FIXED-BED COLUMN ADSORPTION OF FLUOROQUINOLONE ANTIBIOTIC FROM AQUEOUS SOLUTION ONTO SUGARCANE BAGASSE BIOCHAR

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Abstract. The ability of the agricultural residue of sugarcane bagasse to serve as an absorbent material used to remove Ciprofloxacin (CIP), one of strong Fluoroquinolone antibiotic from aqueous solutions in fixed-bed columns was investigated. The properties of biochar sugarcane bagasse were characterized using scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) spectroscopy before and after modification. The results of fixed bed column experiment showed that the shape of the removal efficiency of CIP and exhaustion time was dependent on bed height, flow rate and initial concentration. The maximum adsorption capacity qₑ predicted from Thomas model reached 0.955 mg/g at the flow rate of 1 mL/min, initial concentration of 15 mg/L and bed height of 6 cm. From Yoon-Nelson equation, 3.38 minutes was the time required for 50 % exhaustion of 12 cm bed height column with the flow rate 2 mL/min and concentration 15 mg/L. Thomas and Yoon-Nelson models were in good agreement with the experimental breakthrough curve data.

Keywords: biochar, sugarcane bagasse, adsorption, ciprofloxacin, fluoroquinolone.

Classification numbers: 2.3.1, 3.3.2, 3.4.2.

1. INTRODUCTION

Antibiotics are probably the most successful family of drugs to treat several infectious diseases in both human and animals [1], hence antibiotic drugs to be released in large quantities to natural ecosystems [2]. As micro-contaminants, antibiotics in the aquatic environment may persist and be transported to reservoirs, supply sources and drinking water treatment plants [3]. The effects and risks of antibiotics in the environment are issues of increasing importance resulting in antibiotics being regarded as toxic and hazardous chemicals [4 - 6].
Ciprofloxacin hydrochloride (CIP) is the second-generation broad-spectrum antibiotics in a group of drugs called fluoroquinolone (1-cyclopropyl-6-fluoro-1, 4-dihydro-4- oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid), its empirical formula is C_{17}H_{18}FN_{3}O_{3} and its molecular weight is 331.4 g/mol. Concentrations of CIP in wastewater effluents and surface water were observed to range from ng/L to mg/L. CIP concentration is between 249 and 405 ng/L in wastewater treatment plants have been reported [7] and between 31 mg/L and 50 mg/L in drug manufacturing plants [8 - 10]. Although, the presence of trace levels (ng/L) in wastewater effluents, receiving waters and drinking water sources led to negative impacts on ecological and human health [11 - 12]. Therefore, effective removal method of this compound from discharge streams to the environment becomes an important issue [13].

There are several studies for the removal of CIP from water, for instance adsorption [14, 15], photodegradation [16], photo Fenton oxidation processes [17], oxidation by chlorine and chlorine dioxide [18, 19] and ozonation [20] though batch experiments studies. In which, one of the easiest, most functional, and cost-effective process used as an alternative for organic elimination from aqueous solution is adsorption process. The data obtained during batch adsorption tests is not sufficient to provide accurate scale-up data required in the design of adsorption columns. Fixed bed adsorption has been addressed to eliminate CIP, which using date stones derived granular activated carbon [21] and bamboo based activated carbon [22], not for biochar.

A large amount of agricultural waste is produced yearly, which led to environmental hazards if not treated properly before discharge. There are more 6-7 millions sugarcane bagasse released from industrial scale-up process in Viet Nam [23]. The composition of sugarcane bagasse comprises of cellulose (41 – 55 wt. %), hemicellulose (20 – 27.5 wt. %), lignin (18 – 26.3 wt. %) and other (7 %) [24] in which high cellulose content plays an important factor for adsorption capacity.

The present study is the first case where adsorptive removal of ciprofloxacin has been investigated at various operational conditions in fixed bed column using sugarcane bagasse, namely BSB derived biochar as an adsorbent. The obtained material was characterized by SEM, FTIR. The effect of some parameters process such as bed height; flow rate and the initial concentration of CIP have been studied. The Thomas and Yoon-Nelson model was used also to assess the adsorption kinetics.

2. MATERIALS AND METHODS

2.1. Chemicals

All chemicals and reagents used in the study were of analytical grades and used without further purification. Hydrochloric acid (HCl) and CIP 99 % were purchased from China and Sigma-Aldrich, respectively. All the solutions utilized throughout the experiments were prepared in double distilled water. The 100 ppm stock solution of CIP was prepared by dissolving the desired amount of CIP in the HCl and double distilled water. Further, other solution CIP of different concentration was prepared by subsequent dilution of the stock solution.

2.2. Preparation of material

The carbonaceous precursor used for preparation of biochar was sugarcane bagasse, collected after cane press machine. The collected samples were washed gently several times with
tap water to remove impurities present on the surface and then dried for one week in oven. Dried sugarcane bagasse was cut to uniform size with a diameter of 1 cm, then was calcinated in a furnace at 500 °C in 1.5 hours. After cooling the solid residue to room temperature, they were stored in desiccator for further experiments.

![Image](image1.jpg)

**Figure 1.** Biochar obtained from sugarcane bagasse: a) before and b) after incineration process.

### 2.3. Evaluation of biochar

In this study, microstructure and surface morphology of the adsorbent samples were characterized by a 10 kV HITACHI S-4800 NIHE scanning electron microscope (SEM). To determine the functional groups of the adsorbent, Fourier transform infrared spectroscopy (FTIR) method was applied. The results recorded including spectral that specialize for different bonds or different functional groups. In this research, the FTIR analysis was conducted using FT-IR model 410 JASCO (Japan).

### 2.4. Fixed-bed column adsorption studies

It was shown that adsorption capacity unmodified sugarcane bagasse (USB) lower than biochar sugarcane bagasse (BSB) in difference calcination temperature (200 - 800 °C) in series batch experiments that has been carried out before, therefore, fixed-bed column adsorption experiments for only BSB at 500 °C calcination (highest batch adsorption capacity at 500 °C calcination). The loading behavior of CIP in its dynamic adsorption from solution by BSB could be shown in the form of breakthrough (BT) curves which is usually expressed in terms of normalized concentration, defined as the ratio of outlet adsorbate concentration to the inlet adsorbate concentration \(C_t/C_o\) or the adsorbed solute concentration \(C_{ad}\), which is the difference between inlet and outlet adsorbate concentration \(C_o - C_t\), as a function of time \(t\) for a given bed height. The time taken for outlet concentration of adsorbate to reach the breakthrough point is known as breakthrough time.

Fixed bed column experiment was conducted using a glass column with an internal diameter of 2 cm with height 30 cm. The bottle containing CIP solution was set at higher elevation so that the solution can be transferred at a constant flow rate to the column by gravitation force. A known quantity of BSB packed in the column to obtain the desired bed height of the adsorbent of 6 or 12 cm. The column was then filled up with 5 mm size glass beads in order to provide a uniform flow of the solution through the column and avoid adsorbent loss. CIP solution of known concentrations 15, 20 and 30 mg/L, were pumped upward through the column at a desired flow rate of 1 and 2 mL/min, controlled by a peristaltic pump.
The CIP solutions at the outlet of the column were collected at regular time intervals for analysis and the concentrations were determined using the UV–vis spectrophotometer (UV-1650PC, Shimadzu, Japan) with quartz cuvettes of 1 cm, under a wavelength of 276 nm. All experiments were carried out twice times at least at atmospheric pressure and room temperature.

2.5. Kinetic model

The expressions for the two models as Thomas and Yoon-Nelson used for predicting dynamic behaviour of the fixed bed column are given as follows [21]:

**Thomas model:**

\[
\ln \left[ \frac{C_o}{C_t} - 1 \right] = \frac{k_{Th} q_o m}{Q} - k_{Th} C_o t
\]

**Yoon Nelson model:**

\[
\ln \left[ \frac{C_t}{C_o - C_t} \right] = k_{YN} t - \tau k_{YN}
\]

where \( C_o \) is the effluent concentrations (mg/L), \( C_t \) (mg/L) is the input concentration at time \( t \) (minutes), \( q_o \) is the maximum adsorption capacity (mg/g), \( m \) is the total mass of the adsorbent (g), \( Q \) is volumetric flow rate (ml/min) and \( k_{Th} \) is the Thomas rate constant (ml/min/mg); \( k_{YN} \) is the Yoon Nelson rate constant (l/min), \( \tau \) is the time required for 50 % adsorbate breakthrough (min) and \( t \) is the breakthrough time (minutes).

3. RESULTS

3.1. Characterization of adsorbent materials

The SEM images of USB and BSB are shown in Figure 2. It can be seen that sugarcane bagasse is a mesoporous material with relatively large surface area. Due to the modification process, the structure of the modified and unmodified sugarcane bagasse may be different. Unmodified sugarcane bagasse had a smooth, sheet form and less porous structure on the surface. On the other hand, BSB had broken structure, resulting in more well-developed pores and contained many specific dispersion hole sizes to increase the surface area of adsorbent materials. From the SEM result, it is predicted that BSB has a potential adsorption CIP antibiotic.

![Figure 2. SEM image of (a) USB and (b) BSB at magnification 50 micrometer.](image)

Figure 3 represented the surface functional groups of sugarcane bagasse precursor and BSB. The range of strong absorption at approximately 3350 cm\(^{-1}\) determined by the spectrum of the absorbents can be regarded as the O–H stretching vibration of hydroxyl.
Generally, the absorption range of hydrogen-bonded OH groups is between 3200 and 3650 cm\(^{-1}\) with alcohols and phenols. The adsorption peaks at 2926 cm\(^{-1}\) was attributed to C–H stretching of the aliphatic structure. Bands located at approximately at 1600 cm\(^{-1}\) and 1515 cm\(^{-1}\) were attributed to C=O vibration of carbonyl groups and C=C vibration in aromatic group, respectively, that critical contribution to the adsorption ability. The peaks occurring at 1376, 1254 cm\(^{-1}\) and at 1250 cm\(^{-1}\) were ascribed to the C–H vibration of alkyne groups. Bands located at approximately 1051 cm\(^{-1}\) was attributed to the C–O vibration of the alcohol groups. Many peaks present in the sugarcane bagasse precursor spectrum absolutely disappeared in the BSB spectra while those remaining were weak to a great extent. This is consistent with the breaking of many bonds leading to the liberation and elimination of volatile species and partial aromatization during incineration, leading to increase the surface activated site with CIP antibiotic.

![Figure 3. FT-IR spectra of USB and BSB.](image)

3.2. Absorption of CIP

3.2.1. Effect of operating conditions on column adsorption

**Effect of initial concentration**

The effect of initial concentration of CIP in the range 10–30 mg/L, with the same BSB bed height of 12 cm and solution flow rate of 1 mL/min was displayed in Figure 4a. This figure shows that the breakthrough time decreased with an increase in the influent CIP concentration. These parameters also support this result: as the inflow concentration of CIP increased from 15 to 30 mg/L, the breakthrough time decreased from 270 to 70 min, reduced 3.86 times. Increasing the inlet concentration of CIP reduced the time required to reach the effective bed load as the binding sites became more quickly saturated. It could be associated with the relative increase in concentration gradient. As a result of decrease in exhaustion time, there is a limitation on the adsorbent to continue removing CIP from solution. The overall trend of the breakthrough curve is more flat and gentle, and when the CIP inflow concentration increases, the penetration curve will gradually increase. The similar findings have been suggested for the adsorption of flumequine and levofloxacin antibiotics on commercial and date stones derived granular activated carbon, respectively [21, 25].
Effect of flow rate

Figure 4. The breakthrough curve of effect on influent of (a) CIP concentration, (b) flow rate, and (c) bed depths of CIP adsorption onto BSB absorbent.

The effect of flow rate on the adsorption of CIP onto BSB was investigated by varying the flow rate at 1 and 2 mL/min with a constant BSB bed height of 12 cm and CIP initial concentration of 15 mg/L. It can be observed in Figure 4b that at a higher flow rate, the column was exhausted earlier and the breakthrough curve was steeper. When the flow rate increased from 1 mL/min to 2 mL/min, the exhaustion time decreased from 240 minutes to 150 minutes. The removal efficiency was higher with lower flow rate. For example, after 90 minutes until 180 minutes, the CIP removal efficiency for the flow rate of 1 mL/min was 2 times higher than for 2 mL/min. The phenomenon can be explained that for a higher flow rate, the front of the mass
transfer zone reached the end of the fixed bed more quickly, and the adsorbent was saturated at a higher rate. Similar observations have been reported for fixed-bed adsorption of cephealexin and CIP on granular activated carbon [21, 26].

**Effect of bed height**

Figure 4c, shows the breakthrough curves obtained for CIP adsorption onto BSB at bed heights of 6 and 12 cm, and a constant flow rate of 1 mL/min and initial concentration of 15 mg/L. At bed heights of 6 and 12 cm, the breakthrough times were 45 and 180 min, respectively. The figure displays that the breakthrough curves and exhaustion times increased as bed height increased for adsorbate. The increase in the breakthrough time could be ascribed to the longer distance it takes the mass transfer zone to move from the entrance of the bed to the exit when the bed height is increased. Furthermore, higher uptake of CIP was observed at higher bed height, which could be attributed to rising in the specific surface area of BSB, which provided more fixation binding sites for adsorbate to adsorb. The increase in BSB mass in a higher bed depth also gave rise to an increase in the volume of the CIP solution treated per unit mass of BSB at exhaustion point. Similar observation was also reported by Darweesh *et al.* [21] and Sotelo *et al.* [25] during fixed-bed adsorption study on CIP.

3.2.2. **Breakthrough curve modeling**

In this study, the dynamic adsorption data were used to predict the dynamic adsorption behavior using the Thomas and Yoon-Nelson models.

**Thomas model**

Thomas model assumes plug flow behaviour in the bed, Langmuir isotherm for equilibrium and second order reversible reaction kinetics. It further assumes a constant separation factor but it is applicable to either favourable or unfavourable isotherms. The plots of $\ln(C_t/C_o-1)$ versus time for the adsorption of CIP in different conditions of bed height, initial concentration and flow rate were shown in Figure 5a, b, c. The model constants, $K_{Th}$ and $q_o$, were calculated and reported in Table 1. Thomas rate constant, $K_{Th}$ increased with the decrease of flow rate and initial ion concentration but decreased with the decrease of bed height. On the contrary, for lower bed height, the maximum capacity was higher. The maximum adsorption capacity $q_o$ predicted from Thomas model reached 0.955 mg/g at the flow rate of 1 mL/min, initial concentration of 15 mg/L and bed height of 6 cm. Almost high values of regression coefficients ($R^2 > 0.85$) were determined indicating that the kinetic data fit well with Thomas model. Therefore, the Thomas model is suitable for the adsorption process, indicating that external and internal diffusion are not limiting steps.

**Yoon-Nelson model**

Yoon-Nelson model is based the rate of decrease in the probability of adsorption of each adsorbate molecule. It is assumed to be proportional to probability of adsorption of the adsorbate and probability of adsorbate concentration exceeding the breakthrough concentration on the adsorbent. The plots of $\ln(C_t/(C_o- C_t))$ versus time for the adsorption of CIP in different conditions of bed height, initial concentration and flow rate were shown in Figure 6a, b, c. In addition, Table 1 shows the rate constant, $K_{YN}$ (min$^{-1}$), and the time required for 50 % adsorbate breakthrough, $\tau$ (min), decreased together. It can be seen that the time required for 50 % exhaustion of column increase with the increase of bed height and decrease when the flow rate and initial concentration increase. 3.38 minutes was the time required for 50 % exhaustion of 12 cm bed height column with the flow rate 2 mL/min and concentration 15 mg/L while the
adsorbent in the column with bed height of 12 cm, initial concentration of 10 mg/L and flow rate of 1mL/min did not achieve 50% saturated before 208 minutes. In addition, the correlation coefficient ($R^2$) ranges from 0.8118 to 0.9526 in the Yoon-Nelson model, indicating that the Yoon-Nelson model can also predict the adsorption performance for the adsorption of CIP in a fixed-bed column.

*Figure 5.* Thomas kinetic plot for the adsorption of CIP on BSB at (a) different initial concentration; (b) different flow rate; (c) different bed depths.
To summarize, Thomas and Yoon-Nelson models exhibited good correlation with the experimental breakthrough data for removal CIP using BSB adsorbent. Hence, these models can be used to predict the adsorption performance of CIP in a fixed-bed column.

A comparison of model parameters for removal CIP using date stones derived granular activated carbon (Darweesh et al. [21] and this study showed that column adsorption capacity is 2.094 mg/g ($C_0 = 150$ ppm; flow rate 0.5 mL/min; high bed 25 cm), higher than 0.955 mg/g ($C_0 = 15$ ppm; flow rate 1 mL/min; high bed 6 cm), respectively and saturated time is 65.31 min and 159.29 min, respectively. The double difference in the adsorption capacity can be explained that the material used is activated carbon which has better adsorption capacity than biochar, in addition to the operating conditions with longer retention time in this experiment.

Figure 6. Yoon-Nelson kinetic plot for the adsorption of CIP on BSB at (a) different initial concentration; (b) different flow rate; (c) different bed depths.
Table 1. Parameters of Thomas, and Yoon-Nelson model under different experiment conditions in fixed-bed column obtained from adsorption of CIP by BSB absorbent.

<table>
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<th>Co (mg/L)</th>
<th>Q (mL/min)</th>
<th>H (cm)</th>
<th>Thomas $K_{TH} \times 10^4$ (mL/min/mg)</th>
<th>$q_0$ (mg/g)</th>
<th>$R^2$</th>
<th>Yoon-Nelson $K_{YN}$ (min$^{-1}$)</th>
<th>$\tau$ (min)</th>
<th>$R^2$</th>
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<td>0.0208</td>
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<tr>
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<tr>
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4. CONCLUSIONS

The adsorptive removal of CIP from aqueous solution by BSB using fixed bed column system has been investigated. From FRIR and SEM results, it is predicted that BSB has a potential of antibiotics adsorption. The results of fixed bed column experiment showed that the shape of the removal efficiency of CIP and exhaustion time was dependent on bed height, flow rate and initial concentration. When the bed height increased from 6 g to 12 g, the adsorption efficiency increased 50%. The removal efficiency increased more than 3 times when the initial concentration decreased from 30 mg/L to 15 mg/L. Similarly, as the flow rate decreased from 2 mL/min to 1 mL/min, CIP removal efficiency increased 2 times. Thomas and Yoon-Nelson model are suitable to predict the maximum capacity and time for the adsorbent to be 50% exhausted.

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