprofen were 22.70 and 10.74 mg/g, respectively. This low surface area pinewood biochar (1.35 m^2/g) can adsorb far more adsorbate compared to commercial activated carbons per unit of measured surface area. Methanol stripping achieved 93% and 88% desorption of salicylic acid and ibuprofen, respectively, from the spent biochar, and 76% and 72% of the initial salicylic acid and ibuprofen adsorption capacity, respectively, remained after four full capacity equilibrium recycles.

1. Introduction

Wastewater pollution is an urgent environmental concern. The negative effects of pollution on both humans and the environment have become a subject of intense discussion. Pharmaceutical pollutants are increasingly important and require immediate attention [1]. Pharmaceutical products enter the aquatic environment through municipal waste water treatment, plant effluent, animal excreta, direct discharge of pharmaceuticals into water bodies, and septic tank leakage [2]. Negative effects on humans and animals include the suppression of embryonic cell growth in humans [3], the incapacitation of liver and gills in fish [4], and the inhibition of Gram-positive bacteria [5]. Despite public concerns about the negative effects that pharmaceuticals have on aquatic ecosystems, there are currently no federal laws defining the amount of these chemicals permitted in waste water streams or in drinking water.

Acetylsalicylate is a widely sold "over the counter" drug. Deacetylation of acetylsalicylate produces salicylic acid **1** and its two metabolites (ortho-hydroxyhippuric acid and the hydroxylated metabolite gentisic acid) [6]. Salicylic acid has been found in industrial influent samples in concentrations up to 54 ug/L [7].

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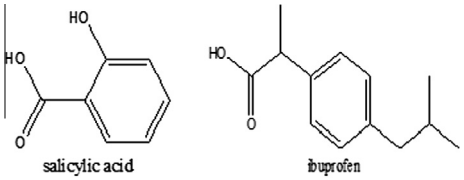
http://dx.doi.org/10.1016/j.cej.2014.12.006
1385-8947/

Ibuprofen **2** is a non-steroidal anti-inflammatory drug with a wide global consumption. It is produced on an industrial scale as a racemate which is generally excreted in the form of conjugates such as 2-[4-(2-hydroxy-2-methylpropyl)phenyl]propanoic acid, 2-[4-(2-carboxypropyl)phenyl]propanoic acid, and 2-phenylpropanoic acid. Ibuprofen is known to have endocrine disruptive activity [8].

Aqueous solutions of these pharmaceutical pollutants have been treated by physical, biochemical and chemical processes [9]. However, these techniques can be expensive. Thus, low cost methods to remove pharmaceutical contaminants from aqueous solution will be well embraced. Low cost adsorbents can be employed to remove recalcitrant compounds from aqueous solution inexpensively and can be effective for removing both organic and inorganic contaminants [10].

The objective of this work is to establish if pine wood biochar can be used to successfully remove ibuprofen and salicylic acid from water. This pinewood biochar is produced by the fast pyrolysis of pine chips in an auger-fed fast pyrolysis reactor used to make bio-oil [11]. Hence, it is available as a byproduct of bio-oil [12], an emerging renewable liquid fuel. If these types of biofuels are eventually produced in large amounts, biochars will be widely available in many locations. Biochars have fuel value (as a coal substitute) or can be used for carbon sequestration or soil conditioners [13,14]. A value-added application as a low cost widely applicable adsorbent [10,15] is desirable and could increase the value of this biofuel byproduct. This research investigates the adsorption behavior of salicylic acid and ibuprofen at different concentrations, pH values, and temperatures.



1 **2**

2. Experiment

2.1. Chemicals and equipment

All chemicals used were either GR or AR-grades. They were purchased from Sigma Aldrich (Saint Louis, MO) unless otherwise specified. Salicylic acid and ibuprofen sodium salt were purchased as white solids with p*K*a's of 2.97 and 4.91, respectively. Salicylic acid's solubility in distilled water is 2 g/L at 293 K, while that of ibuprofen's sodium salt is 100 g/L. However, the solubility of ibuprofen in water is only 21 mg/L in distilled water.

2.2. Preparation of pine wood biochar

The biochar used for adsorption experiments was produced as a byproduct of bio-oil produced by fast pyrolysis of pine wood chips in an auger-fed reactor at a temperature of 698 K using a feed rate of 1–2.5 kg/h [11]. The residence time of the pine wood chips in the hotzone was 20–30 s and the approximate gas residence time in the reactor was 2 s. The chips were preheated to between 383 and 393 K, and a proprietary heat transfer method was used to speed the temperature rise to 698 K in the hotzone. The powdered biochar was collected from the system by capturing it in an enclosed pot after moving past the hotzone. After subsequent removal from this container at room temperature, it was washed several times with distilled water to remove salt impurities and water-soluble organic residuals. Biochar was sieved to a particle size distribution of 100–600 μm (0.1–0.6 mm), and moisture was removed by heating to 383 K for 12 h. The adsorbent was then stored in a closed vessel at 338 K for several days until needed.

2.3. Char characterization

2.3.1. FT-IR

The infrared spectrum of powdered biochar was obtained using a Thermo Nicolet 6700 FT-IR spectrometer. A total of 64 scans were taken from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1}.

2.3.2. Scanning electron microscopy (SEM)

A JEOL JSM-6500F FE-SEM operated at 5 kV was used to examine the biochar's surface morphology. The sample was coated on a carbon stub attached to carbon tape and then sputtered-coated under argon with a 5 nm layer of platinum. The coated sample was then mounted into a sample holder for SEM analysis.

2.3.3. Transmission electron microscopy (TEM)

The biochar was examined using a JEOL model 2100 TEM operated at 80 kV. A small amount of adsorbent was mixed with 100% ethanol, sonicated for about 4 min, and allowed to stand for 24 h. A drop of this suspension was applied to a carbon film on 300 mesh copper grid and allowed to dry in air before TEM analysis.

2.3.4. Surface area measurements and elemental analysis

The biochar's BET surface area (1.35 m^2/g) was determined using a Gemini 2375 V 1.00 surface area analyzer. Biochar elemental analysis, using a CE 440 elemental analyzer (Exeter Analytical, Inc.), found 73.14% C, 3.27% H, 0.32% N with the remaining percentage being 23.27%. Ash content was 3.98% using ASTM D1506-99 method. Thus, this char's oxygen content was ~19%.

2.3.5. Zero point charge determination

Zero point charge was determined using 0.01 M NaCl aqueous solutions with pH values ranging from 2 to 10 at pH intervals of 2. About 10 mL was added to 0.1 g of the biochar and the mixtures were swirled for 48 h. pH was adjusted using either 0.1 N HCl or 0.1 N NaOH solutions. The supernatant was decanted and its pH measured using an ORION model 210 pH meter. The point of zero charge was obtained by plotting supernatant pH verses the initial solution pH.

2.4. Adsorption studies

The adsorbate concentrations were varied from 25 to 100 mg/L for kinetic studies. Kinetic studies for ibuprofen and salicylic acid adsorption were carried out at pH values of 3 and 2.5, respectively, at 298, 308, and 318 K. A known amount of biochar was added to 25 mL solutions containing different adsorbate concentrations in 40 mL amber glass vials. Samples were then swirled at 200 rpm for 16 h. After equilibration, the samples were filtered through Whatman No. 1 filter paper. The amount of adsorbate remaining in the filtrate was determined at their λ_{max} wavelengths of 220 nm for ibuprofen and 298 nm for salicylic acid. Samples were analyzed in duplicate and their average absorbances used. The amount of adsorbate removed per gram of adsorbent was obtained by:

$$q_e = \frac{V(C_o - C_e)}{M} \quad (1)$$

where q_e is the amount of adsorbate (mg) removed per gram of adsorbent, C_o and C_e are the initial and equilibrium adsorbate concentrations (mg/L) in solution, V is the solution volume (L), and M is the biochar weight (g).