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Adsorption of ciprofloxacin and norfloxacin from aqueous solution onto granular activated carbon in fixed bed column

Teeba M. Darweesh, Muthanna J. Ahmed*

Department of Chemical Engineering, University of Baghdad, Baghdad, Iraq

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ABSTRACT

Carbonization of *Phoenix dactylifera L* stones followed by microwave K_2CO_3 activation was adopted for preparation of granular activated carbon (KAC). High yield and favorable pore characteristics in terms of surface area and pore volume were reported for KAC as follows: 44%, 852 m^2/g, and 0.671 cm^3/g, respectively. The application of KAC as adsorbent for attraction of ciprofloxacin (CIP) and norfloxacin (NOR) was investigated using fixed bed systems. The effect of flow rate (0.5–1.5 ml/min), bed height (15–25 cm), and initial drug concentration (75–225 mg/l) on the behavior of breakthrough curves was explained. The fixed bed analysis showed the better correlation of breakthrough data by both Thomas and Yoon-Nelson models. Inlet drug concentration was of greatest effect on breakthrough data compared to other fixed bed variables. Experimental and calculated breakthrough data were obtained for CIP and NOR adsorption on KAC, thus being important for design of fixed bed column.

1. Introduction

Pharmaceutical compounds have been recognized as a hazardous class of organic pollutants due to their extensive use and long term effects towards aquatic environment (Ashfaq et al., 2016). Antibiotics constitute a group of pharmaceuticals that is widely used to treat several infectious diseases in both human and animals (Moussavi et al., 2013). About 30–90% of the given antibiotic dose can remain undegradable in the human or animal body, and is largely excreted as an active compound (Pouretedal and Sadegh, 2014). Ciprofloxacin and norfloxacin antibiotics are belonging to the Fluoroquinolones (FQs) family. These antibiotics are heavily used in medical and veterinary practice (Van Doorslaer et al., 2014). The presence of FQs residues in effluents from households, hospitals, and pharmaceutical industries is a major cause of acute and chronic toxicity, as well as the emergence of resistant bacteria (Prutthiwanasan et al., 2016). Consequently, removal of FQs residues from the environment is a crucial issue.

Many techniques have been used for treatment of FQs-rich effluents such as electrochemical oxidation (Zhu et al., 2016), biodegradation (Cˇvancˇarová et al., 2015), photodegradation (Sturini et al., 2015), catalytic degradation (Feng et al., 2016), micro-extraction (Ebrahimpour et al., 2012), oxidation (catalytic degradation) (Guo et al., 2016), and adsorption (Ferreira et al., 2016). Of these processes, it has been demonstrated that adsorption is a simple, effective, and economical method to remove low concentration FQ pollutants from waters (Tan et al., 2013). Adsorption is the widely used method for removal of a broad range of FQs pollutants due to its simple design, easy operation, and relatively simple regeneration. It has been detected that activated carbon is the efficient adsorbent for removal of FQs as compared to zeolite (Maraschi et al., 2014), clay (Sturini et al., 2016), silica (Liang et al., 2016), and carbon nanotube (Yu et al., 2016), because of its large surface area, micro-porous nature, and high adsorption capacity (Ahmed and Theydan, 2014).

Adsorption of FQs represented by ciprofloxacin and norfloxacin on activated carbons has been explained in many studies using batch operation (Sun et al., 2016, 2014; Wang et al., 2015; Peng et al., 2015; Liu et al., 2011, 2013; Yu et al., 2016). However, fixed bed adsorption of these FQs compounds on activated carbons has not been addressed by researchers. The data obtained during batch adsorption is not sufficient to provide accurate scale-up data required in the design of adsorption columns. Therefore, adsorption of many pharmaceutical groups like cephalosporin (Nazari et al., 2016), quinolones (Patiño et al., 2016; Sotelo et al., 2013), non-steroidal anti-inflammatory (Álvarez-Torrellas et al., 2016; Katsigiannis et al., 2015; Torrellas et al., 2015; Sotelo et al., 2014, 2012a; Dubey et al., 2014), tetracyclines (Álvarez-Torrellas et al., 2016), β-lactam (Yaghmaeian et al., 2014; Burkerta et al., 2011), sulfonamide (Zuo et al., 2016), analgesic drug (García-Mateos et al., 2015), and β-blocker (Sancho et al., 2012; Sotelo et al., 2012b, 2012c) has been studied by column adsorption systems, in which breakthrough curves are determined, and that is

* Corresponding author.
E-mail address: muthanna.ja@gmail.com (M.J. Ahmed).

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useful for determination of the operating life span of the fixed adsorbent bed.

The present study is the first case where sorptive removal of FQs in terms of ciprofloxacin and norfloxacin has been investigated at various operational conditions in fixed bed column reactor using date stones derived active carbon as an adsorbent. Date stones have been utilized as precursors due to their renewability, availability and favorable lignocellulosic composition including 42% cellulose, 18% hemicellulose, and 11% lignin (Ahmed and Theydan, 2012). Moreover, several adsorption models, such as the Bohart–Adams model, the Thomas model, and the Yoon–Nelson model have been applied for analysis of experimental breakthrough curve data with the aid of nonlinear regression analyses in order to get the suitable model with least error for measuring the adsorptive capacity of the adsorbent.

2. Materials and methods

2.1. Materials

Date stones (DS) were isolated from date fruits, frequently washed with tap water, and then dried in an oven at 110 °C for 24 h. After crushing and sieving, a fraction of 1–2 mm particle size was utilized as a precursor for preparation of activated carbon. Potassium carbonate (Didactic Company, Espuma) of purity 99.9% was used as an activator. Ciprofloxacin (Nanjing Huaxin Biopharm. Company Ltd. China) and norfloxacin (Ajanta pharma limited company, India) with purities of 99.9% were used as adsorbates where Table 1 shows their characteristics.

2.2. Preparation and characterization of KAC

Carbonization of dried DS sample to a solid char followed by its K_2CO_3 chemical activation was adopted as a preparation technique for KAC. Char was prepared by pyrolysis of 20 g dried DS sample using a stainless steel reactor of 3 cm diameter and 15 cm length. The reactor was designed to contain a removable upper cover with 1 mm concentric hole for escaping of pyrolysis gases. The reactor was placed in a furnace operated at 500 °C with a constant heating rate of 10 °C/min for 1 h activation time. Then the char product was withdrawn and allowed to cool.

Char (2 g) was well mixed with 10 ml K_2CO_3 solution at 0.8 g/g impregnation ratio for 24 h at room temperature. The impregnated sample was dried at 110 °C in an oven (Model IH-100, England) and then stored in a desiccator for the next treatment. The dried sample was activated with the aid of a modified microwave oven (MM717CPJ, China) by using a quartz glass reactor, described else-where (Ahmed and Theydan, 2013). After activation step at 540 W radiation power and 8 min radiation time, the activated sample was withdrawn from microwave oven and allowed to cool. The sample was leached with 0.1 M HCl solution for 24 h at room temperature in order to remove the residual of K_2CO_3 activator. Then the samples was filtered and repeatedly washed with distilled water to remove alkalis and organic matters, until the pH of filtrate reached 6.5–7. The product sample (KAC) was dried at 110 °C for 24 h. The yield of activated carbon was determined as follow:

$$Yield\ (\%) = \frac{WC}{WS} x100 \quad (1)$$

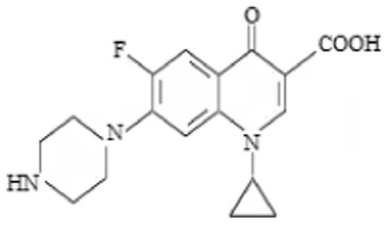
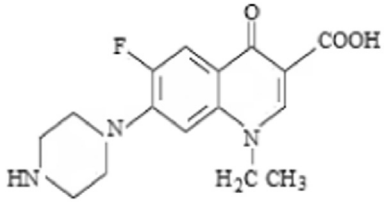
where Wc and Ws are the weights of activated carbon and dried date stones, respectively.

The surface area, total pore volume and average pore diameter of KAC were evaluated. Surface area was determined by the application of BET equation to the adsorption–desorption isotherm of N_2 at 77 K. Total pore volume was evaluated by converting the adsorption volume of N_2 at relative pressure of 0.95 to equivalent liquid volume of adsorbate. Structures of KAC and DS samples were also examined by scanning electron microscopy SEM (VEGA3 TESCAN) and Fourier transforms infrared spectroscopy FTIR (ABB MB3000).

2.3. Fixed bed adsorption

The breakthrough curves for adsorption of CIP and NOR on KAC in terms of effluent to influent concentrations ratio, C/C_o, versus contact time were investigated by carrying out a set of fixed bed experiments at a constant temperature of 30 °C. Granular KAC with a given amount was placed in a glass column of 30 cm length and 1.0 cm internal diameter. The upper and lower parts of column contained plastic pellets to compact the bed and avoid dead volume and channeling. KAC was packed on a plastic sieve placed at the bottom of column. CIP or NOR

Table 1
Characteristics and structure of ciprofloxacin and norfloxacin.

Compound	Structure	Formula	Weight (g mol^{-1})	Solubility[a] (mg/l)	γ_{max} (nm)	Ref.
Ciprofloxacin		$C_{17}H_{18}FN_3O_3$	331.35	150–6190	270	Li et al. (2015); Wu et al. (2010)
Norfloxacin		$C_{16}H_{18}FN_3O_3$	319.33	400–161000	273	Yang et al. (2012)

[a] Solubility at the pH range from 7 to 5.