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Assessment of naproxen adsorption on bone char in aqueous solutions using batch and fixed-bed processes

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ABSTRACT

An integrated analysis of naproxen adsorption on bone char in batch and packed-bed column conditions has been performed. Kinetic, thermodynamic and breakthrough parameters have been calculated using adsorption models and artificial neural networks. Results show that naproxen removal using bone char in batch conditions is a feasible and effective process, which could involve electrostatic and non-electrostatic interactions depending mainly on pH conditions. However, the application of packed-bed column for naproxen adsorption on bone char is not effective for the treatment of diluted solutions due to the low degree of adsorbent utilization (below 4%) at tested operating conditions. The proposed mechanism for naproxen removal using bone char could include a complexation process via phosphate and naproxen, hydrogen bonding and the possibility of hydrophobic interactions via π–π electron. This study highlights the relevance of performing an integrated analysis of adsorbent effectiveness in batch and dynamic conditions to establish the best process configuration for the removal of emerging water pollutants such as pharmaceuticals.

1. Introduction

Carbon-based adsorbents are versatile and the most popular materials for wastewater treatment and water purification due to their physical, chemical and structural properties [1–3]. These adsorbents can be obtained from different precursors and synthesis conditions and, consequently, they can be effectively applied for improving water quality via the removal of a great variety of pollutants, which include dyes, heavy metals, pesticides, arsenic, fluoride, and other inorganic and organic compounds [1,2,4–8]. Specifically, the use of carbon-based adsorbents for water purification is recognized as a prevailing method and it has become the focus of extensive research because of its simple design, easy operation, low cost and high efficiency [9,10]. It has been estimated that almost 80% of the carbon adsorbent production is used for aqueous adsorption processes [9]. Recently, these adsorbents have found applications for the removal of non-traditional water pollutants such as radioisotopes or pharmaceuticals [11,12].

To date, pharmaceuticals are considered as emerging water pollutants due to their widespread use worldwide [13,14]. These pollutants can enter into the sewer system via the human urine and fecal matter and, consequently, they can reach the wastewater treatment plants [12,14]. Recent studies have reported that conventional sewage treatment plants are not effective to remove/degrade these compounds [12,14]. Therefore, pharmaceuticals may be continuously introduced into water resources representing an environmental risk for both ecosystems and human beings due to its toxicological profile, even at trace concentrations [3,12,13,15,16].

The adsorption of pharmaceuticals has been studied mainly at batch operational conditions using activated carbons and other adsorbents such as soils, clays, nanocomposites, hydrous oxides, alumina and silica [3,12,14,17–19]. The adsorption capacity of traditional materials usually ranges from 0.1 to 10 mg/g, depending on the adsorbent, operating conditions and pharmaceutical compound used as solute. On the other hand, few authors have reported on the adsorption of pharmaceuticals at dynamic operational conditions using packed-bed columns [20–22]. It is convenient to highlight that, although the batch experiments provide valuable data about adsorbent effectiveness, including kinetic data and equilibrium uptakes, the evaluation of adsorbent performance at dynamic conditions is fundamental for the process scale up [23]. Dynamic adsorption experiments are necessary to obtain practical information about the adsorption capacity under flow conditions; they are needed to calculate design parameters for real-life applications and to identify the best operating conditions [23]. Note that the quantitative characterization of the adsorbent performance in packed-bed columns also involves the modeling and prediction of the breakthrough curves. Literature indicates that extensive studies in pilot plant scale can be avoided if the breakthrough curves for adsorption columns can be reliably modeled and predicted using laboratory scale measurements

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[20,24]. Traditionally, the adsorbent performance is tested in batch or dynamic conditions, but not in both. However, the integrated analysis of both adsorption systems is fundamental for determining the best configuration and for performing a reliable design of treatment/purification processes used in the removal of priority water pollutants.

With this in mind, the objective of the present study is to assess the performance of bone char as adsorbent for naproxen removal from aqueous solution at both batch and dynamic operating conditions. Naproxen is a member of the arylacetic acid group that exhibits anti-inflammatory and analgesic effects in medical treatments [13,14]. However, this drug is considered as an emerging water pollutant with a high environmental risk [12]. The bone char is a low-cost and high performance carbon-based adsorbent that can be applied for the removal of both organic and inorganic compounds [8,25–27]. To the best of the author's knowledge, this adsorbent has not been used for naproxen adsorption from aqueous solutions. Therefore, batch and dynamic adsorption tests for naproxen on bone char have been studied at different operating conditions and data analysis has been performed to calculate kinetic, thermodynamic and design parameters using both adsorption models and artificial neural networks. The effectiveness of batch reactors and packed-bed columns for naproxen adsorption on bone char has been discussed including the advantages and limitations of each process configuration.

2. Methodology

2.1. Adsorbent description and its physicochemical characterization

Naproxen adsorption experiments were performed using a commercial bone char supplied by Carbotecnia company (Mexico), which is produced from bovine bones. Bone char is considered as a mixed adsorbent constituted by carbon and calcium phosphate in the hydroxyapatite form [26]. In this study, the commercial bone char was washed with deionized water until obtaining a constant pH in washing solution. It was dried and sieved to obtain a mean particle diameter of 0.67 mm (i.e., 20–35 mesh fraction) and this raw adsorbent was employed for naproxen removal. Different characterization techniques were applied for the determination of physicochemical properties of the bone char samples. Specifically, textural parameters of the adsorbent (i.e., surface area, pore size distribution and pore volume) were calculated by N_2 adsorption–desorption isotherm at 77 K using a home-made fully automated equipment designed and constructed by the Advanced Materials group (LMA, Universidad de Alicante), commercialized as N2 Gsorb-6 (www.g2mtech.com). FTIR analysis was performed to identify organic functional groups on adsorbent surface using a Bruker IFS 66/S spectrophotometer with 200 scans and a resolution of 4 cm^{-1}. The physical morphology of bone char was observed with a JEOL JSM-840 scanning electron microscope (SEM) where adsorbent particles were coated with gold.

2.2. Batch adsorption of naproxen and the calculation of kinetic and equilibrium parameters

Naproxen adsorption kinetics and isotherms were obtained at different operating conditions using batch reactors with a mass–volume dosage of 10 mg/mL. These adsorption experiments were performed at pH 5–7 and 20–40 °C using aqueous solutions prepared with naproxen sodium and deionized water. Kinetic adsorption rates were calculated with naproxen initial concentrations of 50, 100 and 200 mg/L and samples were taken from $t = 0.5$ to 24 h; while the adsorption isotherms were obtained using initial concentrations from 20 to 250 mg/L where the equilibrium time was 24 h. The naproxen concentrations were determined using a Hach DR 5000 UV/Vis spectrophotometer at the corresponding characteristic wavelength of naproxen (i.e., 261 nm), and using a linear calibration curve. All the adsorption experiments were conducted in triplicate and the average values were used for data analysis and modeling. The naproxen adsorption capacity of bone char (q, mg/g) was calculated using a mass balance

$$q = \frac{C_0 - C_t}{m} V \tag{1}$$

where C_0 and C_t are the initial and final naproxen concentrations (mg/L) in adsorption experiments, V is the naproxen solution volume (L) and m is the adsorbent mass (g), respectively.

The experimental adsorption data were analyzed using kinetic and equilibrium equations. Specifically, the pseudo-first and pseudo-second order rate constants [28,29] of naproxen adsorption on bone char were calculated and the intraparticle diffusion analysis [30] was performed; while the Freundlich, Langmuir and Sips models were used for isotherm analysis [31–33]. Kinetic and isotherm data modeling was performed via a non-linear regression where the coefficient of determination (R^2) and the mean absolute percentage deviation (E) were considered to measure the goodness of data fitting. Thermodynamic parameters of naproxen adsorption process were calculated using the Gibbs free energy ($\Delta G°$, kJ/mol)

$$\Delta G^\circ = -RT \ln K_c \tag{2}$$

where R is the universal constant of gases (kJ/mol K), T is the temperature of the adsorption process (K) and K_c is the equilibrium constant, which can be calculated as [15]

$$K_c = \frac{C_{Ae}}{C_e} \tag{3}$$

where C_{Ae} and C_e are the equilibrium naproxen concentrations on the adsorbent and in the solution given in mg/L, respectively. Standard enthalpy ($\Delta H°$) and entropy ($\Delta S°$) for the naproxen adsorption were calculated using

$$\ln K_c = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}. \tag{4}$$

These thermodynamic parameters were determined from van't Hoff plot.

2.3. Fixed-bed adsorption of naproxen and the calculation of breakthrough design parameters

Fixed-bed adsorption experiments were performed in polyethylene columns with an internal diameter of 1.8 cm and a length of 15 cm. The bed porosity of packed bed columns ranged from 25 to 30%. All dynamic adsorption experiments were performed at 30 °C and pH 7, which was the best pH for naproxen removal. Adsorption columns were operated at up-flow operation mode using a peristaltic pump and a feed flow rate of 3 mL/min. Naproxen breakthrough curves were obtained by collecting several effluent samples at different operating times. All fixed-bed columns were operated until the outlet column concentration C_t was 95% of the feed concentration C_0. This operating point was established as the saturation/exhaustion condition (t_e) of the bone char. The experimental conditions tested in dynamic adsorption experiments were: the mass of bone char (i.e., 4.5–17 g) and the initial naproxen concentration in the feed (i.e., 1–10 mg/L).

Design parameters of the packed-bed columns were determined from the experimental naproxen breakthrough curves and they were used to characterize the performance of bone char at different dynamic operating conditions. These parameters include the mass transfer zone (MTZ), the breakthrough point time (t_b), the overall adsorption zone (Δt) and the retardation factor (r_f). These parameters are given by

$$\mathrm{MTZ} = L\left(\frac{t_e - t_b}{t_e}\right) \tag{5}$$