BIOCHAR AS A FILTER MEDIA FOR THE ADSORPTION OF
PHARMACEUTICALS FROM WASTEWATER EFFLUENT IRRIGATION WATER

A Thesis in
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by
Marlene Carla Ndoun

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The thesis of Marlene Carla Ndoun was reviewed and approved by the following:

Herschel A. Elliott  
Professor of Agricultural and Biological Engineering  
Thesis Advisor

Heather E. Gall  
Associate Professor of Agricultural and Biological Engineering

John E. Watson  
Professor of Soil Science / Soil Physics

Paul H. Heinemann  
Professor of Agricultural and Biological Engineering  
Head of the Department of Agricultural and Biological Engineering

*Signatures are on file in the Graduate School.
ABSTRACT

Global water shortages due to urbanization and rapid population growth are placing unprecedented pressure on water supplies. The use of treated wastewater effluent has become a valuable solution to preserve water resources but its reuse for irrigation of agricultural lands has led to the widespread presence of pharmaceuticals and personal care products (PPCPs) in the environment and increased public concern over the potential ecotoxicological effects of these contaminants on aquatic life, animals, plants and even humans. This study explores the use of biochars obtained from cotton gin waste (CG) and guayule bagasse (GB) as potential adsorbents for the removal of the following pharmaceutical compounds: acetaminophen (ACT), ibuprofen (IBP), sulfapyridine (SPY), docusate (DCT), erythromycin (ETM) and pseudoephedrine (PED) from aqueous solution. The biochars were prepared through pyrolysis at 350, 500 and 700 °C for 2 h in a stream of N₂ gas. CG and GB biochars were characterized for specific surface area (SA), pH, surface functional groups using FTIR and zeta potential to estimate the point of zero charge (pHₚzc.). An increase in pyrolysis temperature led to an increase in the pH, zeta potential and SA of the biochars. All the biochars showed a net negative charge on their surfaces and an increase in pH was accompanied by an increase in the magnitude of negative charge. Both CG and GB biochars showed strong functionality with the presence of OH, C-H, C=O and C=C groups on their surfaces. The main difference between the biochars was the presence of an additional O-containing functional group on the GB biochar surface, indicating it is less hydrophobic compared to the CG biochars.

Batch adsorption experiments were performed to determine the removal efficiency of CG and GB biochars for the selected pharmaceutical compounds from aqueous solution. Additionally, the effects of contact time and biochar properties on the adsorption capacity were investigated. The results showed that the adsorption of ACT, IBP, SPY, DCT, ETM and PED onto the CG
and GB biochars was influenced by the contact time, solution pH, specific surface area, net charge and functional groups of the biochars. The extent of pharmaceutical adsorption was, in general, positively related to the SA of the biochars. The mechanisms responsible for removal of pharmaceuticals are hydrophobic bonding, hydrogen bonding, π-π electron donor acceptor interactions and diffusion. The lower hydrophobicity of the GB biochars precluded the adsorption of hydrophobic compounds, hence low removal was achieved by these biochars. ACT showed the least removal (<20%) of all the tested biochars due to electrostatic repulsion between the anionic ACT and the negatively charged biochar surfaces. Depending on the pharmaceutical being removed, functional groups of both the biochars and the pharmaceuticals or specific surface areas controlled the adsorption process.

ACT, IBP, SPY, DCT, ETM and PED adsorption studies using the CG700 biochar were also carried out at pH 7 and compared to the adsorption behavior at inherent system conditions (pH 10-11). The removal of ACT significantly improved at pH 7 due to the reduction in electrostatic repulsion between CG700 and ACT molecules. IBP removal decreased from 50% to 35% and the adsorption of SPY decreased from 70% to 30% at pH 7 and the decline is attributed to a decrease in the formation of negative-charge assisted hydrogen bonds. There seem to be no appreciable and consistent differences in the extent of DCT, PED and ETM adsorption for the two pH conditions. The adsorption of pharmaceuticals onto biochar followed pseudo-second order kinetics suggesting the adsorption is controlled by the surface areas of the biochars as well as chemisorption due to electron transfer or sharing. The adsorption data was successfully fitted to both the Langmuir and Freundlich isotherm models although the Langmuir model showed a better fit. The fit of the data to the Langmuir model implies that there was negligible interaction between the pharmaceutical molecules and this favored adsorption by the biochar.
A series of small-scale downflow column tests were carried out using biochar-amended sand media to determine the breakthrough curves for four selected pharmaceuticals: ACT, SPY, DCT and ETM at initial concentrations of 10 mg L⁻¹, a constant flow rate of 1 mL min⁻¹ and a 13-cm bed depth. Breakthrough (time when the column effluent-to-influent concentration ratio was 0.05) occurred in the following order: SPY (1 h), ACT (2 h), ETM (4 h) and DCT (5 h). The ability of CG700 biochar-amended sand filters to remediate ACT, SPY, DCT and ETM was validated by a reduction in contaminant concentration through the column which was confirmed by the high Kᵅ values and maximum bed capacity (qₑ). The breakthrough curves demonstrated that the biochar-amended sand filters have a high affinity for the pharmaceutical compounds and this resulted in slow saturation of the bed occurring after 12 h. These results show that CG and GB biochars could be added to sand filters and have the ability to act as environmentally friendly adsorbents for the removal of pharmaceuticals from treated wastewater used for irrigation.

Lab-scale column data were used to estimate the parameters for a full-scale effluent filtration column. Through scale-up analysis, it was estimated that a total volume of 446 m³ can be treated before the column breakthrough point (Cₑ/C₀ = 0.05) is attained at 22 h with an estimated 39.32 g of ACT removed per kg of biochar. It should be noted that the removal of pharmaceuticals from irrigation water using a full-scale filtration system depends on many system-specific parameters such as the properties of the compounds targeted for removal, the physicochemical characteristics of the biochar, the kinetics of adsorption and the desired pharmaceutical concentrations in the irrigation water.

**Keywords:** Treated wastewater effluent, emerging contaminants, pharmaceuticals, adsorption capacity, percentage removal, pseudo-second-order, breakthrough, biochar-sand filter
TABLE OF CONTENTS

LIST OF TABLES........................................................................................................ viii

LIST OF FIGURES...................................................................................................... ix

LIST OF ABBREVIATIONS......................................................................................... xi

ACKNOWLEDGEMENTS.............................................................................................. xiii

Chapter 1. Introduction............................................................................................. 1

Chapter 2. Literature review..................................................................................... 7
  Introduction.................................................................................................................. 7
  2.1 Emerging contaminants in aquatic systems......................................................... 8
     2.1.1 Sources and Occurrence of ECs................................................................. 8
     2.1.2 Treatment technologies for ECs in wastewater........................................... 10
  2.2 Risk factors for pharmaceuticals to the environment.......................................... 12
     2.2.1 Bioaccumulation......................................................................................... 12
     2.2.2 Potential human effects.............................................................................. 12
     2.2.3 Microorganism resistance......................................................................... 13
     2.2.4 Effects to wildlife....................................................................................... 13
  2.3 Pharmaceuticals in soil receiving treated wastewater......................................... 14
     2.3.1 Fate of pharmaceuticals in soils................................................................. 14
     2.3.2 Factors affecting the degradation of pharmaceuticals in soil..................... 15
  2.4 Uptake of pharmaceuticals by plants................................................................. 16
     2.4.1 Mechanism of uptake and translocation of pharmaceuticals in plants........ 16
     2.4.2 Metabolism of pharmaceuticals in plants.................................................. 16
  2.5 Biochars: Production and characteristics......................................................... 17
     2.5.1 Biomass pyrolysis....................................................................................... 17
     2.5.2 Factors affecting the properties of biochar................................................. 18
  2.6 Pharmaceuticals removal using biochar............................................................. 19
     2.6.1 Adsorption kinetics..................................................................................... 19
     2.6.2 Effect of initial concentration of adsorbate and adsorbent.......................... 19
     2.6.3 Effect of contact time................................................................................ 20
     2.6.4 Adsorption isotherms................................................................................ 20
  2.7 Biochar as a filter media..................................................................................... 21
     2.7.1 Effect of particle size................................................................................ 21
     2.7.2 Effect of porosity....................................................................................... 22
  2.8 Biochar from cotton gin (CG) waste and guayule bagasse (GB)......................... 22
  2.9 Pharmaceuticals of interest................................................................................. 23
     2.9.1 Acetaminophen......................................................................................... 24
     2.9.2 Pseudoephedrine........................................................................................ 24
     2.9.3 Sulfapyridine.............................................................................................. 24
     2.9.4 Ibuprofen.................................................................................................. 25
     2.9.5 Erythromycin............................................................................................ 25
     2.9.6 Docusate.................................................................................................... 26
  3.0 State-of-the-science........................................................................................ 26

Chapter 3. Goals, Objectives and Research Questions............................................ 28
Chapter 4. Methodology

4.1 Phase I: Materials and methods
   4.1.1 Target adsorbates
   4.1.2 Adsorbents
   4.1.3 Characterization of the biochar
   4.1.4 Batch adsorption experiments
   4.1.5 Effect of solution pH

4.2 Phase II: Data analysis
   4.2.1 Kinetic studies
   4.2.2 Adsorption isotherms

4.3 Phase III: Pilot scale study
   4.3.1 Column adsorption experiments
   4.3.2 HYDRUS-1D model

Chapter 5. Results and Discussion

5.1 Characterization of Biochars
   5.1.1 Specific surface area and pH
   5.1.2 Zeta potential
   5.1.3 FT-IR

5.2 Adsorption results
   5.2.1 Acetaminophen adsorption
   5.2.2 Ibuprofen adsorption
   5.2.3 Sulfapyridine adsorption
   5.2.4 Docusate adsorption
   5.2.5 Pseudoephedrine adsorption
   5.2.6 Erythromycin adsorption

5.3 Effect of solution pH
   5.3.1 Acetaminophen
   5.3.2 Ibuprofen
   5.3.3 Sulfapyridine
   5.3.4 Docusate, Erythromycin and Pseudoephedrine

5.4 Modeling kinetics of adsorption
   5.4.1 Kinetics of adsorption at different pH

5.5 Adsorption isotherms

5.6 Column studies results
   5.6.1 Idealized breakthrough curves
   5.6.2 Pharmaceutical HYDRUS-1D Modeling
   5.6.3 Scale-up design

Chapter 6. Conclusion

Appendix. Supplemental Data

References
LIST OF TABLES

Table 1: Occurrence and concentration of various pharmaceuticals in North America modified from Pal et al., (2010) ................................................................. 9

Table 2: Advantages and challenges of different technologies in the removal of ECs.
Modified from Ahmed at al., (2016) ................................................................. 11

Table 3: Physico-chemical properties and structure of pharmaceuticals ................. 33

Table 4: BET surface area, pore size and pH analysis of the biochars .................... 44

Table 5: Zeta potential values for the biochars .................................................. 46

Table 6: Kinetic parameters of pseudo-second order models for the adsorption of ACT, IBP, DCS, PED and SPY onto CG700 ......................................................... 69

Table 7: Kinetic parameters of pseudo second order models for the adsorption of ACT, IBP, SPY, DOC, PED and ETM at pH 7 and 10 ........................................... 71

Table 8: Related parameters Langmuir and Freundlich isotherm model for erythromycin and docusate adsorption on to CG700 ..................................................... 73

Table 9: Parameters for the column adsorption of ACT, DOC, ETM and SPY by CG700 biochar .............................................................. 78

Table 10: Parameters for full-scale column system ............................................. 82

Table 11: Kinetic parameters of pseudo first order models for the adsorption of IBP, SPY and DOC onto CG500 biochar ............................................................. 86

Table 12: Lab-scale column data used to estimate the full-scale column parameters ... 86
LIST OF FIGURES

Figure 1: Methodology flowchart ................................................................. 31
Figure 2: Schematic of batch adsorption experiments ........................................... 37
Figure 3: Schematic of column filter setup for pharmaceutical removal (Modified from Reddy et al., 2014) ................................................................. 42
Figure 4: Zeta potential-pH curves for different biochar samples ......................... 47
Figure 5a: FTIR spectra of CG3550, CG500 and CG700 ........................................ 49
Figure 5b: FTIR spectra of GB350, GB500 and GB700 ........................................ 49
Figure 6a: Removal of Acetaminophen by CG700, CG500 and CG350 ............... 52
Figure 6b: Removal of Acetaminophen by GB700, GB500 and GB350 ................ 52
Figure 7a: Removal of Ibuprofen by CG700, CG500 and CG350 ....................... 53
Figure 7b: Removal of Ibuprofen by GB700, GB500 and GB350 ....................... 53
Figure 8a: Removal of Sulfapyridine by CG700, CG500 and CG350 ................. 56
Figure 8b: Removal of Sulfapyridine by GB700, GB500 and GB350 .................. 56
Figure 9a: Removal of Docusate by CG700, CG500 and CG350 ....................... 59
Figure 9b: Removal of Docusate by GB700, GB500 and GB350 ....................... 59
Figure 10a: Removal of Pseudoephedrine by CG700, CG500 and CG350 .......... 61
Figure 10b: Removal of Pseudoephedrine by GB700, GB500 and GB350 .......... 61
Figure 11a: Removal of Erythromycin by CG700, CG500 and CG350 ............... 62
Figure 11b: Removal of Erythromycin by GB700, GB500 and GB350 ............... 62
Figure 12a: Removal of Acetaminophen at pH 7 and 10 .................................. 65
Figure 12b: Removal of Ibuprofen at pH 7 and 10 ......................................... 65
Figure 12c: Removal of Sulfapyridine at pH 7 and 10 ..................................... 66
Figure 12d: Removal of Docusate at pH 7 and 10 ......................................... 66
Figure 12e: Removal of Pseudoephedrine at pH 7 and 10 ............................... 66
Figure 12f: Removal of Erythromycin at pH 7 and 10 ................................. 66
Figure 13a: Langmuir adsorption isotherms of ETM, DOC and SPY removal by CG700... 72
Figure 13b: Freundlich adsorption isotherms of ETM, DOC and SPY removal by CG700... 72
Figure 14: Idealized breakthrough curves for column adsorption experiments (Modified from Yanyan et al., 2018)................................................................. 74
Figure 15: Breakthrough curves for the column adsorption of ACT, DOC, ETM and SPY by CG700 biochar................................................................. 76
Figure 16a: Pseudo-second order kinetic for the adsorption PED, DCS, ETM, IBP, SPY and ACT onto GB700................................................................. 89
Figure 16b: Pseudo-second order kinetic for the adsorption PED, DCS, ETM, IBP, SPY and ACT onto GB500................................................................. 89
Figure 16c: Pseudo-second order kinetic for the adsorption PED, DCS, ETM, IBP, SPY and ACT onto GB350................................................................. 89
Figure 17a: Pseudo-second order kinetic for the adsorption PED, DCS, ETM, IBP, SPY and ACT onto CG700................................................................. 89
Figure 17b: Pseudo-second order kinetic for the adsorption PED, DCS, ETM, IBP, SPY and ACT onto CG350................................................................. 89
Figure 18a: Kinetic plots for pseudo second order for the adsorption PED, DCS, ETM... 90
Figure 18b: Kinetic plots for pseudo-first order for the adsorption of IBP and SPY...... 90
Figure 19a: Pseudo-second order kinetic for the adsorption PED, DCS, ETM, IBP, SPY and ACT onto CG700 at pH 7................................................................. 90
Figure 19b: Pseudo-second order kinetic for the adsorption PED, DCS, ETM, IBP, SPY and ACT onto CG700 at pH 10................................................................. 90
LIST OF ABBREVIATIONS

ACs: Activated Carbons
ACT: Acetaminophen
AOPs: Advanced Oxidation Processes
BET: Brunauer–Emmett–Teller
CG350: Cotton gin waste pyrolyzed at 350 °C
CG500: Cotton gin waste pyrolyzed at 500 °C
CG700: Cotton gin waste pyrolyzed at 700 °C
COD: Chemical Oxygen Demand
DCT: Docusate
DI: Deionized
DOC: Dissolved Organic carbon
ECs: Emerging Contaminants
EDCs: Endocrine Disrupting Compounds
E2: 17β-estradiol
EE2: 17α-ethinylestradiol
ETM: Erythromycin
FT-IR: Fourier-Transform Infrared Spectroscopy
GB350: Guayule bagasse pyrolyzed at 350 °C
GB500: Guayule bagasse pyrolyzed at 500 °C
GB700: Guayule bagasse pyrolyzed at 700 °C
IBP: Ibuprofen
K_ow: Octanol-water partition coefficient
LD: Levodopa
NF: Nanofiltration
PED: Pseudoephedrine
PNECs: Predicted No-Effect Concentrations
pHzpc: pH point of zero charge
pK: Acid dissociation constant
PPCPs: Pharmaceutical and Personal Care Products
PFO: Pseudo First Order
PSO: Pseudo Second Order
RO: Reverse Osmosis
SEM: Scanning Electron Microscopy
SMX: Sulfamethoxazole
SPY: Sulfapyridine
SA: Specific Surface Area
STPs: Sewage Treatment Plants
USDA: United States Department of Agriculture
USEPA: United States Environmental Protection Agency
USGS: United States Geological Survey
UV: Ultraviolet
WHO: World Health Organization
WWTPs: Wastewater Treatment Plants
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CHAPTER 1. INTRODUCTION

The occurrence of toxic emerging contaminants (ECs) in groundwater due to rapid urbanization, population growth, increasing agricultural activities and industrialization is one of the most significant environmental problems around the world. ECs are chemicals and microorganisms which have been detected in the environment and can potentially cause toxic effects in aquatic and human life at environmentally relevant concentrations (Ahmed et al., 2017; USGS, 2015). There are several classes of ECs including pesticides, industrial additives, flame retardant, endocrine disrupting compounds (EDCs) but pharmaceuticals and personal care products (PPCPs) are often the components present at high concentrations in surface and groundwaters (Daughton, 2004). The abundance of PPCPs in the environment is attributed to the continuous human use of these compounds due to increase in the aging population and progresses in healthcare. Additionally, wastewater treatment plants (WWTPs) are not efficient at removing many of these chemicals, leading to the abundance of various PPCPs and EDCs in wastewater effluents (Gros et al., 2010; Sui et al., 2011).

The World Health Organization (WHO) estimated that in 2025, two-third of the world’s population could be living in regions with limited access to water. Agriculture is the sector which requires the most water and will be negatively impacted the shortage. In an attempt to limit the damages, treated wastewater or reclaimed water has become an effective solution to preserve water resources especially in arid regions of the United States. Reclaimed water is wastewater from homes, offices, hospitals and industries that has undergone treatment to remove impurities such as nutrients and pathogens. Reclaimed water can be successfully used for irrigation because even after treatment, it still contains nitrogen and phosphorus that contribute to plant growth (Kinney et al., 2005). For example, in 2009, 13% of municipal
wastewater in California was recycled and 37% was reused for agricultural irrigation (SWRCB, 2009).

While the use of treated wastewater effluent (water discharged from wastewater treatment plant after undergoing various treatment processes) presents multiple economic and environmental benefits, there are various associated potential risks, such as the food safety risk from ECs, particularly PPCPs. When treated wastewater is used for agricultural irrigation, contaminants such as PPCPs in reclaimed water may be introduced into the crop from the soil through root uptake and translocation, leading to accumulation of these contaminants not only in the soils and the roots but also in edible parts of the plant (Bartha et al., 2010). Erythromycin which is a commonly used antibiotic was found to accumulate over five months in soil irrigated with reclaimed water (Kinney et al., 2005), while six tetracyclines, 4-epianhydrotetracycline, doxycycline, and six quinolones accumulated in soil during a one-month period of reclaimed water irrigation (Wang et al., 2014). Continuous accumulation and perseverance of these chemicals in the environment can lead to several ecotoxicological risks such as interference with endocrine systems of higher organisms, intersex characteristics in organism such as fish and microbiological resistance among bacterial populations (Belhaj et al., 2015).

Additionally, continuing concerns regarding possible population-level impacts of pharmaceuticals in wastewater effluents has contributed to a search for sustainable and cheap technologies which will result in the effective removal of pharmaceuticals from reclaimed water. Although many researchers have explored various physical technologies such as micro and ultra-filtration, nanofiltration, reverse osmosis (Deegan et al., 2011; Luo et al., 2014) and chemical (coagulation, ozonation, photocalysis) and biological (activated sludge, microalgae reactor) treatments, these methods have several disadvantages. These include relatively high
cost of operation and maintenance due high energy demands and consumption, membrane fouling, sludge disposal issues, formation of oxidative by-products and the corrosive nature of finished water (Benner et al., 2013; Matamoros et al., 2015).

Recently, activated carbons (ACs) have been explored as potential materials for the adsorption of pharmaceuticals from wastewater. ACs are versatile adsorbents that are particularly effective in the adsorption of organic and inorganic pollutants from aqueous solutions. However, adsorption using activated carbon poses several problems including the need for high-energy requirements during processing, and a substantial negative environmental footprint. In contrast, adsorption techniques using biochar, which is an inexpensive, readily available and environmentally friendly adsorbent has proven to be an excellent solution for treating wastewater effluents (Lui et al., 2012; Inyanga et al., 2015; Tan et al., 2015; Klinar, 2016; Taheran et al., 2016; Ahmed et al., 2017; Lin et al., 2017).

Biochar is a stable carbon (C)-rich, energy dense by-product synthesized through the pyrolysis of waste biomass in the absence of oxygen (Lehmann and Joseph, 2009). Biochar can be used for several environmental and energy related applications. Applications include land remediation and contaminants immobilization (Ahmad et al., 2014; Mohan et al., 2014), soil fertilization (Chan et al., 2008), greenhouse gas emission reduction (Singh et al., 2010) and adsorption of organic and inorganic pollutants (Kasozi et al., 2010; Nhamo et al., 2017; Yan et al., 2017). Over the years, biochar has been produced from a variety of feedstocks ranging from crop residues, animal manure, wood biomass, sewage sludge, food waste and municipal solid waste. The use of biochar as an alternative to ACs presents several economic and environmental advantages. Biochar can be used to mitigate waste streams because the source material for the production of biochar is generally limited to waste residues thereby decreasing
the pollutant load to the environment. In addition, the production of biochar emits less greenhouse gases (−0.9 kg CO$_2$-eq. for one kg of biochar) compared to the production of ACs (6.6 kg CO$_2$-eq. for one kg of AC; Alhashimi and Aktas 2017). Unlike ACs, biochars can be used with no further treatment or activation and this reduces the cost of production and disposal since deactivation is not required. Biochar has been employed as an adsorbent and it has the ability to compete with ACs for the removal of contaminants from water due to its microporous structure, high carbon content, and specific surface area. In addition, the adsorption ability of biochar is enhanced by the presence of carboxy, hydroxyl and phenolic groups on their surfaces which facilitate the interaction between organic and inorganic contaminants in water (Uchimiya et al., 2011b).

The properties, characteristics and quality of the biochar such as particle size and shape, specific surface area, pore size and distribution as well as elementary composition mainly depend on the feedstock type and pyrolysis conditions (residence time, temperature, heating rate and reactor type; Yahya et al., 2015). For example, a study conducted by Kearns et al. (2014) on the adsorption of the herbicide 2,4-dichlorophenoxyacetic acid to biochar from synthetic solution found that increasing the pyrolysis temperature of the biochar positively influenced the adsorption capacity. The presence of functional groups on the surface of the biochars increase adsorption potential for organic pollutants. Endocrine-disrupting compounds and pharmaceutically active compounds were shown to have greater adsorption to the higher surface area and pore volume of oxygen-free activated biochar (Jung et al., 2013). Results from the potential use of biochar as a filter media for urban storm-water runoff demonstrated that biochar filters effectively remove total suspended solids, heavy metals, nutrients, polycyclic aromatic hydrocarbons, and E. coli. (Mohanty and Boehm, 2014; Reddy et al., 2014). It was also reported that biochar has very high adsorption capacities of pesticides (atrazine, simazine,
acetochlor) with sorption coefficients as high as 1400 L kg⁻¹ (Spokas et al., 2009; Zhen et al., 2010) leading to its potential use as an adsorbent to treat agricultural wastewater effluents. Biochar is an excellent adsorbent for hydrophobic organic compounds such as aromatics because of its high hydrophobicity, high charge density and aromaticity (Wang et al., 2016). Moreover, biochar can be added to bioreactors to remove contaminants from water. Ashoori et al. (2019) studied the use MCG biochar-amended woodchip bioreactors to remove nutrients, metal and trace organic contaminants from urban runoff. The results indicated that woodchips bioreactors were able to remove NO₃, Cd, Cu, Ni and Pb from water and the addition of 33% dry weight biochar to the bioreactors will result in adsorption of trace organic contaminants with breakthrough for the least adsorbed contaminant occurring after 26 years.

The cotton gin and guayule industries are viable sources of biomass for the production of biochar. The production of textiles from cotton gin accounts for approximately 2.5 million tons of cotton gin waste being generated every year (Maglinao et al., 2015). A minimum 200 metric ton per day of guayule bagasse is discarded from the production of latex and biofuels from the guayule plant (Sabaini et al., 2018). The enormous quantities of waste generated present several economic and environmental problems such as the cost (tipping fee) associated with landfills. As a result, the transformation of cotton gin waste and guayule bagasse into value-added products such as biochar for water and wastewater treatment purposes presents opportunities for research.

The overarching objectives of this study were divided into three main phases. The first phase involved (i) understanding the effect of pyrolysis temperature and contact time on the physicochemical characteristics and sorption ability of cotton gin waste (CG) and guayule bagasse (GB) biochar; (ii) conducting batch adsorption experiments to investigate the ability of the
biomass-derived biochar to remove pharmaceuticals from reclaimed water and (iii) determine the effect of pH on the removal efficiency of the biochar. The second phase included performing kinetics studies and adsorption isotherms to understand the adsorption rate and determine the adsorbent demonstrating the maximum adsorption capacity. Following the selection of the suitable biochar, the prime focus of the third phase involved lab-scale column experiments to examine the practical addition of biochars to off-the-shelf micro-irrigation sand filters and to obtain the maximum bed capacity ($q_c$). The HYDRUS-1D program was used to model the breakthrough profiles for the adsorption of the pharmaceuticals compounds and to determine the sorption coefficient ($K_a$).
CHAPTER 2. LITERATURE REVIEW

Introduction

The purpose of this review is to provide in-depth and up-to-date overview of the presence and distribution of emerging contaminants (ECs) in general and pharmaceuticals in particular in the environment, abundance of pharmaceuticals in the soils and plant uptake of pharmaceuticals in connection to the use of treated wastewater effluent in agriculture and the application of adsorptive materials for the removal of pharmaceuticals prior to agricultural irrigation.

Pharmaceuticals and their degradation byproducts are being increasingly detected in the environment. Although the human health and ecological risks of plants contaminated with low levels of pharmaceuticals are still far from clear, based on the adverse effects of pharmaceuticals observed on non-target organisms such as aquatic organisms, potential risks still exist through food intake of pharmaceutical-contaminated crops by humans or animals. Application of treated wastewater can lead to: accumulation of pharmaceuticals in the soils (Borgman and Chefetz, 2013), transport to nearby surface water bodies, leaching to groundwater, and uptake by plants.

A limited number of studies show that pharmaceuticals can undergo extensive transformations after being taken up by plants. However, the scarcity of knowledge regarding the presence and perseverance of pharmaceuticals in edible parts of the plant after uptake, severely underestimates the potential human exposure to these chemicals via dietary intake (Wu et al., 2015). All these factors underscore the need to remove these compounds, not only from drinking water, but also in the wastewater treatment process to avoid the release to receiving waters. The technology options in eliminating these contaminants such as adsorption using
biochar, oxidation via chlorination and ozonation, activated sludge treatment and membrane filtration have been discussed and employed (Bolong et al., 2009). Each removal option has its own limitations and benefits in removing trace contaminants such as pharmaceuticals, however biochar has proven to have potential as removal technology.

2.1. Emerging contaminants in aquatic systems

Emerging contaminants as defined by the United States Geological Survey are *any synthetic or naturally occurring chemicals or any microorganisms that are not commonly monitored in the environment but have the potential to enter the environment and cause known or suspected adverse ecological and/or human health effects* (USGS, 2015). Pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs) are examples of emerging contaminants. Up to 90% of oral drugs pass through the human body and end up in the wastewater stream (Virginia Tech, 2010). PPCPs (soaps, cosmetics, fragrances, etc.) also find their way into wastewater during usage. Endocrine disruptors are substances that may interfere with the function of hormones in the body. Trace amounts of these contaminants are being discovered in both drinking water and wastewater worldwide. Conventional wastewater and recycled water treatment plants are only partially effective in removing or degrading ECs, leading to their discharge into the environment with treated wastewater effluent, recycled water, and sludge from the wastewater treatment plants.

2.1.1. Sources and Occurrence of ECs

ECs are generally released into the aquatic environment by point sources. The principal sources include drugs excreted or disposed to domestic sewage systems or leaky landfills, effluents from hospitals and industries, septic tanks, and runoff from animal husbandry and aquaculture sites (Pal et al., 2010). It has also been observed that even a minor source such as individual
households which discard their expired and unused medicines through the sink and drains can add to the level of pharmaceuticals in the water.

Table 1. Occurrence and concentration of various pharmaceuticals in North America. (Source: Modified from Pal et al., 2010).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Effluent WWTP/STP (ng/L)</th>
<th>Freshwater-rivers, canals, seawater (ng/L)</th>
<th>Lowest PNEC (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Antibiotics</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trimethoprim</td>
<td>&lt;0.5-7900</td>
<td>2-212</td>
<td>1000</td>
</tr>
<tr>
<td>Ciprofloxacin</td>
<td>110-1100</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>5–2800</td>
<td>7-211</td>
<td>20,000</td>
</tr>
<tr>
<td><strong>Analgesics and anti-inflammatory</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naproxen</td>
<td>&lt;1-5100</td>
<td>0-135.2</td>
<td>3700</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>220-3600</td>
<td>0-34</td>
<td>5000</td>
</tr>
<tr>
<td>Ketoprofen</td>
<td>12-110</td>
<td>-</td>
<td>15.6×10^6</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>&lt;0.5-177.1</td>
<td>11-82</td>
<td>10,000</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>47.2-180</td>
<td>70-121</td>
<td>-</td>
</tr>
<tr>
<td>Acetaminophen</td>
<td>-</td>
<td>24.7-65.2</td>
<td>9200</td>
</tr>
</tbody>
</table>

**Antiepileptic**

| Carbamazepine          | 111.2–187                | 2.7-113.7                                   | 25,000             |

ND—not detected dashed line—not reported
PNEC—predicted no-effect concentration
WWTP—wastewater treatment plants
STP—sewage treatment plants

Table 1 shows the concentration of various pharmaceuticals obtained from a literature survey of effluents from a Sewage Treatment Plants (STPs) or Wastewater Treatment Plants (WWTPs) and surface waters (Pal et al. 2010). A general trend occurs whereby there is a decrease in the concentration of pharmaceuticals from STP and WWTP effluents as they are discharged in freshwater bodies. The decline is due to processes such as dilution, biotransformation, photolysis, sorption, volatilization, and dispersion in aquatic environments. The lowest predicted no-effect concentration (PNECs) of the antibiotics trimethoprim and ciprofloxacin on the most sensitive species such as daphniids, fish and algae are much lower than effluent concentrations which suggest the need for an improvement in the wastewater
treatment facilities. It is critical that the concentration of pharmaceuticals in treated wastewater effluents be reduced to values lower than PNEC values before the water is released to receiving water bodies in order to prevent harmful effects on aquatic life.

2.1.2. Treatment technologies for ECs in water and wastewater

Various methods have been explored for the removal of ECs from wastewater and they typically involve adsorption, advanced oxidation processes (AOPs), activated sludge treatment, UV photolysis, nanofiltration and reverse osmosis membranes (Rossner et al., 2009). A review by Bolong et al. (2009) revealed that methods involving adsorption by activated carbon and advanced oxidation were effective for removing some EDCs and PPCPs. Adsorption by powdered activated carbon has the potential to remove up to 90% of EDCs (Schafer et al., 2003). The removal of EDCs and PPCPs by ozone oxidation involves the reaction of ozone itself or the formation of hydroxyl radicals which react with the substrates. Dissolved organic carbon (DOC) has a strong influence on the oxidation process using ozone, leading to the effective degradation of PPCPs and EDCs in water containing low DOC (Huber et al., 2005). Activated sludge treatment can rapidly convert aqueous organic compounds into biomass but not all compounds such as steroid estrogens are completely broken down or converted to biomass (Patrovic et al., 2003). Advanced treatment methods such as UV photolysis for the removal of EC have been employed. One study showed that UV photolysis was able to remove 50–80% of target compounds but required a hundred times greater than the typical disinfection dose (Adams et al., 2002). Membrane filtration technologies such as reverse osmosis (RO) and nanofiltration (NF) have been shown to eliminate ECs. Comparatively, RO will give almost complete removal, but the higher energy consumption makes it unfavorable (Yoon et al., 2006). Overall, each removal option has its own limitation and benefit in removing trace contaminants such as ECs, but adsorption via activated carbon
Table 2. Advantages and challenges of different technologies in the removal of ECs.

(Source Ahmed at al., 2016).

<table>
<thead>
<tr>
<th>Treatment process</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbons</td>
<td>A wide range of ECs removal from wastewater</td>
<td>Competitive effects of surface site and/or pore blocking lower removal efficiency.</td>
</tr>
<tr>
<td></td>
<td>Removal of residual disinfection/oxidation products</td>
<td></td>
</tr>
<tr>
<td>Activated sludge</td>
<td>Lower capital and operational costs than advanced oxidation process (AOPs)</td>
<td>Low efficiencies for pharmaceuticals and beta blockers</td>
</tr>
<tr>
<td></td>
<td>More environmentally friendly than chlorination</td>
<td>Large amount of sludge containing ECs Unsuitable where COD levels are greater than 4000 mg L⁻¹</td>
</tr>
<tr>
<td>Advanced Oxidation Process (AOP)</td>
<td>Selective oxidant favoring disinfection and sterilization properties.</td>
<td>Interference of radical scavengers</td>
</tr>
<tr>
<td></td>
<td>Major ancillary effects on removal of ECs such as EDCs, pharmaceuticals, PCPs and pesticides</td>
<td>Energy consumption issues, operational and maintenance cost</td>
</tr>
<tr>
<td></td>
<td>Short degradation rate</td>
<td>Formation of toxic disinfection by-products</td>
</tr>
<tr>
<td>Photocatalysis (TiO₂)</td>
<td>Sunlight can be used by avoiding UV light</td>
<td>Interference of radical scavenger</td>
</tr>
<tr>
<td></td>
<td>Degrading persistent organic compounds</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High reaction rates upon using catalyst.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low price and chemical stability of TiO₂, catalyst and easier recovery</td>
<td></td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>Useful for treating saline water and WWTP influents</td>
<td>High cost of operation</td>
</tr>
<tr>
<td></td>
<td>Can remove dye stuff and pesticides</td>
<td>High energy demand, membrane fouling and disposal issue</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>Useful for treating saline water and WWTP influents</td>
<td>Limited application in pharmaceutical removal</td>
</tr>
<tr>
<td></td>
<td>Can remove PCPs, EDCs and pharmaceuticals</td>
<td>High energy demand, membrane fouling and disposal issue</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Corrosive nature of finished water and lower pharmaceutical removal</td>
</tr>
</tbody>
</table>

has shown to have potential as removal technology. This is attributed to the fact that adsorption treatment is easy to design and operate and it does not produce toxic by-products (Tong et al.,
2010). The advantages and challenges of different processes for the removal of ECs are outlined in Table 2.

2.2. Risk factors for pharmaceuticals in the environment

2.2.1. Bioaccumulation

The exposure of pharmaceuticals can result in bioaccumulation, thus making them toxic to aquatic and terrestrial organisms. Bacterial communities, plants, insects and fish are most impacted by the occurrence of pharmaceuticals in the environment. The octanol-water partition coefficient ($K_{ow}$) is the main factor used to explain the bioaccumulation of a compound (Streets et al., 2006). The $K_{ow}$ is a measure of hydrophobicity that determines sorption and accumulation. Hydrophobic compounds with log $K_{ow}$ values higher than or equal to 3 are more likely to bioaccumulate organisms, leading to potential human risk from the consumption of these contaminated organisms (Goldstein et al., 2014).

2.2.2. Potential human effects

Several studies have documented the effects of pharmaceuticals on animals, however, the effects to humans are still debated and require more studies. Human exposure to pharmaceuticals is equally harmful and can occur through various routes. An important exposure route is through drinking water. Glassmeyer et al. (2017) discovered that out of the 84 chemicals monitored from nine drinking water treatment plants (DWTPs) from eight states across the U.S., 21 were detected at least once in treated drinking water. A study conducted by Wu et al. (2014) determined that for vegetables that were grown in a section irrigated by treated wastewater, about 64% of edible samples were found to contain at least one PPCP. PPCPs were found to interfere with the endocrine system by mimicking, blocking or also disrupting function of hormones, affecting the health of humans (Ozaki, 2004). Studies have indicated that poor
sperm quality in humans was associated with exposure levels of disinfection by-products (Izsatt et al., 2013). Human exposure to pharmaceuticals is also attributed to an increase in testicular, prostate, ovarian and breast cancer and reproductive malfunctions (Michael, 2001).

2.2.3. Microorganism resistance

Human and veterinary medicine has been extensively used for the treatment and prevention of infectious diseases (Boxall et al., 2003). Many pharmaceutical compounds are not fully degraded in wastewater treatment processes, indicating that antibiotic residues potentially accumulate in the environment during the use of treated wastewater for irrigation. The occurrence of pharmaceuticals in the environment could possibly result in the selection of antibiotic resistance among bacterial populations present in these environments (Negreanu et al., 2012). Antibiotic resistance can also develop to chlortetracycline in human and animals which, in turn, necessitates the prescription of higher dosages of antibiotics and finally invention of new compounds (Davis et al., 2006). For example, Tamiflu, the effective antiviral for avian influenza, can escape sewage treatment plants and even UV radiation cannot substantially degrade it (Fick et al. 2007). Thus, there is a concern that Tamiflu and its metabolites may be released into the aquatic environment and lead to increased resistance of the bird-flu virus.

2.2.4. Effects on wildlife

Pharmaceutical levels observed in environmental waters are not far below the doses that cause toxic effects in animals by interfering with their growth, reproduction and development. For example, the psychiatric drug oxazepam at environmentally relevant concentrations has been found to cause an increased feeding rate, reduction in sociability, and heightened activity in wild European perch (Brodin et al., 2013). The ecotoxicological effects of pharmaceuticals that
lead to the decline in the population of organism include, thinning of eggshells of birds and fish, reproductive system interference in fishes, reptiles, birds and mammals, and alterations in the immunologic system of marine mammals (Esplugas et al., 2007).

2.3. Pharmaceuticals in soil receiving treated wastewater

2.3.1. Fate of pharmaceuticals in soils

Pharmaceuticals find their way into the soils when treated wastewater effluent is reused for irrigation or when sewage sludge is applied as a fertilizer to agricultural land. When pharmaceuticals are found in soils, their sorption and transformation can result in the formation of bound residues, which have much reduced bioavailability. Less than 4.2% of the initial spiked amount of carbamazepine (Li et al., 2013) and less than 73-93% of the initial spiked amount of acetaminophen (Li et al., 2014) were converted to bound residue in soils. Once in soil, pharmaceuticals can be degraded and transformed as a result of biotic and abiotic reactions, leading to changes in their chemical structure. Biodegradation (Xu et al., 2009), photodegradation (Kawabata et al., 2013) and hydrolysis (Mitchell et al., 2014) have been reported to play a major role in the removal of pharmaceuticals from environments. During decomposition, a part of the compound in soil may undergo mineralization (i.e. converted to CO₂), which is viewed as complete detoxification. For example, acetaminophen, which is one of the most widely used over-the-counter and prescription pain medicines in the United States, was found to mineralize in the soils throughout a 120-d aerobic incubation period (Li et al., 2013). So far little information is available on mineralization of pharmaceuticals in soil due to the limited availability of ¹⁴C-labeling compounds (Wu et al. 2015). Fraction of pharmaceuticals in the soil may be available for migration leading to the leaching of pharmaceuticals to groundwater or drainage water. Evidence of movement in soils was shown through the
detection of sulfamethoxazole, carbamazepine and meprobamate in leachate or runoff from turf grass soils irrigated with non-spiked tertiary treated wastewater (Bondarenko et al., 2012).

2.3.2. Factors affecting the degradation of pharmaceuticals in soil

The chemical structure and physicochemical properties of the pharmaceuticals have a major effect on their biodegradation kinetics in soils. For example, weak acid pharmaceuticals such as ibuprofen, benzafibarte and naproxen exhibited faster degradation rates in soils irrigated with treated wastewater compared to non-ionic pharmaceuticals carbamazepine, caffeine, sulfapyridine and metoprolol which were recalcitrant and accumulated in soils. The fast degradation rate of weak acid pharmaceuticals is attributed to the presence of the carboxylic groups that are more prone to microbial degradation (Grossberger et al., 2014). Degradation of pharmaceuticals is impacted by soil properties such as the organic carbon content. Xu et al. (2009) reported that a high organic carbon content in soil reduced the bioavailability of chemicals and hence inhibited their biodegradation in the soil. Also, fluctuations in the microbial community and activity in soils have a major effect on the degradation capability of pharmaceuticals in different soils (Lin and Gan, 2011). Biosolids also have an effect on the degradation of pharmaceuticals in soils. Biosolids amendment usually increases the organic matter content in the soil leading to increased sorption of pharmaceuticals onto the soil and decreased bioavailability (Li et al., 2013). Monteiro and Boxall (2009) determined that biosolids-amended soils generally inhibit the degradation of pharmaceuticals thereby prolonging their availability in soils.
2.4. Uptake of pharmaceuticals by plants

2.4.1. Mechanism of uptake and translocation of pharmaceuticals in plants

In the past few years, there has been an increase in the number of publications on plant uptake of pharmaceuticals, indicating that once present in the agricultural environment, various pharmaceuticals have the potential to be taken up by crops (Wu et al., 2010). Once the pharmaceuticals are found in the soil, they are taken up by the plants through root uptake and translocation and the properties of the pharmaceuticals play a vital role during the process. For example, for nonionic pharmaceuticals, the effect hydrophobicity plays an important role in their uptake by plants. Compounds with log $K_{ow}$ of 2.45 (carbamazepine) and 2.57 (lamotrigine) were taken up at higher concentrations than the hydrophilic sulfapyridine and caffeine (log $K_{ow}$ of 0.35 and −0.07, respectively; Goldstein et al., 2014). For basic and neutral pharmaceuticals, there was a significant correlation between the translocation factor and the transpired masses. This relationship implies that the movement of basic and neutral pharmaceuticals from the root of the plant to the leaves is influenced by transpiration (Dodgen et al., 2015). In contrast, the translocation of anionic pharmaceuticals from the root to the leaves will be inhibited due to strong repulsive forces between the root cell membrane's negative electrical potential and the pharmaceuticals.

2.4.2. Metabolism of pharmaceuticals in plants

After being taken up, plants are able to metabolize pharmaceuticals. A study conducted by Bartha et al. (2010) indicated that plant and shoot tissues containing free acetaminophen showed a decrease in the concentration of acetaminophen in both tissues after 24 h and after one week, free acetaminophen almost completely disappeared from the tissues. The results suggested that plants are able to metabolize pharmaceuticals and the mechanisms for detoxification of xenobiotics in plants were closely related to those in the mammalian system.
Moreover, in their field study, Malchi et al. (2014) detected two carbamazepine metabolites in carrots and sweet potatoes irrigated with treated wastewater. These metabolites were found mainly in the leaves, where the concentration of 10,11-epoxide carbamazepine was significantly higher than the parent compound.

2.5. Biochar: Production and characteristics

2.5.1. Biomass pyrolysis

Adsorption using biochar has been used as a treatment technology for the removal of pharmaceuticals from wastewater. Moreover, biochars exhibited similar or even better adsorption capacity than commercially available activated carbons (ACs; Karakoyun et al., 2011; Xue et al., 2012; Zhang et al., 2012; Yang et al., 2014). Biochar can be produced by the thermochemical decomposition of biomass at temperatures of 200–900 °C in the presence of little or no oxygen, a process commonly known as pyrolysis (Demirbas and Arin, 2002). Pyrolysis is a technique that can be optimized in order to obtain high biochar production. It was been demonstrated that the most efficient technique for high biochar yield is slow pyrolysis. Slow pyrolysis is characterized by a slow heating rate and a long residence time which favors the formation of char, with liquid and gaseous products being formed in small quantities (Brown 2009). In slow pyrolysis, the lower heating rate and longer vapor residence time allows those vapors which are produced during the secondary reaction to be removed. This ultimately results in the formation of solid carbonaceous biochar.

Also, pyrolysis is advantageous for the production of biochar because it can treat and convert most biomass and waste directly without any difficulty. One of the major advantages of pyrolysis is the flexibility with both feedstock type and with operating conditions. Change in the pyrolysis conditions can alter the texture and characteristics of the product according to the
intended application requirements. Pyrolysis is also an environmentally friendly process because of the low sulfur and NOx gas emissions (Tripathi et al., 2015).

### 2.5.2. Factors affecting the properties of biochar

A number of feedstocks including crop residues, wood biomass, animal litter, and solid waste have been utilized to produce biochar via pyrolysis and the biochar yield depends on the feedstock type, pyrolysis temperature, and heating rate. The presence of high inorganic content in animal litter and solid waste as indicated by their relatively high ash content, has resulted in a high yield of biochar produced from these biomasses compared to the biochar yield from the pyrolysis of crop residues and wood biomass (Enders et al., 2012). Moreover, heating rate was not a very important factor in determining biochar yield. In contrast, Karaosmanoglu et al. (2000) described a decrease in biochar yield after pyrolysis when the heating rate increased from 5 to 15 °C min⁻¹.

Another factor that plays an important role in changing the biochar characteristics is the pyrolysis temperature. Biochars obtained from the pyrolysis of grass and wood-based biomass demonstrated a significant reduction in grass-based biochar yield at temperatures less than 300 °C. This is due to initial dehydration reactions coupled with the relatively lower lignin content in grass, compared to wood, which caused an earlier thermal breakdown at low pyrolysis temperatures between 200 and 400 °C leading to a reduction in biochar yield. (Keiluweit et al., 2010). Pyrolysis temperature also influences the elemental composition and functional groups of the biochar. A rise in pyrolysis temperature increased C content, whereas H and O contents decreased. Decreased H and O contents with an increase in pyrolysis temperature were associated with lower molar H/C and O/C ratios, indicating dehydration and deoxygenation of the biomass (Lian et al., 2011). There appears to be no significant effect of pyrolysis
temperature on the nitrogen contents of biochars derived from various feedstock. In general, surface area increases with an increase in pyrolysis temperature. Due to the low C content and high molar H/C and O/C ratios, biochars produced from crop residue and wood biomass exhibit higher surface areas compared to biochars from animal litter and solid waste feedstocks (Bourke et al., 2007).

2.6. Pharmaceutical removal using biochar

2.6.1. Adsorption kinetics

Adsorption kinetics are very important, as they do not only determine removal rate of pharmaceuticals from wastewater but also the size and capital cost of an actual adsorption system required for commercial applications. Kinetic modeling is performed to investigate the rate of the controlling steps during the removal of pharmaceuticals from solution by adsorbents. Many different kinetic models have been used including zero order, first order or pseudo-first-order, second order or pseudo-second-order and third order to describe the kinetics of adsorption (Han et al., 2009). For the adsorption of sulfamethoxazole (SMX) and ibuprofen in reverse osmosis (RO), pseudo-first-order and pseudo-second-order models were applied to simulate the experimental data. Both kinetic models fit well to the experimental data with correlation coefficients ($R^2$) higher than 0.89, but the pseudo-second-order model appeared to be a better fit (Lin et al, 2017).

2.6.2. Effect of initial concentration of adsorbate and adsorbent

In order to determine when the adsorption sites become saturated, the initial relative concentrations of the adsorbate and adsorbent should be monitored. Various pharmaceuticals have different equilibrium times at which they reach their maximum adsorption. In general, increasing the adsorbate concentration leads to a reduction in the proportion of available
adsorbate which is adsorbed (removal efficiency). This is attributed to competition and saturation of active sites by the adsorbate. For example, the breakthrough time \( \frac{C}{C_0} = 5\% \) decrease from 37.4 to 25.6 min for sulfamethoxazole, and from 51.8 to 25.5 min for sulfapyridine as the initial concentration of the antibiotics was quadrupled (Tian et al., 2013).

2.6.3. Effect of contact time

The contact time between adsorbate and adsorbent is an important kinetic parameter. In general, for adsorption to be economically practical, it is preferred that the contact time between the adsorbate and adsorbent be kept at minimum while still achieving maximum removal (Ahmed et al., 2015). Increasing the holding time contributes to the formation of well-defined pores in the biochar which results to an increase in surface area and adsorption capacity. For example, the removal efficiency of dimetridazole onto biochar derived from sugarcane bagasse increased from 91\% to 98\% when the time increases from 60 min to 120 min. A similar trend was observed in the adsorption of metronidazole using biochar produced from sugarcane bagasse; the removal efficiency increased from 75 to 89\% as the holding time increased from 60 min to 120 min (Sun et al., 2017).

2.6.4. Adsorption isotherms

Equilibrium isotherms are widely used to represent the relationship between the adsorbed concentration in the adsorbent phase and the dissolved concentration at equilibrium. The Langmuir and Freundlich isotherm models are most frequently used to describe processes in water and wastewater applications. The Langmuir adsorption model is valid for single-layer adsorption. Data related to adsorption from the liquid phase are fitted better by the Freundlich isotherm equation. The Freundlich isotherm accounts for heterogeneous surface energies (Cooney 1999).
A Freundlich isotherm model was used to describe the endocrine disrupting compounds (EDCs): bisphenol A (BPA), atrazine (ATR), 17α-ethinylestradiol (EE2), and pharmaceutical active compounds (PhACs); sulfamethoxazole (SMX), carbamazepine (CBM), diclofenac (DCF), ibuprofen (IBP) on the surface of biochar samples produced from loblolly pine chips at 300 °C. The results indicated that the linear Freundlich isotherm showed a better fit to the data obtained from the adsorption of EDCs onto loblolly pine biochar implying that EDCs allowed multi-layer adsorption with other pharmaceuticals by forming additional hydrogen bonding, which facilitated interactions among pharmaceuticals (Jung et al., 2013).

2.7. Biochar as a filter media

2.7.1. Effect of particle size

Current research on biochar focuses mainly on its use as an adsorbent or a soil cover amendment. However, the use of biochar as a filter media to removal pharmaceuticals from wastewater could present several advantages since biochar possessed many of the characteristics such as high C content and specific surface area which make it suitable for the application. Biochar has a large surface area and a microporous structure (Lee et al. 2010). Consequently, it is expected to have excellent potential as an adsorbent or filter media. However, particle size has been reported to affect the efficiency of biochar to remove organic, inorganic, and microbial pollutants from wastewater (Mohanty et al., 2014). Hanadeh et al. (2017) established that coarse sand biochar is able to remove between 77.4-87.5% of total phosphorus compared to fine sand biochar which achieved removals between 56.3%-84%.
2.7.2. Effect of porosity

Biochars are considered a type of porous media. Typically, biochar porosity has been classified by distinguishing between the micropores (<2 nm), mesopores (2-50 nm), and macropores (>50 nm; (Rouquerol et al., 1994). The particle size, particle morphology, and media compaction influence the size and shape of the pores between the biochar particles. A study conducted by Gray et al. (2014) determined that pyrogenic nanopores (internal pores produced at higher pyrolysis temperatures) provide the majority of the biochar surface area which is needed for nutrient adsorption but only contributes slightly to the total porosity of the biochar sample. Moreover, the study also concluded that less porous feedstocks have the ability to develop greater pyrogenic nanoporosity with an increase in pyrolysis temperatures, thereby rendering these biochars suitable for filtration applications.

2.8. Biochar from cotton gin (CG) waste and guayule bagasse (GB)

The increase population leads to the continuous demand for valuable products such as cotton and rubber to manufacture a wide range of commodities such as textiles, tires and medical equipment. The US is the world’s leading exporter of cotton with production reaching 20 million bales in 2017 (USDA, 2019). Even with the high percentage of cotton being shipped overseas, by-products of the cotton gin industry such as cotton gin waste remains in the U.S. Cotton gin waste is a heterogenous product consisting of lint, dirt, sticks and leaves that is obtain after cotton has been harvested. For every one bale of raw cotton lint (227 kg) produced, about 40-147 kg of cotton gin is generated (Thomasson, 1990) which accounts for approximately 2.5 million tons of waste generated annually (Maglinao et al., 2015). The huge quantity of solid waste has become a major problem for the cotton mills. There is an undeniable need for the conversion of cotton gin waste into value-added products in order to decrease the cost associated with disposal. Cotton gin waste has been studied as an alternative source for
the production of ethanol but little attention has been given to pyrolysis of cotton gin waste to produce biochar.

In 2013, the U.S. consumed 2.7 metric tons of rubber (IRSG, 2013). Most synthetic rubbers are derived from petroleum products and natural rubber from Hevea (*Hevea brasiliensis*) or it is imported from Republic of Korea and China (United Nations Statistics Division, 2014). Recently, the guayule plant which is a desert shrub that grows in arid and semi-arid regions of the U.S. and Mexico has been explored for the production of rubber. Latex can be extracted from the guayule stem to produce rubber but only about 10 % dry weight of the plant goes into latex production and the remaining 90 % is left as bagasse (Boateng et al., 2010). The successful commercialization of rubber from the guayule plant depends on the utilization of most of the bagasse in order to reduce the waste stream associated with production. As a waste mitigation strategy, we explore the use of biochar produced from the pyrolysis cotton gin waste and guayule bagasse as adsorbents to remove contaminants from water.

### 2.9. Pharmaceuticals of interest

Recent attention has been directed towards emerging contaminants (ECs), particularly pharmaceuticals, personal care products and endocrine disrupting compounds that are biologically active but not commonly regulated. The pharmaceuticals chosen for this study include, acetaminophen (ACT), pseudoephedrine (PED), sulfapyridine (SPY), ibuprofen (IBP), erythromycin (ETM) and docusate (DCT). The variety of pharmaceuticals were selected due to their abundance in the environment. Additionally, due to their varying acid dissociation constants pKₐ and octanol water-partition coefficients (log K_{OW}), removal of the pharmaceuticals from water can be as a result of hydrophobic effects, hydrogen bonding and π-π electron donor interactions.
2.9.1 Acetaminophen: C₈H₉NO₂

Acetaminophen (ACT) is the most widely used over-the-counter and prescription pain medicine in the United States (Kaufman et al., 2002). With a pKa of 9.86 and a log Kₐ of 0.48, ACT exists almost entirely in the neutral form at neutral pH. Worldwide annual production of ACT is 1.45 × 10⁵ tons. ACT is not completely mobilized in the human body and therefore ends up in wastewater after irrigation (Kazprzyk-Hordern et al., 2008). In a recent study, ACT was detected in groundwater used for public drinking water supply in California at levels up to 1.89 mg/L (Fram and Belitz, 2011). ACT is able to pass through the conventional treatment process in drinking water treatment plants and react with disinfectants such as chlorine and chloramines to form disinfectant byproducts (Westerhoff et al., 2005).

2.9.2. Pseudoephedrine: C₁₀H₅NO

Pseudoephedrine (PED) is a sympathomimetic drug belonging to phenethylamine and amphetamine chemical classes and is widely used as a nasal decongestant. PED is characterized by a great polarity with a pKᵢ value of 9.74 and log Kₐ of 0.89. Yang et al, (2009) found that 63% of sediments from an urban river in Florida contained PED and the log Kₐ of the compound was found to be directly related to the sorption capability by the sediments. However, to date, the occurrence of PED in the environment has yet to be fully elucidated. Kasprzyk-Hordern et al. (2010) suggested that PED can be present in raw water at maximum concentrations greater than 300 ng L⁻¹ but the concentration does not exceed 30 ng L⁻¹ in wastewater.

2.9.3. Sulfapyridine: C₁₁H₁₁N₃O₂S

Sulfapyridine (SPY) is a sulfonamide antibiotic primarily used for treating human patients. SPY has been shown to bioaccumulate up the food chain and cause several ecotoxicological effects (Göbel et al., 2005). SPY has pKᵢ and pKₐ values 2.3 and 8.43, respectively and a log
Kow value of 0.35. Sulfapyridine (SPY) is a moderately water-soluble and often detected at high concentrations in wastewaters (70–227 ng L\(^{-1}\); Verlicchi et al. 2012). Residues of SPY and their metabolites require a long residence (32–62 days) to be completely degraded (Gros et al., 2010). However, wastewater treatment plants are typically operated at short hydraulic residence times (~40 h; Radjenovic et al., 2009). This leads to presence of SPY in treated wastewater effluents causing potential contamination of receiving water bodies during discharge.

2.9.4. Ibuprofen: C\(_{13}\)H\(_{18}\)O\(_2\)

Ibuprofen (IBP) is a non-steroidal anti-inflammatory drugs (NSAIDs), and is widely used as analgesic and for anti-inflammatory purposes. Due to its widespread applications as an anti-inflammatory drug, IBP is frequently detected in the wastewater treatment plants (Verlicchi et al., 2010). Unfortunately, wastewater and drinking water treatments plants are inefficient in treating pharmaceuticals such as IBP (Xie et al., 2012) and consequently more effective technologies are required to achieve their removal from wastewater and drinking water. Studies have shown that IBP contamination in water can affect reproduction of aquatic animals by influencing the synthesis of eicosanoids, which are important regulators of reproduction in both vertebrates and invertebrates (Hayashi et al., 2008).

2.9.5. Erythromycin: C\(_{37}\)H\(_{67}\)NO\(_{13}\)

Erythromycin (ETM) is widely used to control bacterial infections in both humans and animals. ETM has a pK\(_a\) of 8.88 and log Kow value of 3.06 and is unstable in acidic and alkaline solutions. A study conducted by Kolpin et al. (2002) investigating the occurrence of 21 veterinary and human antibiotic in US streams showed that ETM is most frequently detected in 139 US streams resulting from possible contamination of these sites from human and industrial
activities as well as discharged of treated wastewater. This reiterates the need to remove ETM from wastewater before it is discharged into the environment.

2.9.6. Docusate: C_{20}H_{37}NaO_{7}S

Docusate (DCT) is a synthetic anionic (pK_a = 10.84) surfactant that is marketed as a stool softener laxative. DCT is a hydrophobic surfactant with and log K_{ow} of 5.24. A study by Rosal et al. (2010) investigated the effect of the intercation between DCT with chlorinated pollutants TCP and triclosan on three aquatic organisms (Cyanobacterium anabaena, Pseudokirchneriella subcapitata, Vibrio fischeri). The results showed that DCT increases the toxicity of both chlorinated compounds in all three tested organisms. This accretion effect indicates a potential toxicological risk associated with the co-existence of DCT and other organic pollutants in aquatic environments.

3.0. State-of-the-science

The occurrence of ECs, particularly pharmaceuticals in receiving waters has been the focus of enormous research efforts. Wastewater treatment plants effluent have been considered a primary source of many pharmaceuticals into the environment. Agricultural application of treated wastewater effluents can lead to the accumulation of pharmaceuticals in the soil and eventual uptake and metabolism in plants. The accumulation of these pharmaceuticals in the environment and their detrimental effects to microorganism, animals, aquatic life, plants and human has been highlighted by a number of studies. Additionally, the nature and degree of natural attenuation of pharmaceuticals in the environment are not fully understood and are challenging to predict making it more difficult to assess the potential human and ecotoxicological risk associated with pharmaceutical contamination.
The availability of sensitive analytical instrumentation has made it possible to characterize pharmaceuticals and study their removal by different treatment technologies. Activated sludge treatment, oxidation, UV photolysis, nanofiltration and reverse osmosis membranes can effectively remove pharmaceuticals but there are still deficiencies in the complete removal of pharmaceuticals from wastewater. Conversely, studies involving the adsorption of pharmaceuticals from wastewater using biochar have been investigated. However, scarce attention has been given to the sorption of pharmaceuticals by cotton gin waste and guayule bagasse and their application as a filter media. Laboratory scale studies have demonstrated biochar’s capacity to serve as an environmentally friendly adsorbent in both batch or column adsorption experiments, with pyrolysis conditions and feedstock type influencing the sorption behavior. These experiments may not take into consideration the careful selection of feedstock and pyrolysis temperature involved in producing “designer biochars” to ensure adequate particle and pore size involved in water retention and filtration applications.

This study is therefore aimed at evaluating biochar produced from cotton gin waste and guayule bagasse for the sorption of pharmaceuticals from reclaimed water. Additionally, this study seeks to understand the effect of pyrolysis temperature, residence time and pH on the physico-chemical characteristics and sorption ability of the biochar using adsorption studies. Following the adsorption studies, column experiments were conducted to examine the addition of biochar to sand filters with the prime focus being to investigate the breakthrough point ($C/C_0 = 0.05$), maximum bed capacity ($q_c$) and sorption coefficient ($K_d$). The research findings have implications for incorporating biochar into sand filters to remove pharmaceuticals from treated wastewater effluents used for irrigation.
Numerous processes (activated sludge treatment, nanofiltration, oxidation, reverse osmosis) employed at wastewater treatment plants contribute to the removal of pharmaceuticals from wastewater effluent. However, these methods have proven to be expensive with numerous limitations. A potential solution involving adsorption using biochar has been identified as a remediation technique for the removal of pharmaceuticals from wastewater effluent used in irrigation. The properties of biochar make it suitable for various applications such as soils amendment, carbon sequestration, contaminants immobilization suggest the technology could be used as an adsorbent or filter to remove contaminants from wastewater (Ahmad et al., 2017). The evaluation of this application is necessary to determine the effectiveness of this environmentally sustainable technology for the elimination of pharmaceuticals from wastewater used for crop production.

The overarching goal of this study is to evaluate biochars obtained from the pyrolysis of cotton gin and guayule bagasse as potential filter media for the removal of pharmaceuticals from wastewater effluent irrigation water. In order to attain this goal, the following objectives were addressed:

- Investigate the effect of pyrolysis temperature, reaction time and pH on the physico-chemical characteristics and adsorption ability of the biochars.

- Assess the ability of biomass-derived biochar to remove pharmaceuticals from reclaimed water by conducting batch adsorption experiments.

- Model adsorption results using kinetic models (e.g. pseudo-first or pseudo-second order) and isotherms (e.g. Langmuir and Freundlich) to understand adsorption rate and determine the maximum adsorption capacity.
- Conduct lab-scale column studies and determine the breakthrough curve parameters to investigate the use of biochar-amended sand filters for the removal of pharmaceuticals from treated wastewater effluents used for irrigation.

The project was motivated by the following research questions:

- How do the properties of the biochar (pore size, surface area, functional groups, pH and zeta potential) vary as the pyrolysis temperature increases?
- Can the amount of pharmaceutical adsorbed from aqueous phase be significantly impacted by the pH of the solution?
- What properties of the biochar influence the adsorption rate or capacity and how do they vary with pyrolysis temperature?
- How do the properties of the pharmaceuticals (pK\textsubscript{a}, log K\textsubscript{ow}, functional groups) affect the mechanisms responsible for their removal using biochar?

The rationale for understanding the water quality impacts of biochar-amended filters is to evaluate the benefits for use within the filtration component of an irrigation system for food crops. The central hypothesis is that biochar can enhance the ability of sand filters to improve wastewater quality by adsorbing the pharmaceuticals during the filtration process.
CHAPTER 4. METHODOLOGY

Introduction

The proposed research aims at investigating the potential for biochar to be used as filter media for the removal of pharmaceuticals from treated wastewater effluents. The methods utilized to achieve the aforementioned goals and objectives are divided into three phases as shown in Fig. 1.

The first phase mainly focuses on the selection of pharmaceuticals to be remediated and on biochar characterization studies. This phase involves the selection of the adsorbates (pharmaceuticals), physico-chemical characterization of the produced biochar and conducting batch adsorption experiments to investigate the ability of the biomass-derived biochar to remove pharmaceuticals from reclaimed water.

Phase 2, involves the collection and analysis of data from batch adsorption experiments. Kinetic studies and adsorption isotherms are used to understand the adsorption rate and determine the adsorbent with the maximum adsorption capacity.

Following the selection of the most suitable adsorbent, the key focus of the third phase involves a pilot-scale study using column experiments to investigate the addition of biochar to irrigation sand filters. This phase focuses on determining the $q_c$ and investigating the breakthrough curves to obtain $K_d$ values of four pharmaceutical compounds.
Fig. 1. Methodology flowchart.
4.1. Phase I: Materials and methods

4.1.1. Target adsorbates

Six pharmaceuticals (acetaminophen, pseudoephedrine, ibuprofen, sulfapyridine, docusate and erythromycin) were purchased from Sigma–Aldrich (St. Louis, MO, USA). The variety of pharmaceuticals were selected due to their frequency of occurrence in environmental systems as a result of widespread usage. Additionally, their pKₐ values and octanol water-partition coefficients (log K_{OW}) cover broad ranges meaning that they are subject to varying degrees of removal by hydrophobic effects, hydrogen bonding and π-π electron donor interactions. Detailed physico-chemical properties of the various adsorbents are provided in Table 3.

4.1.2. Adsorbents

Biochar obtained from the pyrolysis of guayule bagasse (GB) and cotton gin (CG) waste were studied to compare their adsorption capacities for pharmaceuticals in batch adsorption experiments. A total of 6 biochar samples were produced from GB and CG waste. The biochar samples were prepared according to Novak et al. (2012). All feedstocks were processed before pyrolysis through air-drying, grinding, and sieving to pass a 6-mm sieve. Between 0.5 and 1.5 kg of ground biomass were placed in a stainless-steel tray or into a crucible and pyrolyzed using a gas tight retort (Lindberg/MPH, Riverside, MI) at three different temperatures 350, 500 and 700 °C for 2 h under a stream of N₂ gas. The resulting biochar samples were referred to as GB350, GB500, GB700, CG350, CG500 and CG700. The biochar samples were ground to pass a 0.5-mm sieve and stored in a desiccator to minimize the absorption of water.
Table 3. Physico-chemical properties and structure of pharmaceuticals.

<table>
<thead>
<tr>
<th>Pharmaceuticals</th>
<th>Molecular formula</th>
<th>Molecular weight (g mol⁻¹)</th>
<th>Water solubility (mg L⁻¹ at 25 °C)</th>
<th>pKₐ</th>
<th>log Kₗw</th>
<th>Molecular Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaminophen (ACT)</td>
<td>C₈H₉NO₂</td>
<td>151.16</td>
<td>15000</td>
<td>9.86</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>Ibuprofen (IBP)</td>
<td>C₁₃H₁₈O₂</td>
<td>206.29</td>
<td>21</td>
<td>4.91</td>
<td>3.97</td>
<td></td>
</tr>
<tr>
<td>Sulfapyridine (SPY)</td>
<td>C₁₁H₁₁N₃O₂S</td>
<td>249.29</td>
<td>268</td>
<td>2.30</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>Docusate (DCT) (Sodium salt)</td>
<td>C₂₀H₃₇NaO₇S</td>
<td>444.56</td>
<td>71000</td>
<td>10.84</td>
<td>5.24</td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Formula</td>
<td>MW</td>
<td>LogP</td>
<td>Ref.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>---------</td>
<td>-----</td>
<td>------</td>
<td>--------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pseudoephedrine (PED)</td>
<td>C&lt;sub&gt;10&lt;/sub&gt;H&lt;sub&gt;15&lt;/sub&gt;NO</td>
<td>165.23</td>
<td>1.6E+05</td>
<td>9.74, 0.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Erythromycin (ETM)</td>
<td>C&lt;sub&gt;37&lt;/sub&gt;H&lt;sub&gt;67&lt;/sub&gt;NO&lt;sub&gt;13&lt;/sub&gt;</td>
<td>733.93</td>
<td>2000</td>
<td>8.88, 3.06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- a (National Center for Biotechnology Information)
- b (Jung et al., 2015)
- c (Ocampo-Perez et al., 2018)
- d (Yao et al., 2017)
- e (Li et al., 2008)
- f (McFarland et al., 1997)
4.1.3. Characterization of biochar

The pH of the biochar samples was measured according to a modified procedure by Angin (2013). Biochar was added to de-ionized water in a mass ratio of 1:20 (10.5 g of biochar + water). The mixture was shaken for 1 h using a mechanical shaker and the pH was measured with a pH meter. BET surface areas and pore volumes of the biochar were determined by the application of the ASAP 2020 automated surface area and porosimetry system and using t-plot analysis software available with the instrument.

The surface functional groups of the biochars were identified according to a modified procedure described by Kloss at al. (2012), using FTIR (Bruker IFS 66/S and Bruker Vertex V70) equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. Experiments were carried out in diffuse reflectance mode on a Praying Mantis diffuse reflectance accessory. Sample powder was placed in a 3 mm diameter 316 stainless steel sample cup assembly and a total of 500 scans were averaged per spectrum at a resolution of 4 cm\(^{-1}\). Experiments were carried out under a constant N\(_2\) purge with a fresh clean KBr reference acquired before each sample acquisition.

The zeta potential values of the samples were measured using Malvern Zetasizer ZS and according to a modified procedure by Johnson et al. (1996). Briefly, the biochar samples were ground and sieved to pass a 34 µm sieve. About 0.015 g of each biochar sample was added to 30 mL of deionized water. To measure the zeta potential at various pH values (4, 6, 8 and 10), the solutions were prepared by adding 0.05 M aqueous solution of HCl or NaOH to deionized water until the desired pH was obtained. Zeta potential was measured three times at each pH (150 scans each time), with the average values reported.
4.1.4 Batch adsorption experiments

The stock solutions (200 mg L\(^{-1}\)) of ACT, IBP, SPY, DCT, PED and ETM were diluted to produce initial concentrations of 10 mg L\(^{-1}\) for each pharmaceutical compound. The initial concentration of the pharmaceuticals in this study are relatively high compared to the typical concentrations in wastewater effluents (ng L\(^{-1}\)-µg L\(^{-1}\)). However, an initial concentration of 10 mg L\(^{-1}\) was chosen for batch adsorption experiments to ensure that the concentrations left after adsorption were still above the limit of detection for the instrument used to analyze the samples. Additionally, pharmaceuticals such as IBP with a low solubility (21 mg L\(^{-1}\)) have the possibility to precipitate at higher concentrations. Single batch adsorption experiments were conducted to determine the adsorption kinetics for pharmaceuticals on the biochar using 125 mL PTFE-lined® bottles containing 0.5 g of biochar (CG700, CG500, CG350, GB700, GB500 and GB350) and 100 mL of working volume of liquid sample containing the pharmaceutical compounds (Fig. 2). The mixtures were agitated at 200 rpm using a mechanical shaker at ambient laboratory conditions (Temperature ≈ 23 °C) and 10 mL of sample was collected after 5, 15, 30, 60, 120, 180, 240 min and 24 h contact times. The experiments were terminated after 24 h because negligible change in the extent of adsorption was observed beyond 24 h. For quality assurance, all adsorption experiments were conducted in triplicates and PTFE-lined® bottles used in batch experiments were covered with aluminum foil to minimize removal through photodegradation. Control experiments were also conducted without biochar to investigate potential contamination or losses due to experimental setup. Collected samples were filtered through a 1-µm Whatman membrane filter and filtrates were analyzed by high-pressure liquid chromatography and mass spectrometry (HPLC-MS).
Sodium azide (NaN₃) was added to each PTFE-lined® bottle to prevent microbial degradation of the samples. The sodium azide interacted with the pharmaceuticals in solution to form adducts which were read as separate peaks during analysis of the samples. These separate peaks gave the impression that removal occurred in the control experiment (no biochar added) even with photodegradation and biodegradation being ruled out as possible removal mechanism. Due to this analytical complication, NaN₃ was not included in further batch experiments. Additionally, most of the pharmaceuticals being adsorbed are antibiotics, so bacterial growth and activity is not expected to be significant.

Fig. 2. Schematic of batch adsorption experiments

The pharmaceutical removal efficiency and amount adsorbed (q; mg g⁻¹) were calculated using equations (1) and (2), respectively.

\[ Removal\ efficiency\ (\%) = \frac{C_0 - C_t}{C_0} \times 100\% \]  \hspace{1cm} (1)
Where, $C_0$ is the initial concentration of pharmaceuticals in solution (mg L$^{-1}$); $C_t$ is the concentration (mg L$^{-1}$) at time $t$ (5, 15, 30, 60, 120, 180, 240 min and 24 h); $V$ is the volume of the solution (L); and $m$ is the mass of the biochar (g).

### 4.1.5. Effect of solution pH

The effect of solution pH on the adsorption of ACT, IBP, SPY, DCT, PED and ETM was studied using CG700 biochar as adsorbent. Out of the six biochars samples in this study, CG700 showed the greatest affinity for all the pharmaceuticals compounds and was therefore chosen to determine the effect of pH on the removal efficiency. Batch adsorption experiments were conducted at the inherent solution pH ranging from 10-11 and at pH 7 to mimic the typically near-neutral conditions of wastewater effluents. The initial pH of the pharmaceutical solutions was adjusted to pH 7 by adding 0.1 M H$_2$SO$_4$. Mixtures of 0.5 g of CG700 biochar in 100 mL of 10 mg L$^{-1}$ stock solution of ACT, IBP, SPY, DCT, PED and ETM were stirred at 200 rpm and then filtered at different times between 5 min and 24 h.

### 4.2. Phase II: Data analysis

#### 4.2.1. Kinetic studies

The kinetics of adsorption of ACT, IBP, SPY, DCT, PED and ETM onto CG700, CG500, CG350, GB700, GB500 and GB350 biochar was initially analyzed using the pseudo-first order (PFO) and pseudo second-order (PSO) kinetic models. The conformity of the experimental data to the models was evaluated using the linear regression coefficients ($R^2$).
The pseudo-first-order model is expressed by equation (3) as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$  \quad (3)

Equation (4) shows the linearized form of the pseudo second-order kinetic rate equation,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \quad (4)

where, $q_e$ and $q_t$ (mg g\(^{-1}\)) are the amounts of pharmaceuticals adsorbed per unit of mass of biochar at equilibrium and at time $t$ (min) respectively, $k_1$ (min\(^{-1}\)) and $k_2$ (g mg\(^{-1}\) min) are the rate constants of pseudo-first-order and pseudo-second-order adsorption respectively. The values of $q_e$ and $k_2$ were calculated from the slopes and intercept of the plots of $\log (q_e-q_t)$ versus $t$ for the pseudo-first order. Similarly, from the pseudo-second-order plot of $t/q_t$ versus $t$, the values of $q_e$ and $k_2$ were obtained from the slope and intercept, respectively.

### 4.2.2. Adsorption isotherms

Adsorption isotherms of SPY, DCT and ETM on CG700 biochar was performed at inherent solution pH varying from 10-11 at room temperature. The pharmaceuticals were selected according to their removal by CG700 which was in the order DCT $>$ ETM $>$ SPY. 0.5 g of CG700 biochar was added to SPY, DCT and ETM solutions (100 mL) of varying initial concentrations (2, 10, 20, 40 and 50 mg L\(^{-1}\)). Solutions were stirred for 24 h at a speed of 200 rpm to reach equilibrium and then filtered. The equilibrium data obtained from the study were fitted to the Langmuir and Freundlich isotherms. The Langmuir model describes a monolayer adsorption of molecules onto a surface having a finite number of adsorption sites of the same energy, which are equally available for interaction. The linear form of the Langmuir equation as shown by equation (5):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e}$$  \quad (5)
where, \( C_e \) (mg L\(^{-1}\)) is the concentration of pharmaceuticals at equilibrium, \( q_e \) and \( q_m \) are the equilibrium and maximum adsorption capacity respectively (mg g\(^{-1}\)). \( K_i \) is the adsorption equilibrium constant in L mg\(^{-1}\). A straight-line plot of \( 1/q_e \) vs \( 1/C_e \) for the adsorption of the pharmaceuticals was obtained and the maximum adsorption capacity \( q_m \) and the constant \( K_i \) were determined from the slope and intercept of the plot respectively.

The Freundlich model describes multilayer adsorption with interaction between adsorbed molecules onto heterogeneous surfaces, assuming that adsorbent surface sites have a spectrum of different binding energies. Equation (6) shows the linearized form of the Freundlich equation (Goswami et al., 2011).

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

where, \( C_e \) (mg L\(^{-1}\)) is the equilibrium solute concentration in solution, \( q_e \) is the equilibrium adsorption capacity (mg g\(^{-1}\)), \( K_F \) is the Freundlich constant related to adsorption capacity and \( n \) is a measure of adsorption intensity. The values of \( K_F \) and \( n \) were obtained from the intercept and slope and of the plot between \( \log q_e \) and \( \log C_e \). A favorable adsorption tends to have Freundlich constant \( n \) between 1 and 10 (Kumar et al., 2012).

4.3. Phase III: Pilot scale study

4.3.1. Column adsorption experiments

Fig. 3 shows the column setup used for this study. The fixed-bed column experiments were carried out in a glass column with an inner diameter of 1 cm and a length of 60 cm. At the bottom, a layer of glass wool and silica sand with a thickness of 1 cm was fitted. A mixture of 1:1 CG700 biochar-to-sand ratio was obtained and 10 g of the mixture was packed in the same column to obtain a bed
depth of 13 cm. Another layer of sand (1 cm) was placed over the biochar. ACT, SPY, ETM and DCT were selected for the column experiments due to their affinity for CG700 ranging from high (DCT), medium (ETM and SPY) and low (ACT). An initial hypothesis was that breakthrough will occur in the order of ACT < SPY < ETM < DCT since ACT and DCT were the least and most adsorbed compounds, respectively, using CG700. An influent concentration of 10 mg L$^{-1}$ of ACT, SPY, ETM and DCT was pumped to the top of the column and allowed to flow from top to bottom. A constant flowrate of 1.0 mL min$^{-1}$ was maintained using a peristaltic pump. Effluents samples were collected and analyzed for selected pharmaceuticals. The pH of the effluents after adsorption was recorded periodically to monitor any changes that might occur during the adsorption and transport through the column. The breakthrough is defined as the point when the ratios of the effluent-to-influent concentration was 5% ($C_e/C_o = 0.05$; Chauhan and Talib, 2017). The pharmaceutical uptake at 95% ($C_e/C_o = 0.95$) was selected as the saturation point of the column, that is, the point at which most of the surface sites of the biochar are occupied by the pharmaceuticals. The column experiments were stopped when saturation point and column exhaustion occurred.

The maximum column bed capacity ($q_c; $mg g$^{-1}$) for the inlet pharmaceutical concentration and flow rate was determined based on equation (7):

$$q_c = \frac{Q}{1000} \int_{t=0}^{t_{total}} \frac{C_{ads} \, dt}{m}$$  \hspace{1cm} (7)$$

where, $C_{ads}$ is the adsorbed pharmaceutical concentration (mg L$^{-1}$), $Q$ is the volumetric flow rate (mL min$^{-1}$), $t$ (min) is the time and $m$ is the mass of biochar (g) packed in the column.
4.3.2 HYDRUS 1-D model

The HYDUS-1D model was used to simulate the transport of ACT, DCT, ETM and SPY through the column. The model was implemented assuming equilibrium solute transport and a single kinetic site (biochar). HYDRUS calculate numerical solutions for one-dimensional vertical transport based on the convection-dispersion equation (CDE) written as (Chotpantarat et al., 2011);

\[
\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \frac{\rho \partial C}{\theta} \pm \left[ \frac{\partial C}{\partial x} \right]_{r,xxn}
\]

(8)
where, $C$ (mg L$^{-1}$) is the concentration of solute in liquid phase; $t$ (h) is the time; $D_L$ (cm$^2$ h$^{-1}$) is the longitudinal dispersion coefficient; $v_x$ (cm h$^{-1}$) is the average linear velocity; $\rho$ (g cm$^{-3}$) is the bulk density of the media; $\theta$ is the volumetric moisture content or porosity for saturated media; $C^*$ (mg g$^{-1}$) is the amount of solute sorbed per unit weight of solid, rxn is the subscript of the last term which accounts for any biological or chemical reaction of the solute (other than sorption). In the current application, this final term was ignored. The HYDRUS-1D model was applied to the data to evaluate pharmaceutical adsorption and transport in the columns to obtain the breakthrough curves and determine the $K_d$ values.
CHAPTER 5. RESULTS AND DISCUSSION

5.1. Characterization of biochar

5.1.1. Specific surface area (SA) and pH

All of the biochar samples were alkaline and biochar pH increased with a rise in pyrolysis temperature (Table 4). The basic nature of the biochar is due to the transformation of C into ash during pyrolysis and alkali salts begin to separate from the organic matrix, increasing the pH (Cao and Harris, 2010). Porous structure (BET surface area and pore volume) of the studied biochar samples were examined by N$_2$ adsorption experiments and are summarized in Table 4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (hours)</th>
<th>Temperature (°C)</th>
<th>Surface area (m$^2$/g)</th>
<th>Total pore volume (cm$^3$/g)</th>
<th>Average pore diameter (nm)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton gin (CG) waste</td>
<td>2</td>
<td>350</td>
<td>2.40</td>
<td>3.10E-03</td>
<td>4.07</td>
<td>9.46</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>500</td>
<td>2.06</td>
<td>6.06E-03</td>
<td>9.65</td>
<td>10.13</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>700</td>
<td>16.33</td>
<td>1.15E-02</td>
<td>3.59</td>
<td>10.93</td>
</tr>
<tr>
<td>Guayule Bagasse (GB)</td>
<td>2</td>
<td>350</td>
<td>0.00</td>
<td>4.00E-05</td>
<td>-</td>
<td>9.54</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>500</td>
<td>0.07</td>
<td>1.70E-04</td>
<td>-</td>
<td>9.89</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>700</td>
<td>5.92</td>
<td>6.59E-03</td>
<td>-</td>
<td>9.93</td>
</tr>
</tbody>
</table>

The SAs of the cotton gin waste biochars are low but increased as the pyrolysis temperature increased to 700 °C. Numerous studies have documented an increasing surface area of biochars with increasing pyrolysis temperatures (Cao and Harris 2010; Uchimiya et al., 2011a; Ahmad et al., 2012; Kloss et al., 2012; Angina 2013, Ding et al., 2014; Goswami et al., 2016; de Caprariis et al., 2017). As the pyrolysis temperature reached 700 °C, the BET SAs and number of micropores
significantly increased resulting from the removal of volatile matter that were either inside or blocking the micropores (Guedidi et al., 2017). Biochars obtained from guayule bagasse did not exhibit good quality SA and porous structure characteristics. This may be attributed to the softening, melting, fusing and carbonization which likely resulted in the pores of the biochar being partially blocked. This would prevent the access of the absorption gas to the pores and therefore lead to lower surface areas and pore volumes (Fu et al., 2011). The biochar samples were washed several times and the degassing temperature was increased in an attempt to obtain better isotherms but this approach was unsuccessful. It seems in this case that the parent biomass composition rather than biochar production procedure mainly determined the specific surface areas of the biochar. Lower surface area of the biochar (Table 4) suggests that CO₂ isotherms may be more suitable for detecting the microporosity of biochar because the surface area might arise primarily from micropores (<2 nm) rather than nanopores (>1 nm; Kasozi et al., 2010).

The SAs of the biochars in this study were generally lower than values for biochars produced from various feedstocks used in other studies, although several biochars are reported to have values less than 10 m² g⁻¹ (Ahmad et al., 2012). Notably, Uchimiya et al. (2011a) reported SAs of biochar obtained from the pyrolysis of cottonseed hull at 350 °C and 500 °C to be 4.7 and 0.0 m² g⁻¹ respectively. These lower SAs can be attributed to the lower H/C ratio. The formation of extensive cross-linkages during pyrolysis results in oxygen-rich and hydrogen-poor substances that are less graphitized leading to lower SAs (Bourke et al., 2007).

SAs for both corn cob and corn stover biochars obtained at 500 °C were 0.0 and 3.1 m² g⁻¹ respectively. Such low SAs do not preclude substantial adsorption of organic pollutants. Cao and
Harris (2010) reported nearly 77% removal of atrazine (1.5 mg g⁻¹ adsorption capacity) by dairy manure derived biochar pyrolyzed at 200 °C with SA of 2.7 m² g⁻¹. The adsorption capacity of salicylic acid and ibuprofen on pine wood chips pyrolyzed at 425 °C (surface area = 1.35 m² g⁻¹) was 22.70 and 10.74 mg g⁻¹, respectively. The absorption process proceeds through imbibition of water and the adsorbates within the solid structure of the biochar, despite its low surface area. A study by Chen and Chen (2009), demonstrated that orange peels pyrolyzed at 200 °C for 6 h (SA= 7.75 m² g⁻¹) exhibited the optimum sorption capacity for 1-naphthol (100 mg g⁻¹) at high concentration due to its substantial polymeric aliphatic fraction and high-surface adsorption. Similarly, oranges peels pyrolyzed at 250 °C (SA= 51.6 m² g⁻¹) and 400 °C (SA= 28.1 m² g⁻¹), showed 92.4% (2.66 mg g⁻¹) and 98.1% (28.2 mg g⁻¹) removal of naphthalene, respectively (Chen et al., 2011).

5.1.2. Zeta potential

The zeta potential measurement for the different biochar samples are reported in Table 5 and Fig. 4 demonstrates how the zeta potential varies with pH. The measured zeta potential for cotton gin (CG) and guayule bagasse (GB) were both negative for all pH conditions tested (Table 5), indicating strongly negatively charged surfaces that might facilitate the adsorption of cations over a wide pH range.

<table>
<thead>
<tr>
<th>pH</th>
<th>CG350</th>
<th>CG500</th>
<th>CG700</th>
<th>GB350</th>
<th>GB500</th>
<th>GB700</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
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According to Fig. 4, increasing pH resulted in increasing negative zeta potential of all the biochar samples. A similar trend was observed in the study by Taheran et al. (2016) for adsorption of chlortetracycline on pinewood biochar. Likewise, Essandoh et al. (2015) demonstrated that the magnitude of pine wood biochar negative charge increases by increasing the solution pH. Given the nature of the pH-dependent zeta potential shown in Fig. 4, it was not possible to identify a pH point of zero charge (pH\text{zpc}) for the biochars. Extrapolation of the data suggests a pH\text{zpc} of < 2. The active groups on the biochar surface exist in their positive form when the pH is below the pH\text{zpc} and they shift to their deprotonated form at pH levels above pH\text{zpc}. However, the relevance to the current research is that the biochars carry a net negative charge under all pH conditions of use.

![Zeta potential-pH curves for different biochar samples.](image)

**Fig. 4.** Zeta potential-pH curves for different biochar samples.

### 5.1.3 FT-IR

The FT-IR spectra of the biochar samples were used to characterize the surface functional groups. As shown in Fig. 5a and Fig. 5b, all spectra exhibit the OH, C-H, C=O and C=C, bond stretching...
at 3400, 2850, 1750, 1600 cm$^{-1}$ respectively. The peaks at about 3400 and 3550 cm$^{-1}$ correspond to vibrations of OH groups and were still present in the biochar prepared at 700 °C, but were dramatically straightened at 350 and 500 °C. The stretch at 1770 cm$^{-1}$ is due to the C=O stretching vibrations of the carbonyls (aldehyde, ketones esters, carboxylic acids) both unconjugated and conjugated with aromatic rings (Uchimiya et al., 2011a).

Carboxyl groups contribute to negative surface charges (section 5.1.2) which is essential for cation retention in the aqueous solution. The absorbance peaks between 1400 and 1500 cm$^{-1}$ represent C=C stretching vibrations that are indicative of alkanes and aromatics (Inyang et al., 2010). The C-O stretching (1350 cm$^{-1}$) occurred due to the presence of primary, secondary and tertiary alcohols, phenols, ethers and esters. The peak at wave number near 870 cm$^{-1}$ demonstrates the C-H bending vibration in β-glycosidic linkage (Krishnan and Harris, 2008). This also indicates the presence of adjacent aromatic hydrogen in the biochars.

The absorbance peak at 2850 – 2960 cm$^{-1}$ indicates the presence of an alkyl C-H and the intensity of this group increased at 500 °C and decreased at 700 °C (Fig 5a and b). From these results, it can be suggested that the increase of this functional group results from the conversion of functional groups in a low oxidation state to those in a high oxidation state by means of heat treatment. And the decrease of these functional group at 700 °C was attributed to the release of these groups or conversion to other functionalities.
Fig. 5a. FTIR spectra of CG3550, CG500 and CG700.

Fig. 5b. FTIR spectra of GB350, GB500 and GB700.
The major difference between the CG and the GB biochar is the appearance of the dominant phenolic compound (C-O) in the GB biochar. The phenolic functional group promotes acidity, leading to lower alkalinity of the GB biochar compared to the CG biochar as seen by the pH measurements (Table 4; Lopez-Ramon et al., 1999). The presence of more oxygen containing functional groups in the GB biochar makes it more hydrophilic compared to CG biochar and therefore, the CG biochar might be more suitable for adsorbing non-polar organic compounds (Inyang et al., 2010). Based on the IR spectra the changes of the band positions of the functional groups can be used to interpret the adsorption of pharmaceuticals in terms of the formation of bonds between the functional groups present on the biochar surface and the functional groups of the pharmaceutical compounds.

5.2. Adsorption results
Adsorption is a process governed by several mechanisms operating simultaneously and it is often difficult to precisely identify the role of each mechanism in the adsorbent-adsorbate interactions in a specific system. For interpreting adsorption behavior, it is convenient to consider the overall free energy for the adsorption reaction, $\Delta G_{ads}$, as a combination of terms representing various adsorption mechanisms:

$$\Delta G_{ads} = \Delta G_{elect} + \Delta G_{hydro} + \Delta G_{H-bond} + \Delta G_{\pi-\pi EDA} + \cdots$$

where $\Delta G_{elect}$ is the electrostatic adsorption term, $\Delta G_{hydro}$ accounts for removal from solution due to hydrophobic effects, $\Delta G_{H-bond}$ accounts for adsorption due to hydrogen bonding and $\Delta G_{\pi}$.

$\pi EDA$ accounts for electron-donor-acceptor interactions.
The following discussion will focus on results where the adsorption behavior can be plausibly interpreted in the context of the interplay of these different adsorption mechanisms. The removal of ACT, IBP, SPY, DCT, PED and ETM using CG and GB biochars are illustrated and discussed in the subsequent sections.

5.2.1. Acetaminophen adsorption

The adsorption of ACT by biochar was less than 20% using CG700, CG500, CG350, GB700, GB500 and GB350 biochars (Fig. 6a and 6b). The pK$_a$ of ACT (9.86) and the net negative surface charge of the biochars hindered the removal of ACT due to electrostatic repulsion. At the inherent solution pH (10-11), ACT is mostly neutral or exists in its dissociated form ACT$^-$ (pH > pK$_a$; Nam et al., 2014) while all the biochars have a net negative charge (pH > pHzpc). Thus, a rise in electrostatic repulsion between ACT$^-$ and the biochar surface likely prevented significant adsorption. Similarly, Sumalinog et al. (2018) reported constant ACT removal using activated biochar obtained from municipal solid wastes when the solution pH was in the range of 2-8 with a drastic drop observed as the pH went from pH 10-12 (24.1 to 4.5 mg g$^{-1}$ and removal from 45.2 to 7.1%).

Other possible additional removal mechanisms such as hydrophobic bonding, hydrogen bonding and anion-induced π-interactions exist for acetaminophen with biochar at a given pH. H-bonds can be formed between the surface carbonyl group and the OH group of the ACT. Noncovalent π-interactions are caused by the differing statuses of π systems among the materials (Anslyn and Dougherty 2006). However, ACT removal was minimal due to the fact that hydrophobic bonding
was limited because the ACT became more polar as the solution pH exceeded the pKa (9.86) of the compound. Similarly, at this pH (10-11), ACT mostly exists in its undissociated form, limiting anion-induced π-interactions between ACT and the biochars that would have otherwise aided in its adsorption (Jung et al., 2015).

Furthermore, adsorption behavior due to molecular weight (MW) and surface areas of the biochars may cause an obstruction in the removal of ACT. This is attributed to the fact that the compound with the lowest MW contains more molecules in solution. Assuming similar biochar surface area is needed for immobilization of individual molecules, the compound with the lowest MW would require the highest surface area for complete adsorption. ACT which is the compound with the lowest MW in this study (151.16 g mol⁻¹), will require a significant number of active sites for adsorption to be prominent. Given the low specific surface areas and micro/macro pore volumes present on all of the studied biochars (Table 4), ACT adsorption may have been restricted due the saturation of the active sites.

**Fig. 6.** Removal of Acetaminophen by (a) CG700, CG500 and CG350 and (b) GB700, GB500 and GB350 (Red errors bars < 10%).
5.2.2. Ibuprofen adsorption

The time-dependent removal of IBP on the six biochars is shown in Fig. 7a and 7b. The data indicates that the highest removal of IBP by biochar was observed with the CG700, followed by CG350 and CG500 (Fig. 7a). These results can be correlated with the surface areas of the adsorbents that follows the same trend CG700 > CG350 > CG500 (Table 4). The pyrolysis at 700 °C increased the surface area 8-fold compared to the surface area at 350 °C and this was accompanied by a proportional increase of about 70% in the extent of adsorption. Adsorption plots were characterized by an initial fast rate during the first 4 hours (accounting for 20% -50% using CG700 and CG350 biochars) and slowly reached equilibrium after 24 h signifying a point where there is a defined distribution of the adsorbate between the solid and the liquid phases.

![Graph A](image1.png) ![Graph B](image2.png)

**Fig. 7.** Removal of Ibuprofen by (a) CG700, CG500 and CG350 and (b) GB700, GB500 and GB350 (Red errors bars < 10%).

The mechanism for the removal of IBP can be explained by two factors; the surface charge of the biochars (pHzpc) and the pK<sub>a</sub> value of the IBP (4.9). The experimental pH for the study of IBP varied between pH 10.3-10.8 when using CG700 biochar, 10.2-10.4 for CG500 and 9.9-10.2 for CG350 biochar. At these pH conditions, (approximately 5 units above the pK<sub>a</sub>) IBP exists in its
anionic form. Increasing the pH increases the mol % of anionic form of IBP present in solution. At pH 4 the anionic form accounts for 11 mol%, at pH 5 it accounts for 55 mol% and at pH 7 it represents more than 99 mol%. On the other side, since the solution pH is above the pHzpc of the biochar samples, a negative charge is present on the surface of the biochars (as shown in Section 5.1.2). Consequently, electrostatic attraction cannot be the mechanism responsible for IBP removal by CG700, CG500 and CG350 due repulsive forces existing between the negatively charged biochar surface and the anionic IBP.

A combination of π-π interactions (a specific non-covalent force) and hydrophobic bonding were considered as the mechanisms involved in the removal of IBP by CG700, CG500 and CG350. Electron donor-acceptor complex formation due to π-π dispersive forces between the graphite carbonaceous CG700, CG500 and CG350 biochars and the aromatic ring of the IBP likely enhanced removal. Ocampa-Perez et al. (2019) studied the removal of IBP using chili seeds and the results showed that despite repulsive forces, IBP was still adsorbed on the surface of the chili seeds pyrolyzed at 600 °C, thereby implying that π-π interactions control the adsorption mechanism when the pH is greater than 7. Hydrophobic bonding induced by van der Waals forces between the graphemic planes of the biochar and the hydrophobic IBP molecules (K_{ow} = 3.97) equally aided in the adsorption IBP by the biochars. Moreover, another mechanism responsible for IBP adsorption may be attributed to the formation of hydrogen bonds between the carboxyl groups of the IBP and the (C=O) and (C=C) group present on the CG biochars surfaces as shown by the FTIR spectra (Fig. 5b; Charkraborty et al., 2018).
Differences in adsorption of IBP between CG and GB biochars were correlated to the different physico-chemical characteristics of these biochars. The differences in the physico-chemical properties were predominantly controlled by the inherent molecular configuration of the plant-based biomass feedstock (cotton gin waste and guayule bagasse) which, in turn, would affect the sorption properties of biochar. GB700, GB500 and GB350 are characterized by higher content of O-containing functional groups (Fig. 5b), which renders these biochars more hydrophilic and hinders the formation of hydrophobic bonds. This is explained by the fact that during adsorption, the oxygen groups on the biochar surfaces usually act as the primary adsorption center. Water molecules show a greater affinity for surface oxygen groups on the biochar via hydrogen bonding than to the more hydrophobic IBP molecules. Water molecules are therefore adsorbed on the GB biochars surfaces and act as polarized secondary adsorption centers, promoting further water-molecule adsorption and cluster formation. These clusters form an envelope extending beyond the localized adsorption centers, reducing the accessibility of IBP molecules to the solid particles and in addition, water molecules strongly compete for adsorption sites with IBP on the functionalized biochar surface. As a result, the potential for the formation of hydrophobic bonds between IBP molecules and the GB biochars was strongly inhibited (Wu and Pendleton, 2001). One additional, factor is that low pore volume and specific surface areas of the GB700 (5.92 m² g⁻¹) GB500 (0.06 m² g⁻¹) and GB350 (0.00 m² g⁻¹) compared to the CG700 (16.33 m² g⁻¹), made the active sites less available for IBP adsorption contributing to negligible removal (Fig 7b).

5.2.3. Sulfapyridine adsorption

The adsorption of SPY by the biochars follow the order CG700 > CG350 > CG500 with 70%, 50% and 15% removal after 24 h respectively (Fig. 8a). This trend is correlated to the surface areas of the biochars and the degree of hydrophobicity that follow the same order: CG700 > CG350 >
CG500. The ionic character of SPY varies greatly with pH, as reflected by the acidity constants ($pK_{a1} = 2.3$ and $pK_{a2} = 8.4$). At the inherent solution pH which varied between 8.9-11.2 using CG700 and CG350, SPY exists mainly in its neutral and anionic forms (pH > $pK_{a1}$ and $pK_{a2}$; SPY-) and hydrophobic interaction can occur between the SPY and the negatively charged CG700 and CG350 biochar surfaces (pH > $pHzpc$) leading to its removal from the aqueous phase. However, the amount of SPY adsorbed by CG700 and CG350 as illustrated by Fig. 8a is greater than what would be expected due to hydrophobic bonding alone because SPY has a $log K_{ow}$ value of 0.35. This suggests that in addition to hydrophobic bonding, other mechanisms are responsible for the removal of SPY.

![Fig. 8](image.png)

**Fig. 8.** Removal of Sulfapyridine by (a) CG700, CG500 and CG350 and (b) GB700, GB500 and GB350 (Red errors bars < 10%).

An additional driving force contributing to the removal of SPY is the formation of negative charge-assisted H-bond (-CAHB) between the anionic SPY and the oxygen containing functional groups of the biochars. CAHB occurred due to the fact that the pH of the solution in this study increased as the contact time increased to 24 h. The increase in pH is attributed to the release of OH during the proton exchange between SPY and water molecules and this is followed by interaction of the
SPY molecules with the O-functional groups present on the biochar surface leading to SPY adsorption (SPY + biochar \( \rightarrow \) SPY°=biochar; Teixidó et al., 2011).

Furthermore, some of the sorption of SPY by CG700, CG500 and CG350 can be explained by \( \pi-\pi \) electron-donor acceptor (EDA) interactions. SPY can act as a \( \pi \)-electron acceptor due to the presence of the amino functional group and N and/or O-hetero-aromatic rings (Ahmed et al., 2017). CG700, CG500 and CG350 biochars enriched with C=C, OH, C=O groups act as strong electron donors. Both of these factors facilitated \( \pi-\pi \) EDA interactions between CG700, CG500 and CG350 and SPY resulting in the removal from SPY from solution. Yao et al. (2017) recently proposed that the adsorption of sulfapyridine and sulfamethoxazole onto biochars derived from anaerobically digested bagasse is attributed to \( \pi-\pi \) EDA interactions between graphitic regions of biochars and the sulfonamide group in SMX and SPY. Ji et al. (2009) also proposed that the adsorption of SMX and SPY to graphite and multi-walled carbon nanotubes (MWCNTs) is enabled by \( \pi-\pi \) EDA interactions involving the heterocyclic ring.

The low removal achieved by CG500 (14 % removal after 24 h) compared to CG700 and CG350 might be attributed to the inherent pH of the solution. The pH varied between 8.79-9.30 from the beginning of the experiment to the final time. This is lower than the pH of the inherent solution using CG700 and CG350 (pH between 10.5-11.2 and 9.9-11.1, respectively). Consequently, with the pH being slightly above the pK\(_a\) of SPY (8.4), some of the SPY exists as a neutral species and very few anionic species are present and the ability for hydrophobic interactions to occur is diminished. It is therefore hypothesized that the removal of SPY by CG500 was achieved by only two mechanisms which are hydrophobic interaction and \( \pi-\pi \) EDA interactions instead of the three
mechanisms attributed to the removal using CG700 and CG350 (hydrophobic bonding, CAHB and \(\pi-\pi\) EDA interactions).

From Fig. 8b, it is apparent that the removal of SPY by GB700, GB500 and GB350 is limited. The surfaces of the GB biochars are characterized by an additional phenolic group which is absent on the CG biochar surfaces. The presence of more O-containing functional groups on GB700, GB500 and GB350 may facilitate the formation of dense hydrated layers on the biochar surface (as discussed in section 5.2.2), blocking the pores and restricting SPY adsorption (Zheng at al., 2013). Additionally, these biochars display very low specific surface areas leading to a limited number of active sites capable of participating in adsorption, hence significant removal is precluded.

5.2.4. Docusate adsorption

All tested biochars exhibited some ability to remove aqueous DCT (Fig. 9a and b). The removal of DCT reached 98% using CG700, followed by 85% and 79% using CG500 and CG350, respectively (Fig. 9a). As discussed, the biochar surfaces have a net negative charge reducing the potential for anion adsorption. For DCT to be adsorbed at all, it is likely that hydrophobic effects may be responsible for its removal from solution.

The hydrophobic nature of the CG700, CG500 and CG350 biochars (Table 4), compared to GB biochars, coupled with the relatively high log \(K_{ow}\) (5.24) for DCT aided in its adsorption. DCT has a greater tendency to withdraw from the aqueous phase than the other pharmaceuticals in this study, facilitating hydrophobic effects between the hydrophobic chains of the surfactant DCT and the hydrophobic region of the biochar. In addition, hydrophobic effects can occur between
hydrophobic chains of previously adsorbed DCT and other DCT molecules in solution and this results in increased adsorption (Brown et al., 1998).

**Fig. 9.** Removal of Docusate by (a) CG700, CG500 and CG350 and (b) GB700, GB500 and GB350 (Red errors bars < 10%).

Even the GB biochars showed more than 50% removal (Fig. 9b) after 24 h. Adsorption using GB700, GB500 and GB350 reached 51%, 53% and 66%, respectively. However, GB biochars showed the least removal due to the presence of the additional oxygen containing functional group, leading to a hydrophilic surface which was less prone to the uptake of the hydrophobic DCT. DCT is a hydrophobic compound and is apt to be absorbed by a hydrophobic surface. Therefore, the predominance of oxygen containing functional groups on the GB biochar surfaces, and the reduction of the hydrophobic character of the carbon surface will militate against the formation of hydrophobic bonds between GB700, GB500 and GB350 and DCT. This resulted in lower DCT removal compared to the CG biochars.

Lower temperature biochar, GB350 showed the greatest removal of DCT compared to GB700. Besides the parent feedstock used for the production of biochar, the pyrolysis temperature can also
influence the surface area and natural organic matter (NOM) content of biochar. This will in turn have an effect on the removal of DCT by biochar. Biochars made at lower pyrolysis temperature contain a higher NOM content and can sorb organic compounds through the mechanism of partitioning into the organic phase (Kupryianchyk et al., 2016). Thus, lower temperature GB350 biochar could have higher DCT adsorption potential due to their higher NOM content. The higher sorption of DCT onto lower temperature biochars suggest that surface functional groups on the biochars and NOM may play a more important role in interactions between DCT and biochar than other factors such as specific surface area. No information regarding the adsorption of DCT onto biochar is could be found; therefore, further investigation is needed to determine whether other mechanisms are involved in DCT removal.

5.2.5. Pseudoephedrine adsorption

The CG700, CG500 and CG350 biochars were able to adsorb 76%, 72% and 66% of the aqueous PED in solution after 24 h, respectively (Fig 10a). Fig 10b shows the removal of PED by GB700, GB500 and GB350 reached 25%, 33% and 58%, respectively. Since PED has a pKₐ value of 9.74 and the inherent experimental pH of the solution varied between 10.2 and 11.4 when using the biochars, PED existed in its neutral or anionic form. PED molecules can potentially orient themselves with the N-tail pointing out and the aromatic ring towards the surface and this might favor hydrophobic interactions between the PED and the negatively charged hydrophobic biochars (pH > pHzpc). However, with the very low Kᵦ of PED (0.89), hydrophobic interactions will most likely not be the sole mechanism for the removal of PED from solution. In addition, π-π EDA interactions between the hydroxyl groups present in the biochars directly bonding to the aromatic rings of the PED, resulted in removal from the aqueous phase. Moreover, at very high pH, a dipole
moment is created and allows more PED molecules to move towards the surface of the negatively charged biochars thereby enhancing the removal of PED from solution.

Fig. 10. Removal of Pseudoephedrine by (a) CG700, CG500 and CG350 and (b) GB700, GB500 and GB350 (Red errors bars < 10%).

GB biochars exhibited the least removal due the presence of the dominant phenolic groups which renders the biochars more hydrophilic. Additionally, the removal of PED does not follow the specific surface area trend indicating that adsorption is mostly influence by the surface functional groups and not the availability of surface-active sites. Further investigation is required to gain more mechanistic insights into the removal of PED by CG and GB biochars.

5.2.6. Erythromycin adsorption

The ETM adsorption profiles onto CG700, CG500 and CG350 biochars show 74%, 44% and 37% removal, respectively (Fig. 11a). Using the GB biochars, removal reached 53%, 64% and 50% for GB700, GB500 and GB350, respectively (Fig. 11b). The adsorption of ETM onto the biochars is dominated by rapid diffusion of ETM molecules from the solution to external surfaces of the biochars. This step is followed by gradual adsorption and this is attributed to the diffusion of
ETM molecules into the porous structures of the biochars (Mostafapour et al., 2019). Also, the adsorption of ETM onto the biochars was aided by van der Waals forces resulting in the formation of hydrophobic bonds (Sun et al., 2009). The adsorption of ETM onto microporous resin sepabead SP825 studied by Sun et al. (2009) showed that increasing the temperature and pH of the experiment resulted in decreased K, showing that more ETM molecules were present in the aqueous phase and adsorption occurred due to van der Waals forces.

![Graph A](image1.png)  ![Graph B](image2.png)

**Fig. 11.** Removal of Erythromycin by (a) CG700, CG500 and CG350 and (b) GB700, GB500 and GB350 (Red errors bars < 10%).

Moreover, ETM has the ability of form hydrogen bonds between its hydroxyl moieties and the (C=O) and (C=C) group present on the biochars surfaces. The adsorption of ETM follows the order CG700 > GB500 > GB700 > GB350 > CG500 > CG350. Apart from the CG700, the more hydrophilic GB biochars removed ETM more than the CG biochars. These results indicate that the more O-containing functional groups present on the GB biochar increased the formation of H-bonds leading to greater removal. Moreover, this demonstrates that adsorption might be dominated by the formation of H-bonds and not the availability of active surface sites.
5.3. Effect of solution pH

Solution pH in adsorption is important as it affects both the physico-chemical properties of the pharmaceuticals and the surface charge of the biochars. This parameter plays a role in influencing the different removal mechanisms influencing the interaction between the pharmaceutical and the biochar. To evaluate the effect of pH on pharmaceutical adsorption, batch adsorption experiments were conducted at inherent solution pH (10-11) and at pH 7 using CG700 biochar.

5.3.1. Acetaminophen

Fig. 12a shows that the removal efficiency of ACT using CG700 improved significantly at a pH of 7 (90% removal), compared to the inherent solution pH which varied between 10-11 (10% removal). The surface properties of CG700 play a role in ACT removal, while the solution pH affects the dissociation of functional groups on its surface. At a solution pH of 7, the CG700 carries a net negative charge but the surface is more negative at pH 10 (Table 5). On the other hand, ACT is a weak acid and the neutral species mostly exists at a pH below its pKa (9.86). So, due to a decrease in anionic ACT species at pH 7, while the biochar is still negatively charged, the electrostatic repulsion between the negatively charged CG700 and ACT− will not hinder ACT adsorption and this leads to an increase in removal efficiency. Additionally, at pH 7, the neutral, non-anionic ACT molecules become more hydrophobic thus, hydrophobic interactions are considered to occur and increase removal (Angela et al., 2018). Similar results were demonstrated in literature with ACT being adsorbed more efficiently at a pH ranging from 2-10 and a decrease in adsorption capacity at pH values greater than 10. Lui at al. (2013) studied the adsorption of ACT by animal hair-based activated carbon, and found out that at pH between 2-9, ACT adsorption varied slightly from 88 to 92% but the removal efficiency decreased by 70% when then pH was
above 10. Similarly, the adsorption of ACT using activated carbon from Dende coconut mesocarp showed that the adsorption of ACT was very similar at pH 2 and 6.5 and the adsorption decreased at pH 11 due to the ACT molecule being repelled by the negatively charged carbon surface (Ferreira at al. 2015).

**5.3.2. Ibuprofen**

The effect of solution pH on IBP adsorption was studied using CG700 biochar as adsorbent. The experimental results showed that the adsorption was favorable at inherent solution pH varying between 10-11 with 50% removal and the removal decreased to 35% at a pH of 7. (Fig. 12b). The pH effect can be explained by the surface charge of the CG700 biochar and the pK<sub>a</sub> of IBP (4.91). At pH 6-10, negatively charged species of IBP (greater than 90%) are dominant and the biochar surface becomes increasingly more negatively charged as the pH increases from 6-10 (as discussed in Section 5.1.2), thus there is electrostatic repulsion. However, even when there are repulsion interactions, more of the IBP is absorbed on the surface of CG700 at pH 10 compared to pH 7. These results show that when the pH > 7, mechanisms such as hydrophobic bonding and \( \pi-\pi \) interactions are more dominant and control adsorption of IBP as discussed in section 5.2.2.

**5.3.3. Sulfapyridine**

Fig. 12c shows the effect of pH on the adsorption of SPY to CG700. The removal of SPY increased at a pH of 10 (70% removal) and a significant reduction was observed as the pH decreased to 7 (40% removal). At pH 7, neutral SPY\(^{\circ}\) species dominate whereas at a pH of 10, anionic SPY species exists in solution and the CG700 biochar surface becomes negatively charged. Adsorption at pH 7 was due to \( \pi-\pi \) EDA interactions between SPY and CG700. The increase in SPY removal
with increase in pH to about 10 is attributed to the formation of negative-charge assisted hydrogen bonds (CAHB) along with strong hydrophobic interactions (Section 5.2.3; Xie at al., 2014).

### 5.3.4. Docusate, Erythromycin and Pseudoephedrine

The effect of pH on the adsorption of DCT, PED and ETM is shown on Fig. 1d, 1e and 1f respectively. There were no constant and pronounced differences between the removal of DCT, ETM and PED using CG700 at pH 7 and at pH 10. DCT, ETM and PED are negatively charged at pH 7 and the proportion of negatively charged species increases as the pH rises. Likewise, CG700 surface becomes increasingly more negative as the pH becomes more alkaline. Thus, electrostatic repulsion between negatively charged DCT, ETM and PED and the biochar should be reduced at pH 7 relative to pH 10. However, π-π electron donor acceptor interactions between the π- electrons of the pharmaceuticals and the π- electrons contained in the benzene ring of the CG700 exists throughout the entire pH range. Similarly, hydrogen bonding and hydrophobic bonding between the biochar and the pharmaceutical are still dominant mechanisms and this results in the similar equilibrium adsorption amount after 24 h even at different pH conditions.
5.4. Modeling kinetics of adsorption

Adsorption kinetics is important, as it describes the rate of pharmaceutical uptake. The kinetic parameters provide information for modeling the adsorption processes and to determine the residence time needed to achieve a given amount of pharmaceutical removal in an irrigation sand filter. In this study, both pseudo-first-order (PFO) and pseudo-second order (PSO) kinetic models were employed to model the experimental data but only the PSO results are shown. The kinetic
parameters obtained from the PSO model for the adsorption of ACT, IBP, SPY, DCT, PED and ETM are listed in Table 6 and the plots are shown in Appendix A (Fig. 16, 17 and 18).

From the results, it can be deduced that the PSO model could explain better the adsorption processes onto almost all the biochars because of the high $R^2$ values (greater than 0.75) with the exception of few cases (See Appendix A). It is also observed in Table 6 that the experimental adsorption capacity ($q_{(exp)}$) value was very close to the model-calculated adsorption capacity ($q_{(cal)}$) for ACT, IBP, SPY, DCT, PED and ETM which is consistent with the high correlation of the adsorption of pharmaceuticals onto biochars to the PSO model. The better fit of the experimental data by the PSO model implies that the adsorption of ACT, IBP, SPY, DCT, PED and ETM onto CG and GB biochars was a rate-limited process controlled mainly by the available active sites on the biochar surface rather than the pharmaceutical concentration (Ding et al., 2014).

The results for the PSO model fitting for the adsorption of the ACT onto CG700, GB700 and GB350 biochars are less favorable ($R^2 \leq 0.5$). Similarly, adsorption of IBP on GB700 and GB350 and SPY using GB700 did not show a good fit to the PSO model. The data was equally fit into the PFO but the $R^2$ values were lower than the $R^2$ obtained from the PSO, so the results are not displayed. This unfavorable fit may be attributed to the irregular variation of the adsorption results characterized by very low removal followed by high removal efficiencies and then no removal at all leading to a flat horizontal line showing 0% additional removal after 24 h. The adsorption kinetics do not plateau and determining the $R^2$ and $q_{(exp)}$ becomes difficult.
Adsorption kinetics for the removal of IBP and SPY by CG500 fit the PFO (Appendix A; Table 11) better than the PSO while the removal of DCT, PED and ETM is better explained by the PSO model (Table 6). This suggests that physical sorption involving van der Waals forces contributed to the uptake of IBP and SPY onto CG500 while chemisorption through electron sharing or transfer controls the removal of DCT, PED and ETM using CG500 (Sumalinog et al., 2018). ACT was not adsorbed by CG500 biochar and thus could not be modeled (Table 6). In the case of IBP, the R² value (0.091) for the PFO is still very low as shown in Table 11 in appendix A, but it was better than the R² value obtained from the PSO (0.067). These low R² values come from the little or no IBP being adsorbed during the time period for the experiment and this is marked by a flat horizontal line after 24 h.

No kinetic studies could be found on adsorption of ACT, IBP, SPY, DCT, PED and ETM onto cotton gin waste and guayule bagasse biochars. Nonetheless, other researchers have reported that both the PFO and PSO models could fit for the adsorption of pharmaceuticals onto different adsorbents. The adsorption of ACT onto carbon-based materials using pine residues followed the PSO kinetic model with R² value 0.999 (Galhetas et al., 2014). On the other hand, the use of biochar derived from municipal solid waste to adsorbed ACT showed goodness of fit using both PFO and PSO with R² values ranging from 0.986-0.997 and 0.998-0.999 respectively (Sumalinog et al., 2018). Similarly, Essandoh et al. (2015) explained that the adsorption of IBP onto pine wood biochar follows the PSO kinetic model with an R² value of 0.980. Likewise, the adsorption of IBP onto three different types of biochar fit well to the experimental data with correlation coefficients (R²) higher than 0.89 (Lin et al., 2017). The kinetic mixture of sulfonamide sorption by functionalized biochar followed the PSO chemisorption kinetic model (Ahmed et al., 2017). The
adsorption of ETM using multi-walled carbon nanotubes was better explained by the PSO model compared to the PFO with and $R^2$ value of 0.995 (Mostafapour et al., 2019).

**Table 6.** Kinetic parameters of pseudo second order models for the adsorption of ACT, IBP, SPY, DCT, PED and ETM.

<table>
<thead>
<tr>
<th>Biochar</th>
<th>EC</th>
<th>$q_e^{(exp)}$ (mg g$^{-1}$)</th>
<th>Pseudo second-order kinetic model</th>
<th>$k_2$ (g mg$^{-1}$ h$^{-1}$)</th>
<th>$q_e^{(cal)}$ (mg g$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACT</td>
<td>0.544</td>
<td>0.707</td>
<td>0.215</td>
<td>0.225</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP</td>
<td>0.975</td>
<td>3.331</td>
<td>0.907</td>
<td>0.996</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>CG700</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPY</td>
<td>0.785</td>
<td>3.176</td>
<td>0.766</td>
<td>0.997</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCT</td>
<td>2.086</td>
<td>2.115</td>
<td>2.143</td>
<td>0.999</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PED</td>
<td>1.660</td>
<td>0.819</td>
<td>1.691</td>
<td>0.997</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ETM</td>
<td>1.923</td>
<td>2.034</td>
<td>1.934</td>
<td>0.991</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACT</td>
<td>0.185</td>
<td>3.827</td>
<td>0.157</td>
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<td>IBP</td>
<td>0.093</td>
<td>0.006</td>
<td>6.464</td>
<td>0.028</td>
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</tr>
<tr>
<td><strong>GB700</strong></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>SPY</td>
<td>0.024</td>
<td>28.79</td>
<td>0.017</td>
<td>0.518</td>
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<tr>
<td>DCT</td>
<td>0.989</td>
<td>0.893</td>
<td>1.011</td>
<td>0.972</td>
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</tr>
<tr>
<td>PED</td>
<td>0.553</td>
<td>3.269</td>
<td>0.559</td>
<td>0.992</td>
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</tr>
<tr>
<td>ETM</td>
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<td>5.095</td>
<td>1.398</td>
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<tr>
<td>ACT</td>
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<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
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<td></td>
</tr>
<tr>
<td>IBP</td>
<td>0.109</td>
<td>0.019</td>
<td>2.162</td>
<td>0.067</td>
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<td></td>
</tr>
<tr>
<td><strong>CG500</strong></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>SPY</td>
<td>0.087</td>
<td>0.021</td>
<td>0.625</td>
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<td>DCT</td>
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<td>0.598</td>
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<td>PED</td>
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<td>0.100</td>
<td>1.578</td>
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<td>ETM</td>
<td>0.907</td>
<td>4.740</td>
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<td>ACT</td>
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<td>12.411</td>
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<td>IBP</td>
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<td>71.329</td>
<td>0.015</td>
<td>0.984</td>
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<tr>
<td><strong>GB500</strong></td>
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<tr>
<td>SPY</td>
<td>0.013</td>
<td>96.579</td>
<td>0.013</td>
<td>0.987</td>
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<td>DCT</td>
<td>1.097</td>
<td>2.818</td>
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<tr>
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<td>0.637</td>
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<td>ETM</td>
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<td>5.247</td>
<td>1.757</td>
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<tr>
<td>ACT</td>
<td>0.164</td>
<td>3.216</td>
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<tr>
<td>IBP</td>
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<td>0.511</td>
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<td>CG350</td>
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<td>PED</td>
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<tr>
<td>GB350</td>
<td>SPY</td>
<td>0.285</td>
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<tr>
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<td>1.437</td>
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</tr>
<tr>
<td>PED</td>
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<td>0.314</td>
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</tr>
<tr>
<td>ETM</td>
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<td>1.527</td>
<td>1.185</td>
<td>0.996</td>
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</tr>
</tbody>
</table>

5.4.1. Kinetics of adsorption at different pH

The kinetics for the adsorption of the pharmaceuticals onto CG700 biochar was evaluated at pH 7 and 10 and the kinetic parameters are shown in Table 7 (See Appendix A; Fig. 19 for plots). It was found that the experimental data showed an unfavorable fit into the PFO model (Tables not shown). The experimental data was then fitted into the PSO and a high correlation coefficient were observed ($R^2 > 0.8$) with excellent linearity as compared to PFO equation, and the calculated and experimental $q_e$ values were close to each other at all pH conditions. Therefore, excellent fit of the data to the PSO models indicates that chemisorption may be the rate limiting step of the sorption process at different pH where electrons sharing through hydrogen bonding, hydrophobic interactions and $\pi-\pi$ EDA interactions occur by valence forces between the pharmaceuticals and
CG700 biochar. Moreover, it was seen that the PSO rate constant $k_2$ is lower at pH 7 than at pH 10 for ACT, IBP, SPY, DCT, PED and ETM indicating that adsorption at pH 7 required a higher amount of biochar than at pH 10 to reach the same adsorption efficiency (Ferreira et al., 2015).

Table 7. Kinetic parameters of pseudo second order models for the adsorption of ACT, IBP, SPY, DCT, PED and ETM at pH 7 and 10

<table>
<thead>
<tr>
<th>EC</th>
<th>$q_{e\text{(exp)}}$ (mg g$^{-1}$)</th>
<th>$k_2$ (g mg$^{-1}$ h$^{-1}$)</th>
<th>$q_{e\text{(cal)}}$ (mg g$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACT</td>
<td>2.006</td>
<td>0.264</td>
<td>2.128</td>
<td>0.979</td>
</tr>
<tr>
<td>IBP</td>
<td>0.811</td>
<td>1.019</td>
<td>0.835</td>
<td>0.983</td>
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<tr>
<td>pH 7</td>
<td>SPY</td>
<td>0.693</td>
<td>0.800</td>
<td>0.964</td>
</tr>
<tr>
<td>DCT</td>
<td>1.902</td>
<td>1.437</td>
<td>1.925</td>
<td>0.998</td>
</tr>
<tr>
<td>PED</td>
<td>1.418</td>
<td>0.125</td>
<td>1.613</td>
<td>0.802</td>
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<tr>
<td>ETM</td>
<td>1.752</td>
<td>0.249</td>
<td>1.851</td>
<td>0.949</td>
</tr>
<tr>
<td>pH 10</td>
<td>ACT</td>
<td>0.544</td>
<td>0.707</td>
<td>0.215</td>
</tr>
<tr>
<td>IBD</td>
<td>0.975</td>
<td>3.331</td>
<td>0.907</td>
<td>0.966</td>
</tr>
<tr>
<td>SPY</td>
<td>0.785</td>
<td>3.176</td>
<td>0.766</td>
<td>0.997</td>
</tr>
<tr>
<td>DCT</td>
<td>2.086</td>
<td>2.115</td>
<td>2.143</td>
<td>0.999</td>
</tr>
<tr>
<td>PED</td>
<td>1.660</td>
<td>0.819</td>
<td>1.691</td>
<td>0.997</td>
</tr>
<tr>
<td>ETM</td>
<td>1.923</td>
<td>2.034</td>
<td>1.934</td>
<td>0.991</td>
</tr>
</tbody>
</table>

5.5. Adsorption isotherms

A variation in adsorptive behavior of the CG700 biochar with initial pharmaceuticals concentration was observed. When ETM, DCT and SPY concentrations in the aqueous solutions were increased from 2 to 50 mg L$^{-1}$, adsorptive uptake of the CG700 also increased. Table 8 shows the different isotherm parameters and their corresponding values and it is seen from table 8 that the Langmuir isotherm model (Fig. 13a) exhibited a better fit ($R^2$) to the adsorption data than the Freundlich isotherm model (Fig. 13b). The data obtained from the Langmuir isotherm model produces a
straight line fitted with a higher $R^2$ of 0.989, 0.966 and 0.962 for ETM, DCT and SPY respectively and this clearly suggests that the Langmuir isotherm validates the experimental data for the adsorption of ETM, DCT and SPY onto CG700 biochar. The maximum ETM, DCT and SPY adsorption capacities ($q_m$) were 17.123, 19.685 and 1.221 mg g$^{-1}$ respectively, while the Langmuir constant ($K_L$) obtained from the plot was 0.016 L mg$^{-1}$ for ETM, 0.374 L mg$^{-1}$ for DCT and 1.681 L mg$^{-1}$ for SPY.

The value $q_m$ for DCT suggests a greater affinity between DCT molecules and CG700 compared to ETM and SPY molecules. These results are in accordance with the results from the adsorption of the pharmaceuticals using CG700 with DCT showing the greatest removal of 98% after 24 h (Section 5.2.4). The Langmuir isotherm model for the removal of ETM, DCT and SPY suggest an appreciable pharmaceuticals uptake capacity of CG700 with little free energy involved. The adsorption data fitting the Langmuir isotherm suggests that there is uniform binding energy on the surface of the adsorbent and negligible sorbate-sorbate interaction which in turn facilitates monolayer adsorption (Gong et al., 2008). In Table 8 it is also seen that the data obtained from the
Freundlich isotherm suggests suitability of the model for ETM, DCT and SPY since the $R^2$ values are 0.947, 0.905 and 0.909 respectively. The Freundlich constant ($K_f$) for ETM, DCT and SPY was 0.337, 2.957 and 0.531 mg g$^{-1}$ respectively, and the $n$ value lies between 1 and 10 signifying favorable adsorption by CG700. Similarly, the $K_f$ is greater from DCT than for ETM and SPY showing stronger affinity between DCT and CG700. The Freundlich isotherm model suggests that adsorption of these pharmaceuticals onto the surface of CG700 is considered to be a multi-layer process in which the amount of pharmaceuticals absorbed per unit mass of the CG700 increases gradually.

**Table 8.** Related parameters Langmuir and Freundlich isotherm model for erythromycin and docusate adsorption on to CG700

<table>
<thead>
<tr>
<th>Langmuir isotherm</th>
<th>$q_m$ (mg g$^{-1}$)</th>
<th>$K_L$ (L mg$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETM</td>
<td>17.123</td>
<td>0.016</td>
<td>0.989</td>
</tr>
<tr>
<td>DCT</td>
<td>19.685</td>
<td>0.374</td>
<td>0.966</td>
</tr>
<tr>
<td>SPY</td>
<td>1.221</td>
<td>1.681</td>
<td>0.962</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Freundlich isotherm</th>
<th>$K_f$ (mg g$^{-1}$)</th>
<th>$n$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETM</td>
<td>0.337</td>
<td>1.333</td>
<td>0.947</td>
</tr>
<tr>
<td>DCT</td>
<td>2.957</td>
<td>1.847</td>
<td>0.905</td>
</tr>
<tr>
<td>SPY</td>
<td>0.531</td>
<td>3.632</td>
<td>0.909</td>
</tr>
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</table>

**5.6 Column studies results**

**5.6.1. Idealized breakthrough curves**

A breakthrough curve is a plot of the ratio of the effluent-to-influent concentration ($C_e/C_o$) against the time, volume of treated water or pore volume. Initially, as the contaminated solution flows through the column containing the biochar, the contaminant is adsorbed and the contaminant-free effluent passes out of the column. This continuous as longs as the biochar column has the capacity to adsorb the contaminant. When saturation is reached, the contaminant is detected in the effluent
and its concentration increases gradually until no further adsorption occurs and there is no difference between the influent and the effluent concentration ($C_e/C_o=1$). In general, breakthrough curves are dependent on the relative concentrations of the contaminant, the adsorption capacity of the biochar, the flow rate of the influent solution and the bed depth.

![Breakthrough Curve Diagram](image)

**Fig. 14.** Idealized breakthrough curves for column adsorption experiments (Data points from Yanyan et al., 2018).

For an ideal situation, the breakthrough curves are symmetrical with a traditional S-shape as seen in Fig. 14 and breakthrough points occurring in the order 3 > 2 > 1. Given the results from the batch adsorption experiments (section 5.2), it was hypothesized that the breakthrough points for the adsorption of the pharmaceutical compounds would occur in the order DCT (3) > ETM and SPY (2) > ACT (1) with $K_{d3} > K_{d2} > K_{d1}$. This is explained by the fact that ACT showed the least removal (less than 20% after 24 h) using CG700 and is expected to be detected in the effluent earlier hence an earlier breakthrough point. DCT showed the greatest affinity for CG700 with 98% removal and will take a relatively longer time to appear in the effluent and its $K_d$ value will be the
highest. ETM and SPY showed nearly similar removals in batch adsorption studies and, therefore, their breakthrough points should be fairly similar.

However, more often than not, breakthrough curves for adsorption using biochars are not symmetrical and S-shaped, but have varied degrees of steepness and breakthrough times. The reasons for this are due to heterogeneity of the biochar particle sizes resulting in different packing densities within the bed (Marsh and Rodriguez-Reinoso, 2006), reversible adsorption (desorption) occurring within column and changes in adsorption-related properties such as pH which affect the adsorption mechanism. Moreover, the batch adsorption experiments cannot always be adequately used to explain the results from the column experiments. This is due to the fact that the contact time between pharmaceutical and the biochar in a batch system is very long (> 24 h), whereas, the flow rate in the column experiments might not allow enough contact time to promote the mechanisms responsible for the removal of the pharmaceutical compounds. This results in non-ideal breakthrough curves. The following section will focus on the breakthrough curves obtained from column adsorption experiments of ACT, DCT, ETM and SPY and plausible mechanisms resulting in the deviation of the breakthrough curves for the standard S-shape and in the unexpected $K_d$ values.

5.6.2. Pharmaceutical HYDRUS-1D modeling

The breakthrough curves obtained from the HYDRUS-1D equilibrium model are presented in Fig. 15 and the model parameters are shown in Table 9. The HYDUS-1D equilibrium model was effective in modelling the breakthrough curves with $R^2 > 0.9$. It is important to note that the breakthrough point was assumed to be achieved when pharmaceuticals appeared in the solution at
$C_e/C_o = 0.05$ while, it is assumed that the saturation point was reached when the effluent-to-influent concentration was 95% ($C_e/C_o = 0.95$). Fig. 15 shows the breakthrough points occurred in the order DCT > ETM > ACT > SPY. These results are quite similar to the batch adsorption experiments which demonstrated that DCT was effectively adsorbed to the CG700 (98% removal after 24 h) and will therefore appear later in the effluent. ACT is expected to have the shortest breakthrough and appear first in the effluent since ACT showed the least removal using CG700 (Section 5.2). Instead, SPY was detected earlier and this difference can be attributed to change in the solution pH resulting in shorter breakthrough.

![Breakthrough curves for the column adsorption of ACT, DCT, ETM and SPY by CG700 biochar.](image)

**Fig. 15.** Breakthrough curves for the column adsorption of ACT, DCT, ETM and SPY by CG700 biochar.

Moreover, the breakthrough curves presented in Fig. 15 are not of the traditional “S” shape and the reasons for this phenomenon have been discussed in section 5.6.1. The saturation points for the pharmaceutical compound occurred in the order ACT > ETM > DCT > SPY, with saturation occurring after 12 h indicating that a long period of time is required before the bed reaches exhaustion. Additionally, $K_d$ and $q_e$ values followed the same order as the saturation point.
indicating that the transport of pharmaceuticals through the column would be expected to be retarded to a measurable extent due to adsorption occurring over the entire time examined. It should be noted that breakthrough and saturation occurred relatively faster due to the bed depth being only 13 cm long. With a flow rate of 1 mL min\(^{-1}\), it takes approximately 10 min for the solution containing the pharmaceutical to exit the column. Increasing the bed depth and reducing the flow rate will result in enhanced physico-chemical interaction between the biochar and the pharmaceuticals, thereby increasing the times to breakthrough and saturation. The dispersivity values obtained for all compounds were between 2-5 which is typical for column experiments (Ladu and Zhang, 2011).

SPY showed the shortest breakthrough point, appearing in the effluent after 1 h and attained saturation after 15 h. SPY displayed the smallest \(K_d\) and \(q_c\) values of 6.42 L kg\(^{-1}\) and 23.59 mg g\(^{-1}\), respectively. These results are consistent, because the quicker breakthrough point signifies that less of the SPY is being adsorbed to the biochar surface, hence the minimum \(K_d\) and \(q_c\) values. At the start of the column experiment, most of the SPY existed in its deprotonated form (SPY\(^-\)) at a pH above its \(pK_{a2}\) (8.43). With the solution pH being above the \(pH_{zpc}\) (Table 5), the surface of the biochar has an overall net negative charge. This leads to the adsorption of SPY by hydrophobic interactions, \(\pi-\pi\) EDA interactions and negative charge assisted hydrogen bonding as discussed in section 5.2.3. However, from the continuous monitoring of the effluent pH, it was noticed that the pH decreased to 7.8 (below the \(pK_{a2}\) of SPY). This leads to the SPY\(^-\) being converted to its neutral form. The formation of CAHB is subdued (section 5.3.3) and this results to the movement of SPY through the column and its detection in the effluent after 1 h.
ACT was detected in the effluent and the breakthrough point was achieved after 2 h. This can be explained by the pH of the effluent which impacted the mechanisms responsible for ACT adsorption. Once the column experiments started, the pH of the effluent was approximately 11.2. At this pH which is above the pKa (9.71) of ACT, most of the molecules are present as anionic \( \text{ACT}^- \) and the biochar in the column has a net negative charge (pH> pHzpc). Electrosatic repulsion between the ACT and the biochar causes a decreased in ACT adsorption leading to its presence in the effluent after 2 h. However, ACT showed the longest saturation point (48 h) and the highest \( K_d \) value (20.85 L kg\(^{-1}\)) compared to the other pharmaceutical compounds and this is also accompanied by the largest \( q_c \) value (39.23 mg g\(^{-1}\)). This is attributed to the decline in the pH of the effluent as the ACT solution is being continuously flushed through the column. As discussed in section 5.3.1, the decrease in pH causes ACT to be converted from anionic \( \text{ACT}^- \) to its neutral form which is more hydrophobic. Hydrophobic bonding in addition to dispersive interactions between the \( \pi \)-electrons of the aromatic rings in the CG700 and the \( \pi \)-electrons of the ACT form electron donor-acceptor complexes. This results in continuous ACT adsorption through the column leading to the longest saturation point and high \( K_d \) and \( q_c \) values.

**Table 9.** Parameters for the column adsorption of ACT, DCT, ETM and SPY by CG700 biochar

<table>
<thead>
<tr>
<th>Pharmaceutical</th>
<th>Breakthrough time (h)</th>
<th>Saturation time (h)</th>
<th>Dispersivity (cm)</th>
<th>( K_d ) (L kg(^{-1}))</th>
<th>( q_c ) (mg g(^{-1}))</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACT</td>
<td>2</td>
<td>48</td>
<td>2.5</td>
<td>20.85</td>
<td>39.23</td>
<td>0.957</td>
</tr>
<tr>
<td>DCT</td>
<td>5</td>
<td>16</td>
<td>2.8</td>
<td>18.34</td>
<td>36.21</td>
<td>0.907</td>
</tr>
<tr>
<td>ETM</td>
<td>4</td>
<td>24</td>
<td>3.3</td>
<td>19.28</td>
<td>38.11</td>
<td>0.947</td>
</tr>
<tr>
<td>SPY</td>
<td>1</td>
<td>15</td>
<td>4.1</td>
<td>6.42</td>
<td>23.59</td>
<td>0.958</td>
</tr>
</tbody>
</table>
ETM and DCT showed breakthrough points of 4 and 5 h, respectively. ETM showed a longer saturation point compared to DCT and this is validated by the K_d value for ETM (19.28 L kg^{-1}), being slightly greater than the value for DCT (18.34 L kg^{-1}). The q_c values for ETM (38.11 mg g^{-1}) and DCT (36.21 mg g^{-1}) agree with the K_d values, whereby the q_c value for ETM was larger than the value for DCT. The hydrophobic nature of the DCT (log K_{ow} = 5.24) and ETM (log K_{ow} = 3.06) facilitated the formation of hydrophobic bonds between the CG700 biochar and the pharmaceuticals leading to the adsorption of the DCT and ETM in the column. DCT was expected to show the longest saturation point out of all the studied pharmaceuticals compounds due to its strong affinity for CG700 biochar in batch adsorption experiments (section 5.2.4). However, a changed in the adsorption behavior of DCT was noticed whereby the DCT started to desorb from the column after 24 h and this was indicated by effluent concentrations being greater than the influent concentration (10 mg L^{-1}). The desorption of DCT can be attributed to the formation of micelles which increase the solubility and dissolution capacity of DCT causing it to leach from the column resulting in the shorter than expected saturation point (Brown et al., 1998). Further investigation is needed in order to predict the dissolution behavior of DCT particularly in aqueous systems where partitioning and dissolution need to be considered.

Additionally, hydrogen bonding between CG700 and ETM and the diffusion of ETM molecules into the porous structure of the biochars leads to more ETM adsorption resulting in a later saturation point. Moreover, the pH of the effluents from the fixed-bed column experiments of DCT and ETM decreased to pH 8.2-8.5 with the continuous flow of the contaminated solutions through the columns. However, the change in pH had little effect of the on the breakthrough points because
hydrogen bonding, diffusion and hydrophobic bonding existed throughout the entire pH range (Section 5.3.4).

5.6.3. Scale-up design

As a proof-of-concept, the results from the column adsorption experiments can be used to simulate the performance of a full-scale system using a scale-up approach. Assuming similarity in mass transfer and hydrodynamic characteristics between the lab-scale and full-scale column systems, the breakthrough curves for the two systems are expected to be analogous (Yan et al., 2015). In order to design the full-scale column system, the values of filtration rate (FR) and empty bed contact time (EBTC) calculated from the lab-scale column experiments are used. The lab-scale column experimental data used to estimate the full-scale column parameters are shown Table 12, Appendix A. Biochar density was calculated to be 1.0 g cm$^{-3}$ (Appendix A).

The FR (cm min$^{-1}$) for the lab-scale column was calculated using equation (9).

$$FR = \frac{Q_L}{A_L}$$  \hspace{1cm} (9)

The area of the full-scale column ($A_F$, cm$^2$) and EBTC of the lab scale column ($\tau$, min) were calculated using equations (10) and (11), respectively.

$$A_F = \frac{Q_F}{FR}$$  \hspace{1cm} (10)

$$\tau = \frac{V_L}{Q_L}$$  \hspace{1cm} (11)

The correlation between the bed depth ($H_F$, cm), volume of full-scale column ($V_F$, cm$^3$), mass of biochar required in the full-scale column ($m_F$, kg), breakthrough time for the full-scale column
(t_{BT}, \text{min}) and the volume treated before breakthrough (V_{BT}, m^3) are calculated using the following equations (Jung et al., 2017):

\begin{align}
H_F &= FR \times \tau \\
V_F &= \tau \times Q_F \\
m_F &= V_F \times \rho_B \\
t_{BT} &= \frac{m_B}{m_{CR}} \\
V_{BT} &= B_F \times Q_F
\end{align}

where, \( Q_L \) is the flow rate in the lab-scale (cm³ min⁻¹), \( A_L \) is the cross-sectional area in the lab-scale column (cm²), \( V_L \) and \( V_F \) are volumes of lab-scale column and full-scale column (cm³), respectively, \( \rho_B \) (g cm⁻³) is the density of the biochar, \( m_B \) is the amount of biochar consumed in the full-scale column (kg), \( m_{CR} \) is the biochar consumption rate of the full-scale column (g min⁻¹), \( Q_F \) is the flow rate in the full-scale column (m³ d⁻¹). The \( Q_F \) of 500 m³ d⁻¹ of the wastewater was considered to be remediated through the full-scale column. Detailed calculations obtained from a procedure by Chauhan and Talib (2017) are shown in appendix A.

Table 10 shows the parameters for the full-scale column system estimated from the lab-scale column experiments. The design parameters for a full-scale column system such as the diameter, surface area and bed volume were calculated to be 598.5 cm, 2.73E+5 cm² and 3.54E+6 cm³, respectively. Realistically, a column with a diameter of 598.5 cm and a bed depth of 10 cm will not be ideal, therefore increasing the filtration rate and the EBCT (which determines the bed depth) will lead to an increase in the bed depth and a decrease in the diameter of the column.
In order to remediate 500 m$^3$ d$^{-1}$ of wastewater containing the pharmaceuticals, a total of 1770 kg or 2 tons of biochar is needed in the full-scale column. Biochar is more economical to use as a filter media compared to ACs due to one ton of biochar costing US $246 compared to AC which is estimated to cost US $1500 per ton (Ahmad at al., 2012). Therefore, savings attained by using biochar instead of AC will be approximately US $2500 per day assuming 2 tons of AC are also needed to treated 500 m$^3$ d$^{-1}$ of wastewater. A total volume of 446 m$^3$ can be treated which is equivalent to 89% of wastewater treated before the column breakthrough point ($C_e/C_0 = 0.05$) is attained at 22 h. Additionally, the full-scale column showed 39.32 g of pharmaceutical removed per kg of biochar.

**Table 10: Parameters for full-scale column system**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtration rate</td>
<td>cm min$^{-1}$</td>
<td>1.27</td>
</tr>
<tr>
<td>Column diameter</td>
<td>cm</td>
<td>598.5</td>
</tr>
<tr>
<td>Area</td>
<td>cm$^2$</td>
<td>2.73E+5</td>
</tr>
<tr>
<td>Bed volume</td>
<td>cm$^3$</td>
<td>3.54E+6</td>
</tr>
<tr>
<td>EBCT</td>
<td>min</td>
<td>10.2</td>
</tr>
<tr>
<td>Biochar mass</td>
<td>kg</td>
<td>1770</td>
</tr>
<tr>
<td>Biochar consumed</td>
<td>kg</td>
<td>116.82</td>
</tr>
<tr>
<td>Breakthrough time</td>
<td>h</td>
<td>22</td>
</tr>
<tr>
<td>Breakthrough volume</td>
<td>m$^3$</td>
<td>446</td>
</tr>
</tbody>
</table>
CHAPTER 6. CONCLUSIONS

In summary, this work investigated the adsorptive performance of biochar derived from the pyrolysis of cotton gin (CG) waste and guayule bagasse (GB) at 350, 500 and 700 °C for the removal of acetaminophen (ACT), ibuprofen (IBP), sulfapyridine (SPY), docusate (DCT), pseudoephedrine (PED) and erythromycin (ETM) from aqueous solution. Among the biochars, the CG700 stands out for the highest pharmaceutical removal. The batch adsorption studies showed that the removal of DCT on the CG700 (98%) was significantly higher than the removal of all other pharmaceuticals. The adsorption mechanism of the removal of pharmaceutical compounds is a strong function of the solution pH and these mechanisms involve hydrophobic bonding, hydrogen bonding, π-π electron donor acceptor interactions and diffusion. The kinetics of adsorption was evaluated using both the pseudo-first-order and pseudo-second-order kinetic models and the linearized pseudo-second-order model showed the best fit with the exception of some cases indicating that adsorption was dominated by the availability of surface-active sites and chemisorption through electron sharing or transfer. The equilibrium data for the adsorption of ETM, SPY and DCT using CG700 were also fitted using the linear Langmuir and Freundlich isotherm models. For all the pharmaceuticals, the best fitting of the equilibrium data occurred for the Langmuir isotherm model demonstrating that there was negligible interaction between pharmaceutical molecules and this facilitated monolayer adsorption.

Adsorption of ACT, DCT, ETM and SPY at a concentration of 10 mg L⁻¹ using CG700 was also studied using continuous flow column adsorption experiments (13 cm of bed depth with a constant flow rate of 1 mL min⁻¹). The CG700 biochar showed breakthrough points in the order of DCT (5 h) > ETM (4 h) > ACT (2 h) > SPY (1 h). The CG700 biochar column showed efficient adsorption
of the pharmaceuticals and this is demonstrated by $K_d$ values of 20.85, 18.34, 19.28 and 6.42 L kg$^{-1}$ for ACT, DCT, ETM and SPY, respectively. These results show the potential of using biochar from cotton gin waste and guayule bagasse as an effective adsorbent for the removal of pharmaceuticals from water. CG700 biochar showed a great affinity for the pharmaceuticals compounds in the column with maximum bed capacity ($q_c$) values of 23.59, 38.11, 36.21 and 39.23 mg g$^{-1}$ for SPY, ETM, DCT and ACT, respectively. The long saturation times (> 12 h) and the large $q_c$ values indicate that biochar has an enhanced ability to remove pharmaceutical in a fixed-bed reactor with saturation of the bed occurring after a prolonged period of time depending on the pharmaceutical compound. This reduces the cost of operation and maintenance. These results suggest the practical addition low cost biochar-amended sand filters to improve the quality of irrigation water applied to food-chain crops. The lab-scale data was used for scale-up analysis and design and this approach can provide useful information such as the area, diameter and biochar mass required for a full-scale effluent filtration column.

It must be emphasized that because the adsorption capacity of biochar varies with many of its properties (e.g. SA, surface functionality, charge characteristics), the selection of an appropriate material for incorporation into sand filters depends on the nature of pharmaceuticals targeted for removal. Since most pharmaceuticals are weak acids or bases that are moderately hydrophobic ($\log K_{ow} \approx 0$-4), biochars that are intermediate on the hydrophilic-hydrophobic spectrum may be the best suited for the removal of the various pharmaceutical compounds likely to be found in wastewater effluents. A high surface area is also desirable, since the adsorption capacity of the biochars is positively correlated to the surface area.
Additionally, the utilization of biochar amended sand filters to remove pharmaceuticals from water used for irrigation may lead the way to opportunities for sustainable, low capital water treatment solutions. Biochar sand filters present several advantages such as their convenience for large scale production, ease of regeneration without decrease in adsorption capacity and they can be optimized to improve their removal efficiency. Moreover, the exhausted biochar after filtration can be recycled by burning to produce ash for use as liming agents to enhance soil fertility. Further research is needed to develop biochar filter media that can be effective for the removal of pharmaceuticals by investigating the effect of flow rate and bed depth as well as biochar surface area and particle size. Also, a mixture of biochars from different feedstocks (e.g. bagasse, woodchips, switchgrass etc.) to produce “designer” biochar can be added to sand filters to enhance the quality of the filtered water. This “designer” biochar will possess a variety of adsorption properties which will enable the adsorption of a wide array of pharmaceuticals from water. Modification of the biochars by pelletizing them into bead-like particles using calcium alginate, for example, might increase the particles size leading to a pressure drop across the filter bed and, in turn, reduced pumping cost. The implementation of biochar to sand filters for the treatment of wastewater in general, and water used for irrigation in particular, presents major opportunities for further research.
APPENDIX A. SUPPLEMENTAL DATA

Table 11 Kinetic parameters of pseudo first order models for the adsorption of IBP and SPY onto CG500 biochar.

<table>
<thead>
<tr>
<th></th>
<th>$q_{\text{exp}}$ (mg g$^{-1}$)</th>
<th>$k$ (g mg$^{-1}$ min$^{-1}$)</th>
<th>$q_{\text{cal}}$ (mg g$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP</td>
<td>0.450</td>
<td>0.311</td>
<td>1.047</td>
<td>0.091</td>
</tr>
<tr>
<td>CG500</td>
<td>SPY</td>
<td>0.310</td>
<td>0.170</td>
<td>0.828</td>
</tr>
</tbody>
</table>

Table 12: Lab-scale column data used to estimate the full-scale column parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate (Q)</td>
<td>1 mL min$^{-1}$ (1 cm$^3$ min$^{-1}$)</td>
</tr>
<tr>
<td>Column diameter</td>
<td>1 cm</td>
</tr>
<tr>
<td>Column depth</td>
<td>13 cm</td>
</tr>
<tr>
<td>Biochar density ($\rho_B$)</td>
<td>1.0 g cm$^{-3}$</td>
</tr>
<tr>
<td>Breakthrough volume (at $C_e/C_0 = 0.05$)</td>
<td>120 mL (120 cm$^3$)*</td>
</tr>
<tr>
<td>Saturation volume (at $C_e/C_0 = 0.95$)</td>
<td>2880 mL (2800 cm$^3$)*</td>
</tr>
<tr>
<td>Maximum bed capacity at saturation</td>
<td>39.23 mg g$^{-1}$ (39.23 g kg$^{-1}$)*</td>
</tr>
<tr>
<td>Bed capacity at breakthrough</td>
<td>2.58 mg g$^{-1}$ (2.58 g kg$^{-1}$)*</td>
</tr>
</tbody>
</table>

* Data from ACT column studies

Scale-up design calculations

Biochar density ($\rho_B$) = \( \frac{\text{mass of biochar}}{\text{volume of biochar in the column}} \)

Biochar density ($\rho_B$) = \( \frac{10 \text{ g}}{10 \text{ cm}^3} \)

($\rho_B$) = 1.0 g cm$^{-3}$

(a) Filtration rate of lab-scale experiments

\[ FR = \frac{Q_L}{A_L} \]

\[ Area = \pi r^2 = 3.142 \times 0.5^2 = 0.785 \text{ cm}^2 \]

\[ FR = \frac{1 \text{ cm}^3 \text{ min}^{-1}}{0.785 \text{ cm}^2} \]

\[ FR = 1.27 \text{ cm min}^{-1} \]
The same FR is applied to the full-scale column

(b) Area of the fill-scale column
If the flow rate of the full-scale column is designed to be 500 m$^3$ d$^{-1}$ (3.47 E+5 cm$^3$ min$^{-1}$)

\[
A_F = \frac{Q_F}{FR} = \frac{3.47E + 5}{1.27} = 2.73E+5 \text{ cm}^2
\]

Since, \( \text{Area} = \pi \frac{d^2}{4} = 2.73 + 5 \text{ cm}^2 \), the diameter of the full-scale column can be calculated as

\[
d = \sqrt{\frac{A \times 4}{\pi}}
\]

\[
d = 589.6 \text{ cm}
\]

(c) Empty bed contact time of the lab-scale column
\[
\tau = \frac{V_L}{Q_L}
\]

\[
\tau = \frac{\pi^2 h}{Q_L}
\]

\[
\tau = 10.2 \text{ min}
\]

The volume of the full-scale column is calculated as

\[
V_F = \tau \times Q_F = 3.54E + 6 \text{ cm}^3
\]

(d) Bed depth of the full-scale column
\[
H_F = FR \times \tau
\]

\[
H_F = 12.95 \approx 13 \text{ cm}
\]

The lab-scale and full-scale columns have the same bed depth because the bed depth of the column is set by the EBCT and the FR and both values are the same in the lab-scale and full-scale columns.

(e) Mass of biochar and sand required for the full-scale column
\[
m_F = V_F \times \rho_B
\]

\[
m_F = 3.54E+6 \text{ g}
\]

\[
m_F = 3.54E+3 \text{ kg}
\]

\[
m_F = 3540 \text{ kg}
\]

Since packed column contains a sand-to-biochar ratio of 1:1, 50% of $m_F$ is needed

\[
m_F = 1770 \text{ kg}
\]
(f) Determination of pharmaceutical removal \((q_e)\)

Maximum bed capacity at saturation = 39.23 g kg\(^{-1}\)
\[= 0.039 \text{ kg kg}\(^{-1}\)\]
\[= 0.039 \text{ g g}\(^{-1}\)\]

(g) Fraction of biochar consumed in the full-scale column

Maximum bed capacity at saturation = 39.23 g kg\(^{-1}\)
Bed capacity at breakthrough = 2.58 g kg\(^{-1}\)

Fraction of unconsumed bed \((f)\) = \(\frac{39.23 - 2.58}{39.23} g kg^{-1}\)

\(\text{Fraction of unconsumed bed } (f) = 0.934\)
\(\text{% of unconsumed bed} = 93.4\%\)

\(\text{Fraction of consumed bed} = 1 - \text{Fraction of unconsumed bed} (f)\)
\(\text{Fraction of consumed bed} = 0.066\)

(h) Amount of biochar consumed in the full-scale column \((m_B)\)

Concentration of pharmaceutical = 10 mg L\(^{-1}\) = 0.00001 kg L\(^{-1}\)
Pharmaceutical loading rate = 0.00001 kg L\(^{-1}\) \(\times 3.4 \times 10^5\) cm\(^3\) min\(^{-1}\) \(\times 0.001\) L/1 cm\(^3\)
\[= 0.00347\ \text{kg min}^{-1}\]

Biochar consumption rate \((m_{CB})\) = 0.0034 kg min\(^{-1}\) / 0.039 kg kg\(^{-1}\)
\[= 0.089\ \text{kg min}^{-1}\]

Amount of biochar consumed \((m_B)\) = \(m_F \times \text{Fraction of consumed bed}\)
\[= 1770\ \text{kg} \times 0.066\]
\[= 116.82\ \text{kg}\]

(i) Breakthrough time for full-scale column

\(t_{BT} = \frac{m_B}{m_{CB}}\)
\(t_{BT} = 1312.58\ \text{mins} \approx 1313\ \text{mins}\)
\(t_{BT} = 21.87\ \text{h} \approx 22\ \text{h}\)

(j) Volume treated before reaching breakthrough

\(V_{BT} = B_F \times Q_F\)
\(V_{BT} = 1313\ \text{mins} \times 3.4 \times 10^5\ \text{cm}^3\ \text{min}^{-1}\)
\(V_{BT} = 4.46 \times 10^8\ \text{cm}^3\)
\(V_{BT} = 4.46 \times 10^5\ \text{L}\)
\(V_{BT} = 4.46 \times 2\ \text{m}^3\)
\(V_{BT} = 446\ \text{m}^3\)
Plots of the pseudo-first and pseudo-second-order kinetic models

Fig. 16. Pseudo-second order kinetic for the adsorption PED, DCS, ETM, IBP, SPY and ACT onto (a) GB700, (b) GB500 and (c) GB350.
Fig. 17. Pseudo-second order kinetic for the adsorption PED, DCS, ETM, IBP, SPY and ACT onto (a) CG700 and (b) CG350.

![Graph](image1)

Fig. 18. Kinetic plots for (a) Pseudo second order for the adsorption PED, DCS, ETM and (b) Pseudo-first order for the adsorption of IBP and SPY.

![Graph](image2)

Fig. 19. Pseudo-second order kinetic for the adsorption PED, DCS, ETM, IBP, SPY and ACT onto CG700 at (a) pH 7 and (b) pH 10.
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