Fluoroquinolones antibiotics adsorption onto microporous activated carbon from lignocellulosic biomass by microwave pyrolysis

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A B S T R A C T

Microwave-assisted KOH activation has been adopted to prepare activated carbon from a lignocellulosic biomass, *Albizia lebbeck* seed pods. Fluoroquinolones antibiotics such as ciprofloxacin (CIP) and norfloxacin (NOR) were removed from aqueous solutions by adsorption on prepared carbon. The surface area, micropores volume, and mesopores volume of such carbon were 1824.88 m^2/g, 0.645 cm^3/g and 0.137 cm^3/g, respectively. The effects of pH, adsorbent dose, and contact time on the adsorptive removal process were studied. Maximum removal percentages of 96.12% and 98.13% were achieved for CIP and NOR adsorption, respectively. The best fitting for equilibrium adsorption data of both antibiotics was obtained by the Langmuir isotherm with maximum capacities of 131.14 and 166.99 mg/g for CIP and NOR, respectively. The kinetic data were found to follow closely the pseudo-second order model for both antibiotics. Results of thermodynamic studies showed an endothermic CIP adsorption compared to an exothermic NOR adsorption under examined conditions.

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1. Introduction

Fluoroquinolones (FQs) have been classified among the most important synthetic antibiotics used in human and veterinary medicine [1]. One of the widely used FQs is ciprofloxacin (CIP), which has been identified among the top 10 of high priority pharmaceuticals relevant for the water cycle in general. The persistence of such antibiotic in the environment may induce bacterial resistances as well as present a threat to aquatic organism. Norfloxacin (NOR) is another FQs compound with high antibacterial activity against both gram-negative and gram-positive bacteria through inhibition of DNA gyrase [2]. Application of manure as fertilizer and leaking from septic systems leads to the direct release of NOR into surface water. The presence of such undegradable compound in wastewater may present a risk to human health. FQs have been detected at levels of up to 0.036 and 0.45 μg/l in surface water and wastewater effluent, respectively [3]. Although the amounts of FQs in the aquatic environment are low, their continuous input and accumulation may increase their concentration which constitute in the long term a potential risk for

aquatic and terrestrial organisms. Thus, removal of these compounds from the environment is an important case study.

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 [4]. It has been detected that activated carbon is the efficient adsorbent for removal of FQs as compared to others, because of its large surface area, micro-porous nature, and high adsorption capacity [5]. The main reasons for high cost of commercial activated carbon are the use of non-renewable and expensive precursors like wood and depending on conventional heating production methods [6]. Therefore, in recent years, research has been focused on the use of renewable and cheaper precursors such as agricultural wastes with the aid of low treatment time microwave production technique, in which energy is directly supplied to the carbon bed by dipole rotation ionic conduction inside the particles.

Recently, FQs antibiotics have been successfully removed from aqueous solutions by adsorption on activated carbon prepared from various waste biomasses such as date palm leaflets, peat, cyperus alternifolins, lotus stalk, and Trapa natans husk [7–11]. *Albizia lebbeck* (A.L.) is a common tree in tropical and subtropical regions. It belongs to the pea family (Fabaceae) and produces seed pods which are 20 cm long and 3 cm wide. This high volume waste constitutes an environmental problem and its reutilization is useful. A.L. seed pods are composed of 36.4% cellulose, 18.9% hemicelluose, 13.6% lignin, and 83.1% volatile matter [12]. The high volatile and lignocellulosic contents promote the use of these pods

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as precursors for production of microporous activated carbon with high surface area which revealed its capability for efficient adsorptive removal of cephalosporin antibiotics [13]. The main aim of this work is to investigate the ability of A.L seed pods-carbon for adsorptive removal of FQs antibiotics represented by CIP and NOR from aqueous solutions. The initial concentrations of both FQs used in this study were in the range from 20 to 100 mg/l as adopted by Conkle *et al.* [14]. In addition, the equilibrium isotherms, kinetics and thermodynamics data of the adsorption process were also studied to understand the adsorption mechanism.

2. Materials and methods

2.1. Materials

A.L. seed pods used for preparation of activated carbon were collected from trees located in the region of Baghdad University premises, Iraq. After the removal of seeds, the pods were first washed with water to get rid of impurities, dried at 110 °C for 24 h, crushed using disk mill, and sieved. Fraction with average particle size of 0.8 mm was selected for the preparation. Potassium hydroxide (purchased from Didactic company, Espana) of purity 99.9% was used as a chemical activator. CIP (supplied by Nanjing Huaxin Biopharm. Company Ltd., China) of purity 99.9% and NOR (supplied by Ajanta Pharma Limited Company, India) of purity 99.9% were used as adsorbates.

2.2. Activated carbon preparation

Dried pods (3 g) were mixed with 20 ml of KOH solution of at 1.0 g/g impregnation ratios (weight of activator/weight of dried pods) for 24 h at room temperature. The impregnated samples were next dried at 80 °C until completely dried and stored in a desiccator. For the activation of dried impregnated samples a quartz glass reactor (2.5 cm diameter × 12.5 cm length) was used. The reactor was sealed at one end and the other end had a removable cover connected to a stainless steel pipe of 5 mm inside diameter to allow for the escape of the pyrolysis gases. The reactor was placed in a modified microwave heating apparatus (MM717CPJ, China) and held at radiation power of 620 W for 8 min radiation time. At the end of activation the samples were withdrawn from the apparatus and allowed to cool. Then the samples were soaked with 0.1 M HCl solution such that the liquid to solid ratio is 10 ml/g. The mixtures were left overnight at room temperature, and then filtered and subsequently the samples were repeatedly washed with distilled water until the pH of filtrate reach 6.5–7. After that, the samples were dried at 110 °C for 24 h, and subsequently were weighed to determine the yield of the product. Finally the samples were stored in tightly closed bottles.

The yield of prepared carbon is defined as the ratio of final weight of the obtained product after washing and drying to the weight of dried precursor initially used. The yield was calculated based on the following equation:

$$\text{Yield}\,(\%) = \frac{W_f}{W_o} \times 100 \tag{1}$$

where W_f and W_o (g) are the weights of carbon product and dried pods, respectively.

The characteristics of prepared carbon represented by surface area, micropores and mesopores volumes, and pore size distribution were determined. Surface area was determined from the application of BET equation to the adsorption–desorption isotherm of N$_2$ at 77 K [15]. Micropores volume was determined by applying the Dubinin–Radushkevich equation. The mesopores volume was determined using BJH desorption branch [16] and the pore size distribution was determined from the density functional theory

[17]. NOVAWin2 data analysis software was used to perform these calculations [18]. The morphology of prepared activated and raw material was examined by scanning electron microscopy SEM (300 K Pixel CMOS, China).

2.3. Adsorptive removal

Batch mode adsorption experiments were carried out to show the effects of pH, contact time, and adsorbent dose on the removal percentages of CIP and NOR. Prepared carbon of 250 μm average particle size at different adsorbent dose (0.25–1.25 g/l) was mixed with 20 ml samples of CIP or NOR solutions with different initial concentrations (20–100 mg/l) and different pH (2–12). The mixtures were added to 100 ml Erlenmeyer flasks, and shaken at 200 rpm and 303 K for various contact times (0–150 min). Then, the samples were filtered and the concentrations of CIP or NOR in the filtrate were analyzed by using a UV-Visible Spectrophotometer (Shimadzu UV-160A) at maximum wavelengths of 275 and 272 nm for CIP and NOR, respectively. Each experiment was duplicated under identical conditions, indeed the results of UV analysis were the average of two readings. The removal percentage of each antibiotic was determined by the following equation:

$$\text{Removal percentage}\,(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where C_0 and C_e (mg/l) are the initial and equilibrium concentrations of CIP or NOR solution, respectively.

2.4. Adsorption isotherms

The relation between the adsorbed amounts of CIP and NOR and their equilibrium concentrations at different temperatures was investigated. 20 ml of CIP or NOR solutions with different initial concentrations (20–100 mg/l) was placed in 100 ml Erlenmeyer flasks. Carbon with average particle size of 250 μm was added to each flask and kept in a shaker of 200 rpm at various temperatures (303–323 K). Other parameters such as pH, contact time and adsorbent dose were kept at their best values. The concentrations of CIP or NOR solutions were similarly measured and the uptake of each component at equilibrium, q_e (mg/g), was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{3}$$

where V (l) is the volume of solution and W (g) is the weight of prepared carbon.

The experimental isotherm data of both antibiotics were correlated by the Langmuir, Freundlich, and Temkin and Phyzev [19–21]. These equations can be written as follows:

$$\text{Langmuir isotherm}\quad \frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \tag{4}$$

$$\text{Freundlich isotherm}\quad \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

$$\text{Temkin isotherm}\quad q_e = B \ln A + B \ln C_e \tag{6}$$

where q_L (mg/g) is the Langmuir maximum uptake of CIP or NOR per unit mass of carbon, K_L (l/mg) is the Langmuir constant related to rate of adsorption, K_F ((mg/g)(l/mg)$^{1/n}$) and n are Freundlich constants which give a measure of adsorption capacity and adsorption intensity, respectively, B is the Temkin constant related to adsorption heat and A (l/mg) is the Temkin parameter related to the equilibrium binding energy. Least-squares regression program based on Hooke–Jeeves and Gauss–Newton method was used to analyze experimental data. This program gave the parameters of