

**Sustainable upgrading of wastewater treatment plant through  
enhanced adsorption of micropollutants by waste-based biochar  
activated with *in-situ* emitted greenhouse gas**

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## Abstract

Sustainable upgrading of wastewater treatment plant through enhanced adsorption of micropollutants by waste-based biochar activated with *in-situ* emitted greenhouse gas

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**Concordia University, 2022**

The current world's challenges concerning Sustainable Development Goals (SDG) have introduced new principles in environmental engineering. Wastewater treatment plant (WWTPs) is one of the most important parts of modern cities, which is no exception to following these principles. The daily production of a large amount of biosolids, greenhouse emissions, and the effluent quality concerning EMs have made the wastewater treatment plant the center of attention. Consequently, providing solutions for sustainable upgrading of the wastewater treatment plant is of great importance. Emerging micropollutants (EMs), including pharmaceuticals compounds, personal care products, and metals, have been continuously released into aquatic systems due to their lack of removal from the effluents in conventional wastewater treatment plants. Subsequently, these EMs require advanced treatment such as sorption to decrease their harmful effects on human health and the environment. Adsorbing material is expected to adhere to as many sustainable development standards as feasible. This study investigated the preparation of biochar adsorbent from in-situ produced biosolids and industrial waste, which performance was enhanced with CO<sub>2</sub> generated at the same WWTP. Designing parameters and optimum operation conditions for scaling up the filtration system are determined by setting pilot adsorption column experiments in three stages. In the first stage, adsorptive material preparation was optimized using three different methods. In the second stage, a series of batch tests was conducted to achieve the highest efficiency of pharmaceutical compound adsorption. In stage three, the fixed-bed column was designed to verify the performance of prepared adsorptive material under continuous flow conditions to determine designing parameters for scaling up the system. Then, the removal of micro & micropollutants was investigated in the pilot system. The designed system successfully removed 96.8% of SMX as a ubiquitous pharmaceutical compound in aquatics systems. Furthermore, metals such as Cr, Mn, Zn, and Pb were removed by 20.2%, 69.9%, 53.2%, and 28.7%, respectively. Additionally, chloride, nitrite, nitrate, ammonia, bromide, phosphate, sulfate, sodium, calcium, and magnesium were eliminated by 22.42%, 23.36%, 30.29%, 34.5%, 99.5%, 27.12%, 22%, 14.96%, 36.94%, and 64.56%, respectively. Moreover, the metals usually present in biosolids were also reduced. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy (SEM & EDX) showed that waste-based biochar, formulated using an optimal method, demonstrated specific high porosity with the spherical structure that increased its adsorption capacity. The production of waste-base biochar upgraded with GHG might be conducted on-site in WWTP, where it can be used for the effluent filtration before its discharge to a receptor.

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## **Dedication**

To:

*My beloved daughter who accompanied me on her little feet during this journey  
my husband, and my family.*

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## List of Abbreviation

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AC	Activated carbon
AOP	Advanced oxidation process
BC	Bed capacity
BCH	Biochar
CFCs	Chlorofluorocarbons
CGAC	Commercial granular activated carbon
COD	Chemical oxygen demand
Da	Dalton or unified atomic mass unit
DIW	Deionized water
DOM	Dissolved organic matter
EDCs	Endocrine-disrupting compounds
ED	Endocrine disruptors
EDX	Energy Dispersive X-Ray Spectroscopy
EMs	Emerging micropollutants
EPA	United States Environmental Protection Agency
EU	European Union
GHG	Greenhouse gases
HMs	Heavy metals
HRT	Hydraulic Retention Time
HW	Hard wood
IBU	Ibuprofen
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
MAC	Maximum adsorption capacity
PAC	Powdered activated carbon
PARA	Paracetamol
PAHs	Polycyclic Aromatic Hydrocarbons

PARA	Paracetamol
PBM1	Prepared biochar with method 1
PBM2	Prepared biochar with method 2
PBM3-CO <sub>2</sub>	Prepared biochar with method 3 and activated by CO <sub>2</sub>
PCBs	Polychlorinated Biphenyls
PPCPs	Pharmaceuticals and personal care products
SEM	Scanning electron microscopy
SMX	Sulfamethoxazole
SS: HW	Sewage sludge and hardwood
SS: SW	Sewage sludge and softwood
SS	Sewage sludge
SDG	Sustainable development goals
TSS	Total suspended solids
VEN	Venlafaxine
WAS	Waste-activated sludge
WBB	Waste-based biochar
WWTP	Wastewater treatment plant

# 1. Introduction

## 1.1. Problem statement

Increasing the level of detection (from ng/L to µg/L) of emerging micropollutants (EMs) such as pharmaceutical compounds, personal care products, and hormones in addition to heavy metals in the aquatic environment has prompted governments and researchers across the globe to investigate methods of their elimination (Tran et al., 2020; Guillossou et al., 2019; Reungoat et al., 2012). According to recent research, these pollutants, especially pharmaceuticals compound and heavy metals, can adversely affect human and environmental health even at low concentrations in water bodies (Kasonga et al., 2021). Among the properties of these compounds' bioaccumulation is considered the main factor for alerting the endocrine systems of humans and wildlife. Recent studies have reported hormonal disruption resulting in reproductive system interruption that causes thyroid problems, Alzheimer, cancer, and obesity (Kasonga et al., 2021). These emerging contaminants transfer to the environment through domestic and industrial wastewater (Khan et al., 2020). Recalcitrant properties of EMs will cause the existing water and wastewater treatment systems to be inefficient for their elimination (Heo et al., 2019; Margot et al., 2015), since wastewater treatment plants have been highlighted as the primary source of emerging organic micropollutants (Mailler et al., 2016; Verlicchi et al., 2012 Loos et al., 2013). This inefficient removal of EMs will result in their occurrence in receiving aquatic systems. Consequently, a new approach should be investigated to create alternative technologies to remove these chemicals (Regkouzas & Diamadopoulou, 2019).

Different methods have been investigated for removing EMs (Tiwari et al., 2020; Ben et al., 2018; Y. Yang et al., 2017; Alexander et al., 2012). Activated carbon revealed appropriate results for its high porosity and surface area (Guillossou et al., 2019; Beijer et al., 2017). However, in many cases, to achieve a favorable result, a higher dose of activated carbon or the combination with another advanced treatment should be used to reach a satisfactory removal of EMs (Baresel et al., 2019). Activated carbon is a final product of burned carbon-based materials such as plant, wood, coal, or lignocellulosic precursors (González-García, 2018). However, high costs in large-scale productions should not be underestimated. Hence in recent years, efforts to find a cost-effective and sustainable source of activated carbon have led to the

expanded usage of biochar, a carbonaceous product of biomass pyrolysis, as a cost-effective and sustainable adsorbent in removing emerging micropollutants (Kazemi Shariat Panahi et al., 2020).

Different carbon-based leftover materials can be used for producing biochar from pyrolysis (Kazemi Shariat Panahi et al., 2020). Treated secondary sludge is one of the most favorable materials proposed for producing biochar since it is a cheap and readily available carbon-rich residue that can not only solve sludge disposal in wastewater treatment plants but also reduce carbon footprint (Januševičius et al., 2022; Bolognesi et al., 2021).

However, depending on the application of biochar, its efficiency can be improved through physical, chemical, or microbial engineering procedures. Engineered biochar could be applied for various applications, especially pollution adsorption. Engineering biochar enhances the favorable features of biochar and its efficiency in minimizing the existing inhibitors and impurities (Kazemi Shariat Panahi et al., 2020).

## **1.2. Research objectives**

The main objectives of the existing thesis are a) manufacturing of adsorbing materials and designing the filter based on biochar for removing emerging micropollutants (EMs), considering sustainable use of waste materials and greenhouse gases; b) improving the quality of wastewater treatment plant effluent in order to protect Saint Laurance River against pharmaceutical compounds.

### **Specified objectives are:**

1. Preparation of adequate filtration materials for adsorption of pharmaceutical pollutants.
2. Developing of a method for post-pyrolysis modification of material to enhance its adsorption capacity.
3. Defining the efficiency of the modified waste-based adsorbent in removing target micro-pollutants from various aqueous solutions.
4. Designing and testing filtration column containing modified biochar for verifying adsorption performance of different materials.

5. Verification of modified biochar adsorption of pharmaceutical compounds in the presence of effluent impurities.

### **1.3. Organization of the thesis**

The thesis includes five chapters; chapter 1 contains a brief introduction, including the problem statement and the scope of the research. Chapter 2 reviews the current pertinent literatures on the occurrence of EMs in the WWTPs, the possible innovative technologies for alleviating the environmental stress resulting from EMs in the aqueous environment, and new and sustainable options for removing EMs from WWTP effluent. Chapter 3 presents a detailed description of the methodology, including materials and chemicals, water and wastewater sampling, experimental procedure, and analytical methods. Chapter 4 shows results obtained from laboratory experiments and their discussions. Finally, Chapter 5 provides a conclusion and explores research contributions and recommendations for future work.



## **2. Literature Review**

### **2.1. Emerging micropollutants (EMs)**

The prevalence of refractory micropollutants in the natural environment has become a worldwide concern. Industrial chemicals, pharmaceutically active residues, steroid hormones, personal care items, and other harmful compounds are micropollutants. Most micropollutants come from home, agricultural, medical, and industrial sources and may be identified in aqueous systems at concentrations ranging from a few ng/L to several g/L (Bhatt et al., 2022). The production and usage of chemicals classified as "Micro pollutants" have increased due to the ongoing development of anthropogenic activities (industry, agriculture, health). These emerging pollutants result from uncontrolled urbanization, industrial development, health-care activities, agriculture, and transportation. They comprise a broad spectrum of compounds created by humans that are regarded as essential for modern society (Yadav et al., 2021). Because of its ubiquity, persistence, and toxicity to aquatic systems, EMs contamination is becoming a growing concern worldwide (Tan et al., 2022).

EMs are synthetic persistent organic compounds in the form of nano- to micro concentrations that are not typically monitored in the environment but have the potential to harm the environment and human health. There are more than 700 compounds grouped into 20 classes of emerging pollutants, according to the NORMAN database ([www.norman-network.net](http://www.norman-network.net)): "surfactants, antibiotics and other pharmaceuticals, steroid hormones and other endocrine-disrupting compounds (EDCs), fire retardants, sunscreens, disinfection by-products, new pesticides, pesticide metabolites, naturally-occurring algal toxins," (Vasilachi et al., 2021; Varjani et al., 2020).

For the last few years, EMs have attracted growing public concerns due to their extensive contamination of the environment. EMs are steadily accumulating in drinking and other water sources and food chains which are considered a significant health risk to human and ecological systems. Some major and recognized health effects of EMs exposure are occurring cancers, endocrine disruption, and antibiotic resistance in humans (Varjani et al., 2020). Many researchers have reported on the origins, permanence, incidence, destiny, and environmental implications of EMs (Tang et al., 2019; Gavrilescu et al., 2015; Y. Yang et al., 2017).

## 2.2. Source of EMs in the aquatic system

Emerging micropollutants (EMs) are discharged into the environment from point and nonpoint sources of domestic and industrial activities (Tan et al., 2022; Varjani et al., 2020). Different sources of urban activities generate EMs in the wastewater, including municipal, hospital, and industrial, as well as agricultural runoff. EMs in municipal wastewater originate from pharmaceutical and personal care products such as medicine, detergent compounds, cosmetics, chemicals, etc. People use a variety of chemicals in the bathroom and kitchen in their everyday life, in addition to a wide range of pharmaceuticals and personal care products (PPCPs) that are mixing with other wastes in municipal sewage. For this reason, municipal wastewater is foremost a primary source of EMs (Varjani et al., 2020). During a study on the WWTP effluent in Quebec, sixteen pharmaceutical compounds were detected at a frequency of 100 % (Zojaji 2019). Detected compounds are presented in Table 1.1.

Table 1.1 Detected EMS in WWTP effluent (Zojaji 2019)

Compound's name	Mean Concentration (ng/L)		
	September 13, 2018	September 14, 2018,	September 15, 2018,
Ibuprofen	15.4	18.4	22.7
2-Hydroxy Ibuprofen	512	969	1362
Diclofenac	370	491	578
4-Hydroxy Diclofenac	12.7	25.8	40.4
Sulfamethoxazole	161	201	257
Clarithromycin	39.4	35.1	38.5
Carbamazepine	230	268	394
2-Hydroxy Carbamazepine	760	751	869
Acebutolol	44	35.3	45.9
Venlafaxine	673	713	810
Desvenlafaxine	1141	1229	1484
Fluoxetine	2.5	2.9	3.1
Caffeine	50.2	52.1	117
Estrone	26.1	16.1	40.1
Atrazine	18.4	19.6	20.9
Desethylatrazine	29.4	26.8	32.3

### **2.3. Environmental and health issues related to EMs**

The process of adding micropollutants to the ecosystem is ongoing and typically based on the active concentration of the population, manufacturing, etc. In general, human influences can accelerate the rate of EMs dispersion. Using synthetic organic chemicals in personal care and health-related items has resulted in ever-increasingly harmful environmental concentrations. EMs can infiltrate water bodies and remain above and beyond permissible limits. There is a considerable likelihood that crops watered with polluted water may include EMs, which pose a risk to human health when consumed. On both aquatic and terrestrial species as well as human societies, EMs can have detrimental effects. Endocrine-disrupting substances bring on numerous sexual and reproductive disorders in wildlife and people. Exposure to these substances during fetal and postnatal development may impede endocrine system development and signaling. The consequences of development are long-lasting and occasionally irreversible (Yang et al., 2017; Gogoi et al., 2018; Vasilachi et al., 2021; Bhatt et al., 2022).

The management of EMs in water resources is a crucial topic that needs attention, particularly in ecosystems that are delicate and in places that are fast-growing. (Bhatt et al., 2022) There are strong indicators that micropollutants have long-term consequences on the ecosystem, even if their effects in aquatic settings are still not fully understood. The following factors account for this: (1) their propensity for bioaccumulation into aquatic creatures and human bodies; (2) their toxicity; and (3) their resilience to environmental deterioration (persistence). Thus, controls on their emission and discharge are essential for enhancing the aquatic ecosystem and the quality of surface waters (Chavoshani et al., 2020).

### **2.4. Occurrence of EMs at the conventional WWTPs**

The widespread presence, persistence, and negative consequences of emerging contaminants are essential topics closely linked to wastewater treatment plants (WWTPs), which have been identified as the principal suppliers of emerging micropollutants in water bodies. Because conventional WWTPs were designed to remove nitrogen and phosphate, they cannot remove anthropogenic substances such as emerging micropollutants and their by-products, resulting in their ubiquity in diverse environmental media in the ng/L to µg/L range (Ofrydopoulou et al., 2022). A description of three families of common emerging micropollutants in WWTP

including pharmaceutical compounds, hormones, and heavy metals are presented below

#### **2.4.1. Pharmaceutical compounds**

From environmental concerns, "Pharmaceutical Active Compounds" are of great importance. The widespread use of personal care and medications for human and veterinary use has resulted in their identification in wastewater treatment plant effluents and aquatic systems such as rivers, surface waters, and others. This occurrence has raised awareness of drugs' possible hazards to aquatic ecosystems. According to studies, commonly used analgesic medications such as Ibuprofen (IBU) and Paracetamol (PARA) are available in noticeable amounts in the aqueous environment. In a study conducted by Zojaji et al. (2019), a municipal wastewater treatment facility and its environs were monitored in three sites to evaluate the exposure of the Saint Lawrence River to Ibuprofen and its corresponding 2-Hydroxylated metabolite. According to the findings, both chemicals were found in the Saint Lawrence River at 100% frequency. The concentrations of Ibuprofen (IBU) and 2-Hydroxy Ibuprofen (2-OH IBU) were detected at 3.64- 4.40 ng/L and 330- 713 ng/L, respectively (Zojaji et al., 2019).

There are no legally controlled maximum allowable concentrations of medicines in the environment, which is one of the critical issues related to their discharge into water streams. In the European Commission's current watch list, only a few medications were listed precisely. This list includes four drugs: Macrolide antibiotics, Diclofenac., 17-Ethynylestradiol, and 17-Estradiol (Quintelas et al., 2020). These compounds are pharmacologically active, resistant to degradation, persistent in aqueous systems, have deleterious effects on organisms, and have a detrimental influence on human health. Pharmaceuticals are not a homogeneous set of substances like Chlorofluorocarbons (CFCs), Polychlorinated Biphenyls (PCBs) or Polycyclic Aromatic Hydrocarbons (PAHs); they do not all have the same physical, chemical, structural, or biological qualities. Most medications are polar and were created to perform a specific function in a specific creature (Patel et al., 2019).

Pharmaceuticals have several properties that set them apart from typical commercial compounds, including complicated chemical structures, numerous ionization sites, and polymorphism. Pharmaceutical contaminants differ from most other contaminants in the following ways: (a) having molecular masses of less than 500 Da, although some compounds have higher molecular masses of 128, (b) containing chemically complex molecules with a

wide range of structures, shapes, molecular masses, and functionalities, (c) containing polar compounds with more than one ionizable group, (d) have features and degrees of ionization that depend on the medium's pH, (e) being lipophilic, (f) have modest water solubility. They also can persist in nature, accumulate in living things, and stay physiologically active. For example, Sulfamethoxazole, and Erythromycin, can last for almost a year, but Clofibrac acid lasts for years. Finally, (g) these molecules have a proclivity for adsorption and distribution in a live organism, which alters their chemical structure metabolically (Patel et al., 2019)

#### **2.4.2. Natural and synthetic hormones**

Natural hormones can be spontaneously excreted from the human bodies; estrone (E1), 17 $\beta$ -estradiol (E2), estriol (E3), and testosterone are classified in this group. Synthetic hormones are also employed for various purposes, including reproductive system management, such as 17 $\alpha$ -ethynyl estradiol (EE2). Some of these hormones, including 17-estradiol (E2) and 17-ethynylestradiol (EE2), were designated as "Watch List" in Directive 2013/39/EU due to their severe harm to aquatic life. Both E2 and EE2 are on this list since they are commonly utilized in synthetic estrogenic medications and estrogen replacement treatment (Yien Fang et al., 2019).

These pollutants in water are most often caused by sewage treatment plants effluent and are considered a hazard to aquatic life because of their estrogenic actions. Even at modest doses (ng/L), these compounds have potent negative impacts on various species. For example, when these chemicals reach the aquatic environment, they interfere with fish reproductive, feminization, and vitellogenin synthesis (Amin et al., 2018).

Hormones may be found in the influent and effluent of WWTPs worldwide. The levels of E1, E2, and EE2 measured in influents, for example, varied from 2.4–116, 4–150, and ND-14.4 (expressed in ng/L), respectively. According to Pauwels et al., EE2 concentrations in hospital and residential WWTP samples ranged from 0.2 to 114 ng/L, and E1 ranged from 0.2 to 58 ng/L. In another research E1, E2, and EE2 typical concentrations in effluent were ND-96, ND-30, and ND-5 ng/L respectively (Amin et al., 2018).

In typical WWTPs, the removal efficiency of estrogenic chemicals is inadequate and poor. Studies revealed a broad range of results for E1, E2, and EE2, ranging from 19 to 98%, 62 to 98 %, and 76 to > 90 %, respectively. Biodegradation and sorption, followed by the removal

of excess sludge, are two key processes that may be considered for eliminating estrogens during wastewater treatment operations (Amin et al., 2018).

### **2.4.3. Metallic compounds**

The quantity of inorganic and organic pollutants, including heavy metals, released into surface water and groundwater has grown dramatically due to the exponential development of industrial, agricultural, and mining operations. For example, in the Republic of Korea, 15.3 % of industrial regions discharge significant amounts of heavy metals such as lead (Pb), copper (Cu), and zinc (Zn) through their effluent in the aqueous system. These pollutants are recorded as extremely persistent pollutants in groundwater. Mentioned heavy metals are toxic, non-biologically degradable, and accumulate in groundwater, posing substantial hazards to the ecosystem and human health (Shahrokhi-Shahraki et al., 2021)

Although some heavy metals such as copper and zinc ions are needed for living creatures and are necessary for the regular operation of enzymes in humans, high levels of copper and zinc ions in the body can cause kidney and liver damage and Alzheimer's disease. Similarly, lead may disrupt numerous human bodily systems, including the neurological system, and can cause disorders like anemia (Y. Zhang et al., 2021). Metal toxicity in humans is caused by metal ions binding to biological components such as proteins, enzymes, and nucleic acids. Arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc are metals that accumulate in living things and are persistent, toxic, and carcinogenic (A. Singh et al., 2022).

Heavy metals mainly harm those bodily organs that may store large amounts of metal, such as soft tissues. Metal toxicity also depends on the metal ion's contact route and chemical characteristics when it enters the body (S. Singh et al., 2021). As a result, there is a pressing need for new, cost-effective, and efficient techniques to treat heavy metal-polluted wastewater before it is released into the ecosystem to avoid negative consequences such as buildup in water bodies (S. Singh et al., 2021). The physical, biological, and chemical approaches can be applied to removing heavy metals from wastewater. Filtration, ion exchange, adsorption, coagulation, flocculation, precipitation, oxidation, and membrane separation, are some of the ways that are used for their removal (A. Singh et al., 2022).

## **2.5. Regulations related to Emerging micropollutants**

Increased medical and personal demand for pharmaceutical compounds and personal care products has caused their discharge into the environment (Natarajan et al., 2022). Biochemical sector innovations have overtaken regulatory risk management controls, exposing human and environmental populations to endocrine disruptor (ED) risks and uncertainties. ED exposure comes from everyday products like pharmaceuticals and personal care products. These compounds are intended to treat medical conditions and improve one's aesthetic qualities of life; however, they can bind, block, or mimic hormone receptors, posing a threat to cognitive development and reproductive growth (Della Savia, 2021).

Governments worldwide are changing legislations and negotiating alternative risk management systems to mitigate the adverse effects of environmental exposure. Future laws controlling EDs are predicted, and local governments will be compelled to respond considering expanding international regulatory interests and the Government of Canada's desire to revise the Chemicals Management Plan (Della Savia, 2021). Only a few nations, like the United States and Europe, have implemented legislations and procedures for EMs management. Because hospitals have long been obligated to treat EMs-contaminated wastewater before sending it to the sewage system, this started in hospitals to manage EMs (Varjani et al., 2020).

The United States Environmental Protection Agency (EPA) issued its first regulation in 1985, entitled Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Life and Their Uses. This guideline established the assessment of acute and chronic toxicity of traditional pollutants but not for other contaminants (Varjani et al., 2020).

The European Union (EU) has recently enacted several laws concerning these emerging micropollutants in water supplies. The need for better, cheaper, and more cost-effective treatment methods capable of removing pharmaceuticals from wastewater was underlined in Directive 2013/39/EU (EU, 2013). Then, in 2015, Decision 2015/495/EU established the first chemical watch list, which contained several pharmaceuticals, intending to gather necessary monitoring data to assist future decisions on their inclusion in the priority substances list (Decision 2015/495/EU, 2015). The watch list, which was updated and abolished by Decision 2018/840/EU in 2018, now includes 15 substances of rising concern, including antibiotics and steroid hormones (Decision 2018/840/EU, 2018) (Rocha et al., 2020).

## **2.6. Removing micropollutants in the wastewater treatment plant**

The Wastewater collected by the sewage system contains EMs, so the wastewater treatment plants needed to be equipped with treatment processes for effective EMs removal (Rizzo et al., 2019). Conventional WWTP consists of primary and secondary treatment processes; primary treatment regulates only sedimentation and screening functions, removing around 20% of EMs in the wastewater treatment plant. The polarized EMs need more than screening to be effectively removed from wastewater. After screening, EMs are divided into the aqueous phase and solid phase; for each phase, different treatments are applicable. Available technologies for removing EMs in the aqueous phase in WWTP are activated sludge, anaerobic process, advanced oxidation, membrane, and physical processes. Biological technologies can remove 60% of EMs, and other advanced processes can eliminate 10% -30% of total EMs presented in wastewater treatment plants. The specific processes for removing EMs in solid phase are anaerobic digestion, thermal process, conditioning, and dewatering. Tertiary treatment is an expensive process, so it should be carefully considered. In some situations, for controlling recalcitrant organic compounds, an advanced oxidation process locates prior to the biological units. However, it consumes a considerable amount of energy and chemicals and produces toxic by-products. Another way to control the EMs in the wastewater is using catalysts such as salts and heavy metals, which are also toxic to subsequent biological sections (Varjani et al., 2020).

### **2.6.1. Anaerobic process**

EMs are removed through the anaerobic process by two main mechanisms: biodegradation and adsorption. Biodegradation consists of hydrolysis, acidogenesis, and methanogenesis (Harb et al., 2019). Of these mechanisms, methanogenesis has been revealed to play a significant role in EMs removal (50% overall). However, the degradation process of EMs relies on the characteristics of EMs and certain types of microbes (Bhatt et al., 2022).

According to the research where 20 EMs were studied under anaerobic degradation, Naproxen, Roxithromycin, Sulfamethoxazole, Trimethoprim, 17 $\alpha$ -ethinylestradiol, Fluoxetine, and Citalopram were bio transformed beyond 50%. In contrast, Carbamazepine, Diazepam, Diclofenac, Fluoxetine, and Ibuprofen were recalcitrant, and the removal efficiency was <15%. The anaerobic process has been shown to be ineffective for estrogen removal. Conversely,



sorption was only effective for removing lipophilic EMs of antidepressant Fluoxetine and the musk fragrances such as Galaxolide, Celestolide, and Tonalide. The main drawback of anaerobic systems is their sensitivity to the operational condition; for instance, an excessive number of EMs could impede the anaerobic process; Acetaminophen concentrations ranging from 50 to 1000 mg/L, for example, were found to be toxic to the microbial community in anaerobic systems. This complicates designing and operating anaerobic sections, which should be considered for removing different types of EMs (Varjani et al., 2020).

### **2.6.2. Activated sludge process**

In the activated sludge process, EMs will be eliminated mostly by biodegradation rather than biomass adsorption (Quintelas et al., 2020). Adsorption through activated carbon is accounted for 20% removal of EMs. Biodegradation of EMs in the activated sludge is regulated by aerobic microbial activities stimulated by catabolism and cometabolism. Catabolism is the utilization of organic substances as a source of energy, whereas cometabolism is the transformation of the aimed compounds without using them as a source of energy (Varjani et al., 2020).

A wide range of microorganisms governs activated sludge. These cause degradation of EMs in activated sludge occurs selectively (Chen et al., 2022). As a result, choosing suitable microbial strains is crucial for efficiently eliminating EMs in the activated sludge process. Even the media can impact the removal of EMs; some EMs are removed more efficiently in attached media rather than suspended media. For example, the attached media degraded Ketoprofen, Mefenamic acid, and Valsartan faster than the suspended process. Nevertheless, activated sludge has some disadvantages as it is less effective for EMs compounds with the double aromatic ring, iodide, nitro-, azo-, sulfur-, halogen, and aromatic amine groups. These structures have been revealed to be resilient to biodegradability and even more toxic to microorganisms (Varjani et al., 2020).

### **2.6.3. Advanced oxidation processes**

Although the biological process is a low-cost and well-established technique, it does have drawbacks. Biological processes are ineffective in eliminating recalcitrant compounds such as aromatic hydrocarbons, chlorinated aromatic hydrocarbons, chlorinated phenols, and pesticides. In addition, high concentrations of EMs have toxic effects on the microbial

consortium. Consequently, other methods, such as advanced oxidation, have been applied to remove EMs (Krishnan et al., 2021).

Different oxidation processes, chemical-based, photo-based, or electron-based technologies, have been introduced, such as ultraviolet (UV), Fenton, ozonation, and electrochemical methods. The basis of all these methods is producing hydroxyl radical groups (OH), which can contribute to oxidation reactions. During oxidation, EMs will be removed rapidly and proficiently by hydroxyl radical, even in high concentrations. EMs perform differently to ozonation, UV, and H<sub>2</sub>O<sub>2</sub> processes. The mild sensitive group can be removed more than 87% during advanced oxidation, such as Bezafibrate, Diclofenac, and Gemfibrozil, which can be removed 95% within 2 mins. In contrast, the recalcitrant group such as 2,4-Dichlorophenoxyacetic acid, Clofibrac acid, Ibuprofen, and p-Chlorobenzoic acid are reported to be eradicated only 40% to 60% (Varjani et al., 2020).

In addition to OH, the sulfate radical (SO<sub>4</sub>) has recently emerged as a new, improved oxidation process agent with a more significant oxidation potential (2.5-3.1 V) than OH. It is suitable for a more comprehensive pH range (Q. Yang et al., 2019). This agent was found to be successful in eliminating up to 95% of Carbamazepine, Diclofenac, Atrazine, and Triclosan resistance (Tiwari et al., 2020).

However, EMs removal efficiency is determined by several parameters, including catalyst dose, contact time, and initial EMs concentration (Rodríguez-Chueca et al., 2019). According to the research, in a concentration of 0.5 mM and a contact time of 28 s, removal efficiency of 95% has been reported, while in the concentration range of 0.05 mM and contact period of 9s, a low removal of less than 20% revealed (Varjani et al., 2020).

2,4-Dichlorophenoxyacetic acid, Clofibrac acid, Ibuprofen, and p-Chlorobenzene acid strongly resisted the catalyst-assisted accelerated oxidation process in some circumstances. Metal catalysts (such as Mn<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Ti<sup>2+</sup>) can only boost removal efficiency by 10%. Because this technology uses a lot of energy and chemicals, it is not very cost-effective for wastewater treatment. As a result, the benefits of reagent dose, contact time, and the necessity for sophisticated oxidation procedures must all be carefully considered (Tiwari et al., 2020).

#### 2.6.4. Membrane processes

The membrane process is a revolutionary technology based on using pore size of natural or synthetic fabricated material for removing pollutants from water and wastewater (Khan et al., 2020). Based on membrane pore size and performance, they are divided into different classifications: microfiltration, ultrafiltration, nanofiltration, and reverse osmosis (Van der Bruggen, 2018).

Nanofiltration and reverse osmosis membranes can effectively remove EMs rather than microfiltration and ultrafiltration since their pore size are widely smaller than EMs molecules. The two methods for removing EMS via the membrane process are process optimization and membrane mechanism. Process optimization can happen when the procedure joined with other membrane technologies such as ion exchange, enzyme, and biocatalyst or monitoring and regulating operating factors such as hydraulic retention time and flux. Enzymatic membrane bioreactors (membrane bioreactors combined with enzymes) are used widely for removing hydrophilic EMs. Nanofiltration membranes based on enzymes can remove 92 % to 99 % of EMs, which is 10% to 80% more than ultrafiltration (Varjani et al., 2020; Van der Bruggen, 2018).

The specific mechanisms for nanofiltration are size exclusion, adsorption, and electrostatic contact, whereas the mechanism for ultrafiltration is mostly charge repulsion. Magnetic ion exchange can be combined with ultrafiltration membranes. According to the studies, the hybrid approach can eliminate Carbamazepine 35%-79% instead of the 15 % removal by single ultrafiltration. Hydraulic retention time and flow are the essential operating factors to optimize. The hybrid moving-bed biofilm reactor/membrane bioreactor, for example, was more effective in eliminating EMs at an HRT of 18 hours rather than 24 hours. The membrane material significantly impacts how effective it is at removing EMs. The manufactured material shapes the pore size and hydrophobicity of the membrane. Surfactant, coating, grafting, polymer blend, and plasma increase the membrane's hydrophilicity, reduce clogging, and improve chemical resistance and adsorption. Surprisingly, biocatalysts have lately been combined with membrane material and chemicals. For example, in a study Laccase enzyme was added to polydopamine/polyethyleneimine-coated nanofiltration membrane and contributed to 33.8 % to bisphenol a removal (96.8%) (Varjani et al., 2020).

### **2.6.5. Ion-exchange**

Ion exchange utilizes the substitution of ions with other ions and may thus be used to treat wastewater successfully. Ion exchange resins are molecular materials that may exchange cations and anions. They are typically made up of a cross-linking polymer matrix with functional groups via covalent bonds. Ion exchange resins are synthetic or natural with suitable adsorbents and high mechanical and chemical stability. Many researchers have used cationic exchange resins to remove heavy metal ions such as  $Ce^{4+}$ ,  $Fe^{3+}$ , and  $Pb^{2+}$ . Natural zeolites have a crystalline structure, are made up of aluminum and silicate atoms connected by oxygen bridges and have a high cation exchange capacity for various heavy metal ions. The atoms responsible for zeolites' ion exchange capabilities include  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  (Varjani et al., 2020).

Pepe et al. (2013) investigated using natural zeolite to remove Barium ( $Ba^{2+}$ ) from polluted wastewater. As an exchange ingredient, Chabazite and Phillipsite were used in this resin. For the removal of chromium (VI) and manganese, Kononova et al. (2019) used a variety of cation and anion exchange resins. A macro-porous magnetically enhanced cation and anion exchange resin incorporating magnetic iron oxide and a polyacrylic backbone were effectively deployed to remove dissolved organic matter from natural water. Tang et al. (2021) used a hybrid magnetic ion-exchange resin followed by ozonation to remove micropollutants. Because the ion exchange resin absorbed organic nitrogen and nitrite-nitrogen, ion-exchange treatment before ozonation effectively reduced the formation of ammonia–nitrogen, and nitrate–nitrogen.

### **2.6.6. Filtration and adsorption process**

Adsorption is a mass transfer phenomenon that occurs when gas or solute molecules bind to solid or liquid surfaces. Adsorption is the process of contaminants being captured by an adsorbent using physical and chemical forces. Due to its simple design, ease of operation, cost-effectiveness, and high removal efficiency, adsorption approaches for treating micropollutants in wastewater have recently emerged as a promising alternative to the old procedure. As a result, a broad range of adsorbents for removing micropollutants in wastewater have been studied, including carbon-based, nanoparticle-based, metal oxides, carbon nanotubes, hydroxides-based, natural zeolite, ion exchange resins, and modified and complex adsorbents (Alizadeh Fard & Barkdoll, 2019).

The primary definition of adsorption is a separation process through which specific fluid-phase components are conveyed to a solid adsorbent's surface. Tiny adsorbate particles are usually trapped in a fixed bed during flow, passing through the solid until the solid is almost saturated and efficient separation can no longer be achieved. In this situation, the flow can be shifted to a second bed until the saturated adsorbent is replaced or regenerated. Adsorption performance depends on solid-fluid equilibria and mass-transfer rates. Most adsorbents are incredibly porous materials. Adsorption mainly occurs on the walls of the pores or at specific locations inside the particle. Because the pores are usually microscopic, the internal surface area is much greater than the external area; this may be as large as 2000 m<sup>2</sup>/g. Separation occurs because of differences in molecular weight, shape, or polarity. Stated factors cause some molecules to be added more intensely on the surface than others or because the pores are too small to accommodate the larger molecules (Alizadeh Fard & Barkdoll, 2019). The biochar's kinetic and isotherm investigations for adsorption revealed substantial chemical-sorption interactions on the surface of adsorbent and adsorbate contact. Hydrogen bonding, ion exchange, and electrostatic adsorption all are methods for removing adsorbate (Shao et al., 2021).

Carbon-based adsorbents are widely used in industry, medicine, and wastewater treatment. The most often used carbon-based adsorbent in the restoration of contaminated water bodies is activated carbon, which is produced by the pyrolytic breakdown of any carbonaceous substance. Carbon-based adsorbents have a microporous structure, a higher specific surface area, hydrophobicity, and pore size, which increase their adsorption capacity for a wide spectrum of micropollutants (Mezohegyi et al., 2012).

The literature has several publications on the use of carbon-based adsorbents for the effective removal of micropollutants. Pharmaceutical microcontaminants such as Ibuprofen, Diclofenac, Ketoprofen, and Naproxen were removed using a cost-effective activated carbon adsorbent from olive waste cakes (Baccar et al., 2012).

The adsorption effectiveness of these four micropollutants on activated carbon varied depending on their pK<sub>a</sub> and octanol/water coefficient. In addition, powdered activated carbon (PAC) and granular activated carbon (GAC) are often used in adsorption investigations (Bhatt et al., 2022).

## 2.7. Concentration pattern in fixed bed adsorption

In fixed-bed adsorption, fluid and solid phase concentrations vary with time and position in the bed. Most of the mass transfer occurs at the early stage, where the inlet first contacts the bed. If the solid contains no adsorbate at the start, the concentration in the fluid drops exponentially with distance until it reaches zero before the end of the bed is reached. This concentration profile in the bed is shown by curve  $t_1$  in Figure 2.1, where  $C/C_0$  is the concentration in fluid over that in the feed. After a few minutes, the bed near the inlet is nearly saturated, so most of the mass transfer occurs further from the inlet, so the concentration gradient in the bed becomes more S-shape, as shown in Figure 2.1 by  $t_2$ . The gradient in the following time has been shown by  $t_3$  and  $t_4$ . The region where most of the change in concentration occurs is called the mass-transfer zone, and the limits are often taken as  $C/C_0$  values of 0.95 to 0.05 (Jiang et al., 2017).

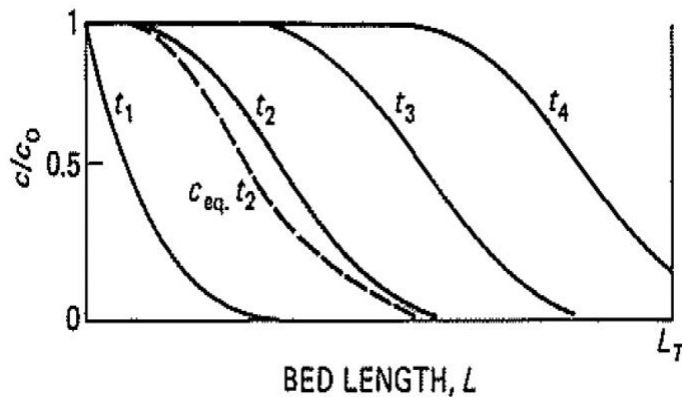


Figure 2.1. Concentration profile in fixed bed (MacCab et al., 1993)

## 2.8. Breakthrough curve

A breakthrough curve is a curve of concentration vs. time for fluid leaving the bed. The concentration of pollutants is nearly zero at time  $t_1$ . By reaching some limitation for fair value, the curve reaches the breakpoint when the adsorbent bed needs to be regenerated. The breakpoint is frequently taken as a relative concentration of 0.05 or 0.2; at this average stage fraction of adsorbate, removal is 0.99 or higher. If adsorption were continued beyond the breakpoint, the concentration would rise quickly to about 0.5 and then more gradually, as shown in Figure 2.2.

This S-shaped curve is comparable to those for the internal concentration profiles, and it is often approximately symmetrical. In equilibrium conditions, it can be shown that the area between the curve and a line at  $C/C_0$  equal to 1.0 is proportional to the solute adsorbed. In addition, the adsorbate concentration is proportional to the rectangular area to the left of the dashed line at  $t^*$ , the ideal adsorption time for a vertical breakthrough curve. For a symmetrical curve,  $t^*$  is the time when  $C/C_0$  reaches 0.5 (MacCab et al., 1993).

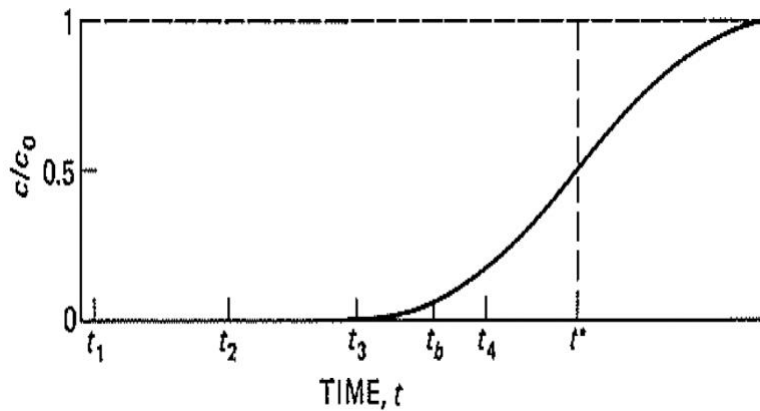


Figure 2.2 Breakthrough curve (MacCab et al., 1993)

## 2.9. Sludge-based carbon adsorbents

### 2.9.1. Sludge generation, stabilization, and disposal

Wasted activated sludge (WAS) is the sludge generated during the biological treatment of wastewater, particularly by secondary clarifier, which goes for a supplementary treatment, which also called biosolids. An increase of the urban population leads to a constant rising of wastewater flow to WWTPs, and subsequently to increase of sludge production. Furthermore, discharge of runoff to sewage system increase suspended solids content (Wei et al., 2020). In the European Union, yearly sewage sludge (SS) output climbed from 5.5 million tons per year (Mton/year) in 1992 to more than 10 Mton/year in 2010. In 2010, annual output (dry-weight basis) in the United States (USA) was about 8 Mton/year, and in China it was 9 Mton/year (Li et al., 2016).

Managing a large amount of biosolids has become a significant environmental concern. Several approaches have been used to address this challenge and avoid biosolids deposition in

landfills (Awasthi et al., 2016). Currently, the most common methods for sludge processing include incineration, land application, sanitary landfills, and the manufacturing of construction materials. Meanwhile, thickening, conditioning, dewatering, digesting, composting, and disinfection are common treatment methods for sludge volume reduction, nutrient recycling, as well as energy and value-added-product recovery (Wei et al., 2020).

Composting is one of popular and cost-effective methods of biosolids management, which allows organic waste to be bio-converted into a well-stabilized, value-added product. The disadvantages of composting include nitrogen loss and greenhouse gas (GHG) emissions during organic waste decomposition, as well as a potential presence of heavy metals (HMs) and salts in the final product (Wei et al., 2020).

Biochar, which is made from biomass waste pyrolyzed under low oxygen conditions, has lately been proposed as a means of reducing GHG emissions and stabilizing heavy metals (HMs). Several studies have shown that biochar amendment is one of the most effective methods for reducing HMs mobility and increasing composting rates (Chen et al., 2010; Sonoki and Bastida, 2012; Zhang et al., 2014). During the composting of biosolids, researchers have also observed the influence of the biochar concentrations on ammonia emissions and decrease of GHG emissions (Steiner et al., 2010; Jindo et al., 2012; Malinska et al., 2014).

Biochar may also be used in composting to minimize nitrogen loss, enhance porosity, and increase water holding capacity, making it a cost-effective and ecologically friendly solution for the residual, underutilised components of waste biomass (Czekala et al., 2016). Biochar addition can enhance the biodegradation of organic waste, according to Dias et al. (2010) and Steiner et al. (2010), with a 64 percent reduction in ammonia emissions and odors during the composting of poultry manure. Biochar's capacity to lower GHG and  $\text{NH}_4^{++}\text{N}$  emissions, as well as the bioavailability of HMs during the composting of biosolids combined with agricultural wastes, has been documented in previous research (Sonoki and Bastida, 2012; Zhang et al., 2014; Czekala et al., 2016).

### **2.9.2. Sludge-based carbon adsorbent (Biochar)**

In the environment outlined, waste-based adsorbents have emerged as a viable alternative to activated carbons (AC) derived from non-renewable sources (Silva et al., 2019). Biochar is a



carbonaceous porous substance formed from biomass, with the carbon component's amount and chemical composition varying depending on the parent material. Agricultural leftovers, wood waste, animal dung, and sewage sludge have all been used to make biochar (Saxena et al., 2017; (Zojaji et al., 2019); Stella Mary et al., 2016; Bera et al., 2018; Mohan et al., 2018).

The biochar production from SS aligns with the objective of long-term resource recovery. It encourages the use of wastewater in a circular economy (Zojaji et al., 2020). Thermochemical conversion of SS to biochar addresses two main challenges: lowering disposal costs and acting as a resource for removing harmful pollutants from water and wastewater. Biochar is an economically feasible material for wastewater treatment because of its reusability and accessible availability, regardless of the season (Gopinath et al., 2021).

### **2.9.3. Biochar production principles**

Sewage sludge includes a significant quantity of biomass that may be turned into biochar and bio-oil using thermochemical methods. Hydrothermal carbonization and pyrolysis are the most extensively used processes for biochar formation (Gasc o et al., 2018). The hydrothermal carbonization method, as the name implies, happens in the presence of water at ambient pressure and low temperatures, requiring no moisture removal prior to the synthesis of biochar. On the other hand, the pyrolysis process necessitates the total removal of water molecules since the moisture content of the biomass increases the pyrolysis heating time (Tripathi et al., 2016).

Drying is usually done in the open air and may be done in a variety of methods, such as keeping the temperature between 100 and 105°C for 24 hours or keeping the temperature between 25 and 30°C for a few weeks (Chen et al., 2019; Zielinska et al., 2015). For achieving a high heating rate, the dewatered sludge must be crushed to tiny particles in addition to drying. Various pyrolysis procedures have been utilized to produce biochar, depending on the temperature maintained and the residence period. Slow pyrolysis (300–800°C; heating rate of 1°C/s), rapid pyrolysis (500–1000°C; heating rate of 10–200°C/s), and electromagnetic induction-based pyrolysis have been the main techniques among the many pyrolysis processes (Chen et al., 2015; Zojaji et al., 2020; Xue et al., 2019; Zielinska et al., 2015).

The physicochemical characteristics of biochar are influenced by several factors, including the pyrolysis method utilized and the presence of additional components in the pyrolysis process.

Apart from using SS as a single feedstock, other researchers have experimented with combining different feedstocks to increase biochar characteristics (Chen et al., 2019; Kończak, et al., 2019; Zojaji, 2019).

#### **2.9.4. Production of biochar from waste materials (sludge-hardwood)**

Zojaji (2019) used waste materials containing woodchips from a wood mill and sludge from WWTP to produce biochar. Hardwood (HW) chips were added at 50% (w/w%) to the dried sludge (SS). Powder KOH was added to the mixture at a 1:1 ratio (by weight). The mixture (without water) was poured into crucibles, then placed in the furnace. The pyrolysis of samples was carried out in a high-temperature tubular furnace (MTI, OTF-1200X-III). Nitrogen gas flow was set at 2 L/min and fed through the furnace constantly. The sample was heated to 750 °C at a rate of 10 °C per minute. The maximum temperature was held for 60 minutes. Since it is predicted that most of the potassium and its related by-products remained inside the carbon matrix and blocked the pores after pyrolysis, biochar should be cleaned to improve its adsorption ability. As a result, the carbonaceous product must be washed to remove these residues. According to his study, wood chips and leftover sewage sludge were discovered to be suitable primary components for the creation of novel adsorptive materials. The novel waste-based adsorbents showed a large surface area and a well-established pore structure. The degree of microporosity was increased by 16% as a result of the co-activation of sludge and hardwood residues as compared to the adsorbent made only from secondary sludge (sludge-based biochar). Also, the strength of the surface acidity and yield of products were boosted after wood addition.

#### **2.9.5. Biochar characteristics**

##### **2.9.5.1. Surface area and porosity**

Surface area and porosity are significant physical features of biochar, and they play a vital role in various biochar applications specially in wastewater treatment. Engineered biochar with a highly porous structure and an enormous surface area has attracted much interest. The main affecting parameters are biomass feedstock composition and pyrolysis temperature. It is proposed that lignocellulosic biomass, mainly wood and woody, is an excellent choice. Furthermore, moderate temperatures (400–700 °C) are ideal for pore structure growth. (Leng

et al., 2021). This increase in surface area is due to the elimination of volatile organic materials, which causes pores to open up, allowing for more surface area (Gopinath et al., 2021). In a study by Zojaji et al., a biochar adsorbent was made using a one-step carbonization-activation process using potassium hydroxide. In order to make carbon adsorbents, biosolids and two types of residual wood materials derived from hardwood and softwood were employed as precursors. The pore structure analysis utilizing physical adsorption of nitrogen gas was used to characterize the carbon materials that had been manufactured. The findings revealed that carbon adsorbents with high surface areas (more than 1000 m<sup>2</sup>/g) can be made and that combining wood residues with biosolids can improve the textural qualities of the final carbon product. For example, an adsorbent made from biosolids, and hardwood waste had a surface area of 1565 m<sup>2</sup>/g. However, an adsorbent made solely from biosolids had a surface area of 1325 m<sup>2</sup>/g.

Furthermore, the final carbon adsorbent's output yield rose once the woodchips were added. Because of the large surface area of carbon adsorbents produced, co-activation of biosolids and woodchips might be a viable option for recovering two distinct waste streams. This is especially significant in a region like Canada, where both leftovers and traditional disposal techniques like landfilling are under public and regulatory criticism (Zojaji et al., 2020)

Other activation, particularly chemical activation, is extensively utilized, which showed successful results for increasing biochar surface area and porosity. Other treatment procedures, such as carbonaceous materials coating, ball milling, and templating, can also be used to improve the results (Leng et al., 2021).

#### **2.9.5.2. Ash content**

As the pyrolysis temperature rises, the ash produced also rises. Furthermore, the ash concentration of biochar produced by pyrolysis of biosolids is often more extensive than that of biochar produced by pyrolysis of other types of biomasses (Zielinska et al., 2015). This is owing to sewage sludge's high mineral concentration, which is absorbed into the ash at higher temperatures. The acid washing technique decreases the ash concentration in biosolids-generated biochar by removing mineral components (Li et al., 2018). Because of the absence of degraded volatile organic matter, the biochar produced at high temperatures has a greater ash concentration (Zhang et al., 2019). The ash content of biochar pyrolysis from WAS at 400,

500 and 600 °C of pyrolysis has been reported at 42.2, 56.3, and 67.3%, respectively, compared to that biochar made from maize straw and coconut shell in a study by Zhang et al. (2019).

### **2.9.5.3. pH**

At high pyrolysis temperatures, the pH of biochar, regardless of the biomass source, rises to a higher pH value. In most circumstances, biomass is acidic or neutral. However, following the creation of biochar, it becomes alkaline due to a decrease in the number of acidic groups at higher temperatures and the cleavage of alkali metal salts from the organic matrix of the biomass. The pH value of biochar produced from SS ranges from 8.7 to 11.1, while the initial pH of SS has no effect on the final biochar pH (Gopinath et al., 2021).

### **2.9.5.4. Elemental Analysis**

Elemental analyzers can be used to detect the content of C, H, O, N, and S in biochar. In contrast, inductively coupled Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or energy-dispersive X-ray spectroscopy (EDS) can be used to assess the existence of metal content in biochar (Gopinath et al., 2021). With higher pyrolysis temperatures, the carbon content will increase (S. Wei et al., 2019). Increased pH, surface area, pore-volume, ash, fixed carbon, Ca, Mg, and Zn concentrations, and the production of stable Ca supply minerals were all seen with higher pyrolysis temperatures (calcite and oxalate) (Figueiredo et al., 2021).

The ratio of these elements to C changes with temperature. Tang et al. (2019) used anaerobically digested sludge to investigate the change in biochar characteristics at different temperatures. According to scientists, the carbonization impact and the transformation of organic nitrogen caused a rise in the C/N. However, due to the significant dehydration process at higher temperatures, the H/C, and O/C ratios declined. The decreased values of the ratios mentioned above indicate that biochar's hydrophilic nature has deteriorated. Furthermore, a lower H/C value indicates strong aromaticity, indicating stability and degradation resistance (Huang et al., 2017).

Copper, cadmium, arsenic, chromium, zinc, mercury, and lead were found in secondary WAS (produced after the activated sludge process) in quantities of 0.15, 0.02, 26.61, 21.51, 0.51, 0.06, and 56.42 mg /kg, respectively, in a study by Srinivasan et al. (2015). The presence of these elements differs depending on the source of WAS (Gopinath et al., 2021).

## **2.9.6. Biochar application in water and wastewater treatment**

### **2.9.6.1. Biochar as an adsorbent**

Biochar derived from SS has been shown to be an effective adsorbent in the removal of a wide range of pollutants from synthetic and real wastewaters, including emerging contaminants, dyes, heavy metals, and other industrial chemicals (Zojaji 2019; Leng et al., 2015; Liu et al., 2020; Shimabuku et al., 2016; Tang et al. 2019). Researchers have also described the enhancement of biochar materials' adsorption properties through procedures such as magnetization, impregnation with various metallic and non-metallic elements, and co-pyrolysis with other biomass materials (Saadat et al., 2018; Tang et al., 2019; Wei et al., 2019; Yang et al., 2016). The intrinsic qualities of the adsorbent, adsorbate and ambient circumstances are the primary determinants of adsorption (Gopinath et al., 2020). The intrinsic qualities of the adsorbent, adsorbate and ambient circumstances are the primary determinants of adsorption (Gopinath et al., 2020).

### **2.9.6.2. Removal of emerging contaminants**

Researchers reported adsorptive removal of emerging pollutants, including phenolic compounds and pharmaceuticals using both original and modified biochar. During the study conducted by Zojaji, venlafaxine (VEN) sorption from an aqueous solution onto the novel adsorbent generated from a combination of sewage sludge and hardwood (SS: HW) was compared to a commercial granular activated carbon (CGAC). According to their report, the SS: HW had a maximum sorption capacity of 131.57 mg /g, whereas the CGAC had a maximum sorption capacity of 25.57 mg/g. Then, using real WWTP effluent, SS: HW adsorption efficiency was effectively tested, but CGAC failed to remove a mixture of EMs from the real matrix. According to the findings, the novel micro-mesoporous sludge-based adsorbent might be a valuable tool for polishing WWTP effluent and maintaining the quality of surface water resources (Zojaji 2019).

Shimabuku et al. (2016) compared the adsorption of Sulfamethoxazole on sewage-derived biochar to that of other adsorbents such as wood-based biochar and powdered activated carbon (PAC). Due to the presence of dissolved organic matter (DOM) in the wastewater, high-ash

sludge-derived biochar (54.2–82.4 %) was shown to have a lower fouling impact than low-ash wood-based biochar (1.3–3.1 %) and PAC (6.3 %).

According to the scientists, the ash concentration was also linked to the pore size distribution and the presence of oxygen groups. The sludge-derived biochar with a high ash content had more microporosity than the adsorbent with a low ash level. The oxygen-to-carbon ratio of the adsorbents has been reported to be 0.18 to 1.27 for sludge biochar. This ratio for wood biochar is 0.07 to 0.5, and for powder-activated carbon (PAC) is 0.05. Intrinsic features of the biochar are important in target compound removal such as pore size distribution and the presence of oxygen-based functional moieties. Minor competing effects of DOM were seen in the removal of Sulfamethoxazole by sludge-generated biochar (Gopinath et al., 2020)

Kalderis et al. (2017) investigated using biochar made from SS, wood chips, and fuel/demolition waste for removing 2,4-Dichlorophenol. According to their study pH-dependent electrostatic attractions and non-covalent interactions were the primary mechanisms for pollution elimination. In another study by Wei et al. (2019) removing medicines, namely Tetracycline and Doxycycline, were investigated using iron-loaded sludge-derived biochar using a hydrothermal procedure. The iron-loaded biochar showed high surface areas with a particle size of roughly 10 nm and the presence of hydroxyl, carboxyl, and aromatic groups on the surface. Tetracycline and Doxycycline have maximum adsorption capacities of 104.86 mg/g and 128.98 mg/g, respectively.

Tang et al. (2019) used secondary sludge as a precursor for making alkali-acid modified magnetic biochar that was calcined at 800°C and had the maximum adsorptive removal of Tetracycline of 286.9 mg/g. According to their report, the synergetic effects of interactions are of great importance. Stacking interactions and high pore filling are responsible for Tetracycline removal by alkali-acid modified magnetic biochar. According to Yang et al. (2016) the pyrolysis temperature and the activator/dried sludge ratio are the most important elements determining the surface properties of ferric-activated biochar generated from secondary sludge at 750°C to remove tetracycline from aqueous solution.

### **2.9.6.3. Heavy metal removal**

The poisonous nature of heavy metals (HMs) and their influence on the ecosystem and human health have prompted much interest in heavy metal removal from contaminated water and wastewater streams using biochar in recent years (Kamali et al., 2021).

Researchers have looked at the removal of numerous heavy metals and metalloids, such as As, Cd, Pb, Hg, Cr, and Cu, as well as the methods by which different biochar remove them. Tan et al. (2015), investigated the adsorption of Cd on biochar generated from municipal secondary sludge pyrolyzed at 900°C and found that the maximum adsorption capacity was  $42.80 \pm 2.38$  mg /g with a 0.2 percent adsorbent dose. The removal was influenced mainly by the pH of the solution, with around 20 mg/g adsorption capacity recorded for pH less than 2.0 and about 40 mg/g adsorption capacity observed for pH more than 3.0. Surface precipitation and ion exchange interactions were credited with the removal process (Kamali et al., 2021).

The inefficiency of traditional treatment techniques for treating this type of hazardous substances has led to new advancements in the use of biochar for removing HM, exhibiting more efficient and economically viable solutions than activated carbon, notably for chromium and zinc (Shakoor et al., 2020). The effectiveness of several forms of biochar in removing HM from polluted streams has been investigated. For sorption investigations on arsenate (As (III)) and arsenate (As (V)), Khan et al. (2019) employed Japanese oak wood-derived biochar. In this study, As (V) adsorption was marginally greater than As (III) adsorption (84 and 81 percent, respectively).

### **2.10. Engineered biochar**

Activation or modification of biochar to improve its physicochemical qualities has arisen as a new trend, despite pristine biochar's suitable performance in environmental applications (Wang, Ok, et al., 2020). As a result, the phrase 'engineered biochar' describes materials that have been manipulated or activated for specific objectives via physical, chemical, or biological methods (Kazemi Shariat Panahi et al., 2020; Ok et al., 2015; Wang et al., 2017).

Recently there have been attempts to activate biochar using gas, steam, microwaves, acids, alkalis, and oxidants (Panwar & Pawar, 2020; Sajjadi et al., 2019). Another option is to construct composites using co-pyrolysis or post-pyrolysis modification (Mandal et al., 2020;

Tan et al., 2016). In the co-pyrolysis, enhancement agents, such as metal oxides and minerals, are added to the charcoal feedstock before pyrolysis. However, more research tends to use post-pyrolysis biochar alteration. Because the biochar-making process is carried out at high temperatures, the possibility of introducing specific compounds is restricted. For example, biochar–goethite composites with great arsenic (As) adsorption and immobilization characteristics could only be made by post-pyrolysis modification since the external agent will be deactivated at over 260°C (Ammasi, 2020; de Faria & Lopes, 2007).

Green fabrication is a new trend in biochar composite synthesis that corresponds to the green chemistry concept. In this case, safer chemicals and gentler reaction conditions should be used (USEPA, 2017). Zhang et al. (2020) employed banana peel extracts rather than hazardous sodium borohydride (NaBH<sub>4</sub>) as the external agent to form a biochar-iron oxide composite. Produced engineered biochar showed more effective results in adsorbing target chemicals than pristine biochar. Zhang et al. (2020) used a one-step hydrothermal approach to make the biochar composite, decreasing the reaction temperature to 180°C.

Yek et al. (2021) investigated a new approach to integrate self-purging microwave pyrolysis and pyrolytic activation to convert empty fruit bunch (EFB) into microwave modified biochar (MB). They investigated performance of steam and CO<sub>2</sub> as activating agent to produce MB to treat actual landfill leachate via batch and continuous adsorption operation. They applied CO<sub>2</sub> as an activator on the solid waste materials in their pyrolysis system in a high heating rate and process temperature of up to 170°C/min and 600 °C, respectively. MB produced via CO<sub>2</sub> activation (MB-CO<sub>2</sub>) showed significantly higher surface area (95.6 m<sup>2</sup>/g) and mass yield (92.0 wt. %) compared to that produced via steam activation (MB-Steam).

## **2.11. Problematic greenhouse gas (GHG) produced by WWTP**

New issues are being considered to ensure the long-term viability of WWTPs in terms of cost and environmental effect. Energy usage and greenhouse gas (GHG) emissions are two characteristics that have emerged as significant determinants of the WWTPs' overall performance. WWTPs have been highlighted as possible sources of anthropogenic GHG emissions, contributing to climate change and air pollution in recent research (Campos et al., 2016). Biological wastewater treatment methods release carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and nitrous oxide (N<sub>2</sub>O) into the atmosphere. CO<sub>2</sub> is also emitted while producing the energy



necessary for plant operation (Zhan et al., 2018).

Demir & Yapıcıoğlu (2019) investigated GHG emission sources in a municipal wastewater treatment plant. According to their research, CO<sub>2</sub> is one of the main emitted gases in the WWTP. Because of biogas reusing, these facilities do not release CH<sub>4</sub> into the environment. The grit chamber, aeration tank, and secondary sedimentation tank were all reported as direct emission sources of GHGs during the treatment process. The aeration tank was the plant's primary source of GHGs. Only the plant's power usage acted as an indirect emission source. There was no GHG emission to the atmosphere owing to the anaerobic sludge digestion process since all the biogas produced was reused. Overall GHG emissions were lowered by recovering biogas and reusing it as energy.

The emissions into the atmosphere are zero if 100% of the biogas is reused. In recent years many works have been done for reusing and controlling CH<sub>4</sub> and biogas produced in WWTPs. Still, an adequate and sustainable management of CO<sub>2</sub> has not been well implemented yet, so such management requires immediate attention. Decreased CO<sub>2</sub> emission and the entirely (or partially) of its usage on-site required the development of new technologies.

## **2.12. Sustainable development goals and wastewater treatment plants**

Sustainability's social, economic, and environmental pillars can steer a route toward sustainable urbanization (United Nations, 2019). The deployment of sustainable infrastructure to support residents' economic and social welfare without hurting the environment is necessary for planned urbanization (Adshead et al., 2019). Currently, investments are insufficient and unsustainable to cover infrastructure gaps, particularly in emerging and underdeveloped countries; it is anticipated that investments needed to create sustainable infrastructures to meet the 2030 Agenda would cost roughly \$90 billion (Bhattacharya et al., 2015). As a remedy, Alcamo (2019) has suggested that coordinated measures for mutually beneficial Sustainable Development Goals (SDGs) and objectives be implemented. Previous publications have highlighted the links/interdependencies of SDG #6 with other SDGs, such as SDG # 11, in the context of wastewater infrastructure, which is an essential component of urban infrastructure. The links and interdependencies between the SDGs and their objectives and sustainable wastewater infrastructure are summarized in Figure 2.3.(Kanchanamala Delanka-Pedige et al.,

2021) Historically, the primary purpose of wastewater infrastructure has been to provide cleanliness and preserve the environment by collecting wastewater and treating it at the end of the pipe to fulfill discharge regulations. Traditional wastewater infrastructure does not achieve several SDGs in the context of the 2030 Agenda (Zhang et al., 2019). According to the UN water assessment of worldwide progress on SDG #6 objectives, the world will not be able to fulfill the targets by 2030 at the current rate of development. It has been proposed that economic and long-term wastewater infrastructure technologies be created for deployment in fast-increasing cities and to replace old infrastructure in wealthy countries (Kanchanamala Delanka-Pedige et al., 2021).

Since sustainability-based wastewater infrastructure selection cannot guarantee long-term survival or continuous and stable operation, it is critical to consider the priorities/potentials and constraints of each nation/region/decision-maker when deciding on the best treatment option. For example, even if some high-tech wastewater infrastructures enable resource recovery (energy, nutrients, and high-quality effluents) to improve sustainability, they may be out of reach for developing countries; and even if they were, insufficient operation and maintenance contribute to frequent system failures, endangering people, and the environment. In contrast, despite their financial and scientific potential, certain emerging green technologies may not be acceptable in wealthy countries due to resource constraints (Kanchanamala Delanka-Pedige et al., 2021).

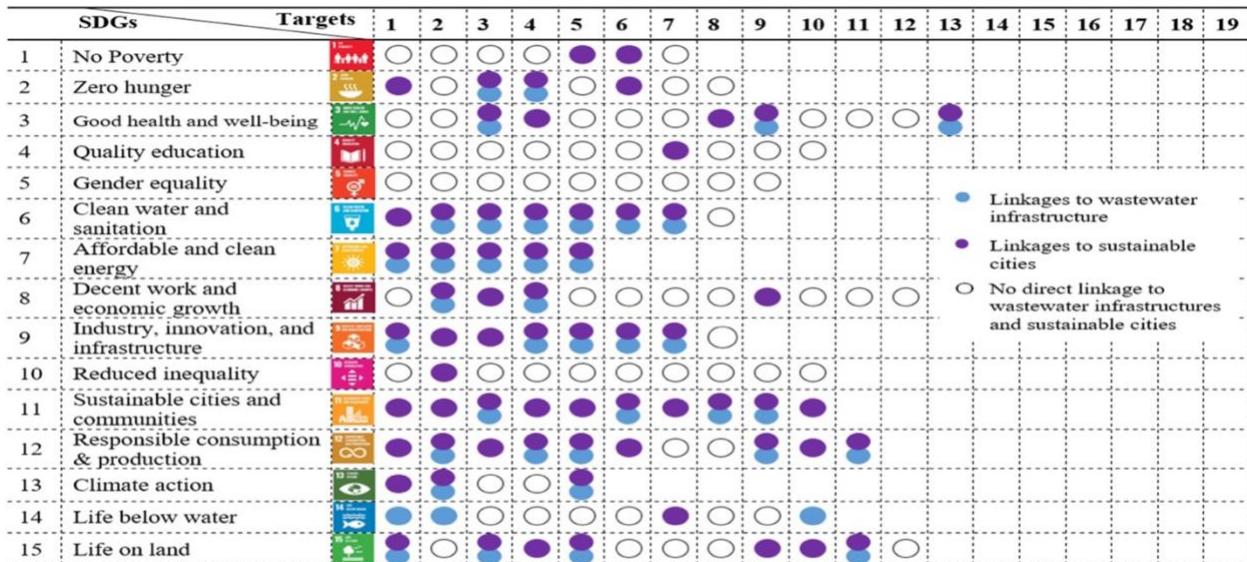


Figure 2-3 Interdependencies of wastewater infrastructures, sustainable cities, and other SDGs. (Kanchanamala Delanka-Pedige et al., 2021)

### **3. Methodology**

#### **3.1. Introduction**

Removing EMs from a WWTP's (RAEBL Régie d'Assainissement des Eaux du Bassin de Laprairie) effluent in Quebec province by a sustainable adsorbent (biochar) has been investigated in this study. According to Zojaji (2019), the current biological treatment within mentioned WWTP is unsuccessful in eliminating EMs. Sixteen of the thirty EMs examined were found in the wastewater effluent at quantities ranging from a few ng/L to g/L. This results in dumping huge amounts of micropollutants into the Saint Lawrence River regularly. Pharmaceutical substances, their metabolites, hormones, herbicides, and transformed products are some of detected Ems. Among reported EMs, Sulfamethoxazole (SMX) and Venlafaxine (VEN) are in the highest concentration (Zojaji 2019).

In the present study, waste-based biochar (WBB) was used for removing EMS, specially SMX, and metals. Biochar prepared according to the previous study (Zojaji 2019) where hardwood chips and wastewater treatment biosolids were combined with potassium hydroxide (KOH), and then pyrolyzed through single step carbonization activation at 750 °C. To enhance biochar's adsorption capacity, the remaining potassium and its relevant by-products should be washed, which might block the pores after pyrolysis. Furthermore, besides having excellent adsorption ability, the material used for effluent filtration should demonstrate a neutral pH value. To achieve defined objectives, the study was conducted in three phases which are presented in the methodical approaches.

#### **3.2. Methodical approaches**

**Phase1:** Preparation of filtration materials for adsorption of pharmaceutical pollutants.

**Phase 2:** Conducting batch tests to maximize prepared materials' efficiency.

**Phase 3:** Designing and testing filtration column to verify and maximize the performance of different adsorptive materials.

### **3.3. Sampling procedure**

A WWTP (with an activated sludge system located in the City of Saint Catherine (Quebec), was chosen as a supplier of primary materials in this study. Subsequently, dewatered and stabilized biosolids and treated effluents came from the same WWTP source. Please note that Zojaji used that same effluent source for his EMs measurements.

### **3.4. General descriptions of the selected WWTP**

Selected WWTP (RAEBL Régie d'Assainissement des Eaux du Bassin de Laprairie) serves five municipalities in addition to several nearby industries (equal to 240,000 inhabitants). The COD load to the treatment plant originates in almost 50% of municipal and 50% of industrial sources. The treatment system in the WWTP consists of the following operation units: automatic screening (two bar racks), grit and grease removal (2 units), four premixing ponds, four aeration basins, and clarifiers (3 units). The plant's average hydraulic retention time (HRT) is 24 hours. The WWTP discharges its effluent at the mean flow of 65,000 m<sup>3</sup>/day to the Saint Lawrence River (SLR). At the sampling time, the plant was working in its normal conditions, which was assessed by analyzing the wastewater effluent quality parameters.

The system was designed to stabilize the sludge anaerobically and dewater it by centrifuge; however, during this study, the anaerobic reactor was out of service. Generally, the treated secondary sludge is disposed off in a landfill or incinerated. The production of biosolids (treated sludge) in this plant is approximately 1731 tons per month. The WWTP recognizes the produced biosolids as waste material, which management counts for high operation costs.

### **3.5. Providing waste-based filtration adsorbent (biochar)**

#### **3.5.1. Preparing of waste-based biochar**

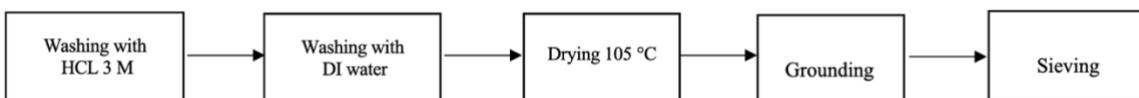
Biochar used in this work was generated during last study (Heidari, 2020) based on the method defined in section 2.9.4 (Zojaji 2019). The biochar was made using single-step carbonization in a large scale. The wasted materials only were used as a precursor of biochar. The biosolids (dewatered/stabilized sludge) were collected when loaded onto trucks for disposal. The hardwood residue (HW) was gathered from a Mirabel (Quebec) wood mill. According to Zojaji (2019), hardwood precursor shows better adsorption results. All primary materials, including

stabilized sludge and hardwood wastes (HW), were dried to a consistent weight in the oven at 105 °C. The pyrolysis was applied on an industrial scale, biochar for large scale test was produced from the mixture of sludge-hardwood-KOH (2:1:2) at  $550 \pm 1^\circ\text{C}$  by increasing the temperature of biomass at the rate of  $10^\circ\text{C}/\text{min}$  in the presence of nitrogen for 60 minutes.

This industrial prepared biochar required post preparation because of high pH. According to Zojjaji, nutria pH (6-7) is the best condition for the adsorption, so the industrial produced biochar should be adjusted. Unfortunately, due to inadequate mixing and unequal distribution of temperature, the adsorptive materials showed lower capacity (see results in section 4-1-1) so post-modification of pyrolysis was required. In addition, the surface area and pH were required to be improved. Subsequently, adequate methods for adsorptive material preparation were designed.

### 3.5.2. Preparation of biochar with Method 1 (PBM1):

Method 1 consists of washing biochar with acid HCl 3M twice, then rinsing with DI water, and subsequently drying in the oven at  $105^\circ\text{C}$  overnight. Subsequently, dried and cooled biochar is grounded and sieved (Figure 3.1). Sieve numbers are mentioned in appendix 1 in Table A-1 to A-3.



*Figure 3.1 Method 1 of biochar preparation*

### 3.5.3. Preparation of biochar with Method 2 (PBM2)

Method 2 of biochar preparation was conducted in the following steps: i) media crashing, ii) washing with HCl 1.5 M, iii) soaking in DI water for 12 hours, iv) drying in the oven at  $105^\circ\text{C}$  overnight, v) grounding, vi) sieving (Figure 3.2).

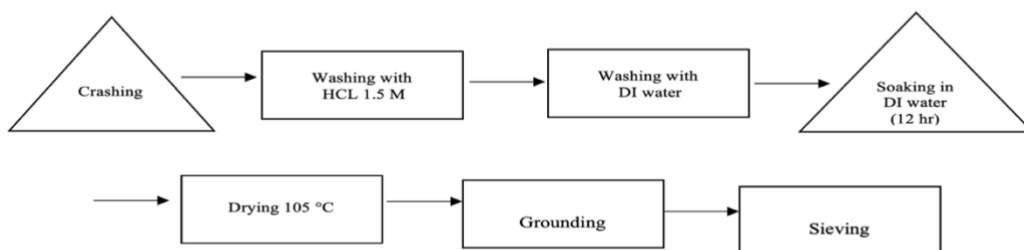


Figure 3.2 Method 2 of biochar preparation

### 3.5.4. Preparation of biochar with Method 3 and activating with CO<sub>2</sub> (PBM3-CO<sub>2</sub>):

Method 3 of biochar preparation was more complicated but demonstrated the best adsorption properties. The following steps of the preparation procedure were applied in this case: i) media from pyrolysis were crashed, ii) washed with HCl 1.5 M, iii) soaked in DI water for 12 hours, iv) CO<sub>2</sub> applied to the biochar (Figure 3.3), v) dried in the oven, vi) grinding, vii) sieving.

A special reactor for activation of biochar with CO<sub>2</sub> was designed. It was a setup consisting of a cubic batch reactor (polyvinyl chloride plastic box) with a volume of 1250 cm<sup>3</sup>. The gas flow rate of 2 L/min passed through the biochar for 20 minutes (Figure 3.4).

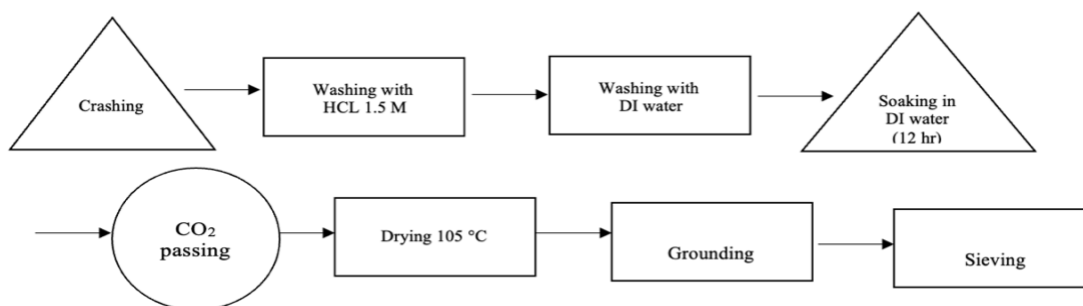


Figure 3.3 Method 3 of biochar preparation

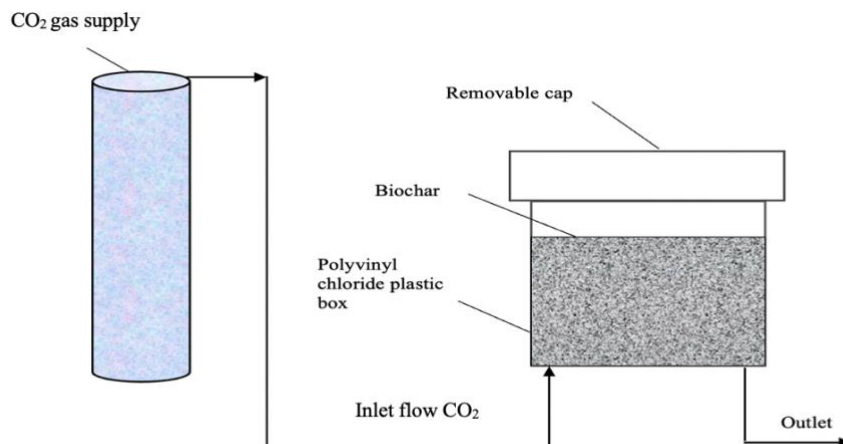


Figure 3.4 Device developed for biochar activation with CO<sub>2</sub>

Application of such method permitted on decrease of biochar pH and increase of carbon contentment. In addition, the beneficial change of shape of biochar particles was observed.

### 3.6. Optimizing biochar gasification:

Optimizing gasification is very important, enhancing productivity and reducing energy consumption on a bigger scale. In this regard, a certain amount of DI water (250 mL) was added to 250 g of washed biochar then CO<sub>2</sub> was applied to the mixture according to the previously described Method (the flow rate of 2 L/min of CO<sub>2</sub> for 20 minutes), and pH tested at the end of each experiment. After each experiment, the amount of water decreased, and the biochar increased. The optimum point is the highest amount of used biochar for activation and the lowest amount of DI water with a neutral pH value.

### 3.7. Batch tests

#### 3.7.1. Adsorption of pharmaceutical compounds

To investigate the effect of the preparation method on the adsorption efficiency, batch tests were performed. For this purpose, adsorption of VEN, and SMX on washed biochar with Method 1 (PBM1) and prepared biochar with Method 2 (PBM2) were investigated. To this end, PBM1 and PBM2 were screened to the fraction of a diameter between 0.3 mm and 0.5 mm. All the adsorbents were kept inside the desiccator until their use. Ultrapure water obtained from Milli-Q water purification systems was used for the solution's preparation. Adsorption

experiments were carried out in 125 mL amber jar glass containing 60 mL of aqueous solution polluted with 30 mg/L of a selected pharmaceutical compound. Based on Zojaji (2020) 48 h-contact time was enough to reach equilibrium for sorption, so the samples were shaken on the reciprocating-orbital shaker (Thermolyn Aros 160) at the constant rotating speed of 250 rpm. Additionally, a blank sample was used in each experiment to ensure that there is no interference and losses in the tests.

### **3.7.2. Effect of pH on adsorption efficiency**

Since the value of pH plays an essential role in the adsorption process, a series of batch tests was conducted to examine the effect of pH on the adsorption of a selected pharmaceutical compound on PBM1 and PBM2 materials. For this purpose, the adsorption concentration (50 mg/ L), agitation rate 250 rpm, room temperature  $27\pm 5$  °C, and contact time of 24 h were maintained constant, while pH varied from 3 to 11 to investigate its effect on the adsorption.

## **3.8. Designing and testing the filtration columns**

### **3.8.1. Solution preparation for column test**

Instance samples of wastewater effluent were collected in WWTP and transferred to the lab. All samples were kept at the temperature of 4°C in the refrigerator until their use in batch or column tests. Each sample was removed from the refrigerator 3 hours before the experiment to reach room temperature. Then, 30 mg/L of SMX was added to the effluent to investigate the pharmaceutical compound adsorption.

### **3.8.2. Components of the filtration column**

A fiberglass column was used to carry a bed height of 24 cm with an internal diameter of 10 cm in every experiment. The column was rinsed with deionized water (DIW) and sterilized with ethanol ( $C_2H_5OH$ ). At the bottom of the column, a circular fiberglass mesh was installed. Once the column was packed with the adsorbent, the top of the biochar was covered with filter paper of 0.45  $\mu m$  size to ensure uniform distribution of water in the column.

The two ends of the column were sealed with commercial silicon and covered with plastic covers. The effluent feed and filtrate discharge were done through adequately situated valves. A PVC container was used to carry the feed solution. The feedwater was pumped using a



Master flex peristaltic pump (model no. 77919-35, USA).

### **3.8.3. Description of the filtration column experiments**

The biochar prepared with Method 2 (PBM2) was used in column experiments 1, 2, and 3 (EXP1, EXP2, and EXP3), where the volume of biochar increased in each experiment. Washed biochar by Method 3 was applied in the filtration column in experiment 4 (EXP4). Biochar prepared by Method 3 encountered the CO<sub>2</sub> to examine the effect of CO<sub>2</sub> on the adsorption performance. During all experiments, the total height of 24 cm of the filtration column was kept constant.

In EXP1 (Figure 3.5), gravel and sand were used in combination with the biochar (gravel 12 cm, sand 8 cm, and biochar 4 cm). In EXP2 (Figure 3.6), gravel was removed from the column, and the remained part was filled with sand (a total of 14 cm), where the height of biochar was 10 cm. Finally, in EXP3 (Figure 3.7), the full height of 24 cm was filled with sole biochar. In EXP4 (Figure 3.8), the full height of the column was filled with biochar washed with Method 3 (i.e., activated biochar with CO<sub>2</sub>).

Before using gravel and sand in the experiments, they were washed with hydrochloric acid 3M to remove impurities, rinsed with DI water, and dried in the oven at 105 °C overnight. Before starting the column experiments, distilled water was passed through the column to remove potential impurities from the column.

The packed column was subjected to rinsing several times with deionized water (DIW) until the leachate pH stabilized at a particular level, indicating that the column was clean and suitable for an experiment.

To find optimum operation conditions for the column, three different flow rates (25, 15, and 10 mL/min) were used in each experiment. The adsorption capacity, exhaustion time (time of bed saturation, T<sub>s</sub>), breakthrough time (T<sub>b</sub>), length of the unused bed (LUB), adsorption capacity at breakthrough time (q<sub>b</sub>), and adsorption capacity at exhaustion time (q<sub>s</sub>), were measured for different heights of biochar materials and flow rates.

### **3.8.4. Column test experiment 1 (EXP1)**

During column test experiment 1 (EXP1), the ratio of filtration of 3:2:1 for a total height of

24 cm considered. It was 12 cm of gravel, 8 cm of sand, and 4 cm of washed biochar (3:2:1). The biochar was prepared with Method 2 (PBM2).

Figure 3.5 shows the experimental system for EXP1. The effluent from WWTP, polluted with 30 mg/L SMX, was accommodated in a PVC barrel to be pumped throughout the column. A 25, 15, and 10 mL/min flow rate passed through the column. Column leachate samples were collected immediately after the filtration and every 3 hours until exhaustion time.

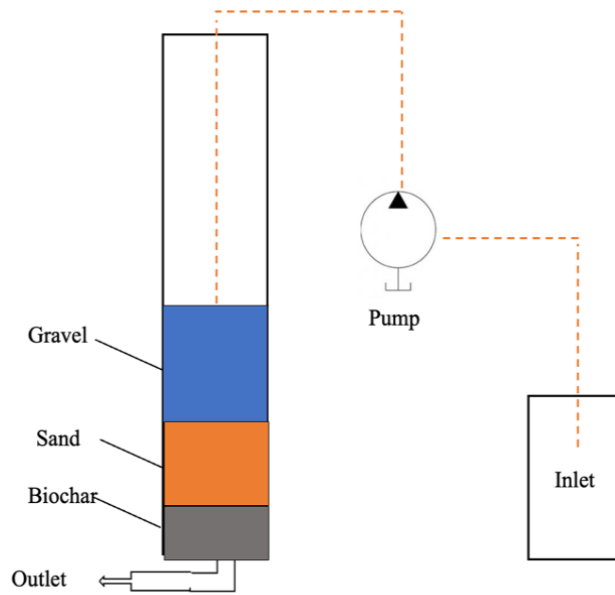


Figure 3.5 System used for column test EXP1

### 3.8.5. Column test experiment 2 (EXP2)

In experiment 2, the portion of gravel was substituted with sand; the total heights of sand and biochar were 14 cm and 10 cm, respectively (Figure. 3.6). Thus, the ratio of sand volume to biochar volume in the filter was 1.4:1. The preparation of biochar followed Method 2 (PBM2). The effluent from WWTP containing 30 mg/L of SMX was filtrated through the column at a flow rate of 25,15 and 10 mL/min, while leachate samples were collected at the initial stage and every 3 hours until exhaustion time.

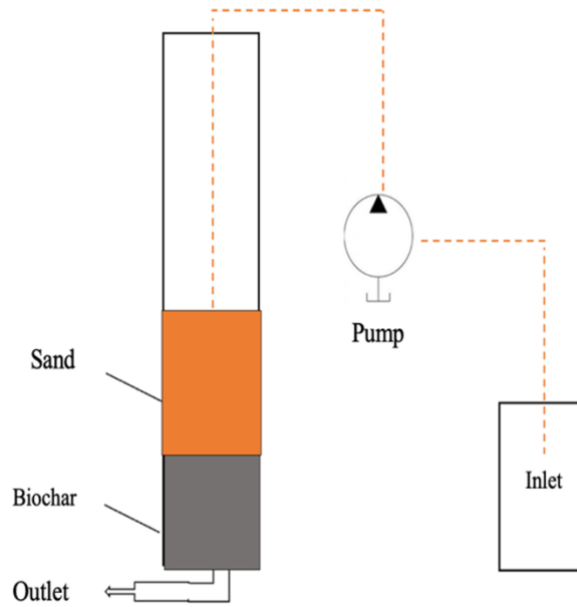


Figure 3.6 System used for column test EXP2

### 3.8.6. Column test experiment 3 (EXP3)

In experiment 3 whole column to a height of 24 cm (Figure. 3.7) was filled with biochar prepared using Method 2 (PBM2). The effluent's flow rate (25, 15, 10 mL/min) containing 30 mg/L SMX as in EXP2 was applied, and the leachate samples were collected at the beginning of the filtration process, and every 3 hours until exhaustion time.

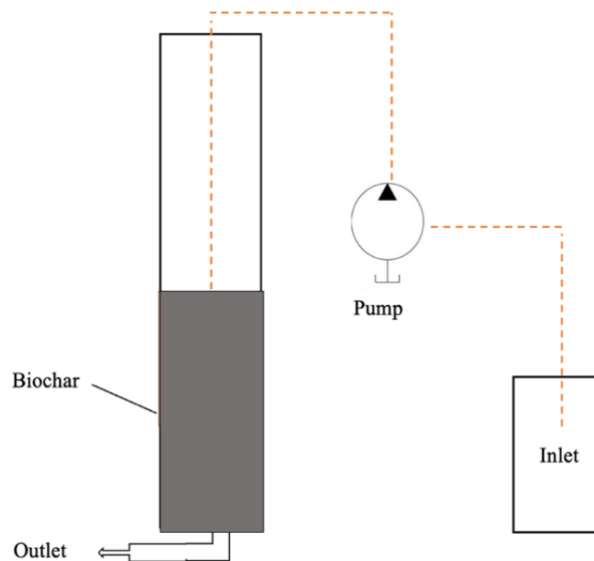


Figure 3.7 System used for the column test EXP 3

### 3.8.7. Column test experiment 4 (EXP4)

The column in EXP4 was also filled with biochar until the height of 24 cm (Figure. 3.8). However, biochar was prepared using Method 3 and activated by CO<sub>2</sub> (PBM3- CO<sub>2</sub>). The effluent containing 30 mg/L of SMX was filtrated through the column with a flow rate of 25, 15, and 10 mL/min. Leachate samples were collected initially and every 3 hours until exhaustion time. Subsequently, the samples were analyzed using UV-Vis spectrometry.

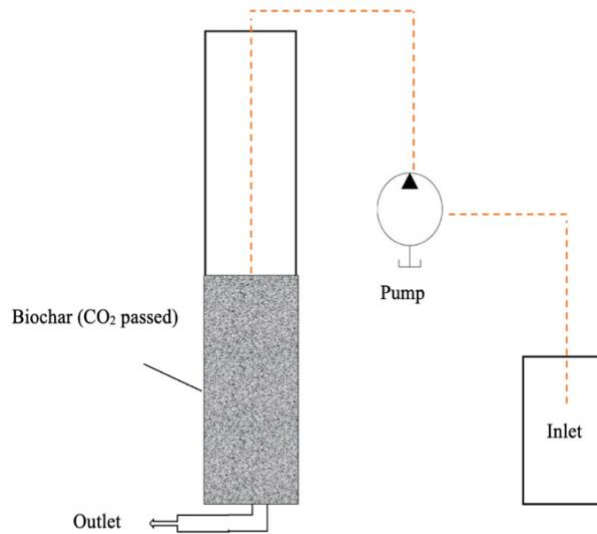


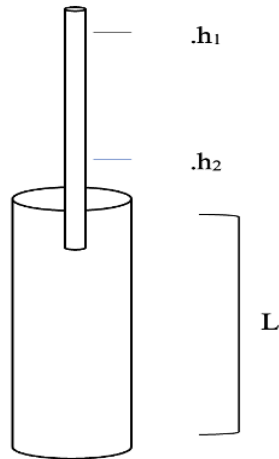
Figure 3.8 System used for column test EXP 4

### 3.9. Hydraulic parameter designing of the column

In order to find permeability of the biochar ( $k$ ) Darcy's law has been used (Helwany, 2007; (Liu et al., 2016).

$$k = \frac{aL}{At} \ln \frac{h_1}{h_2} \quad (3-1)$$

A cylinder was filled with the biochar and compacted, then a calibrated tube was put above it to let water come and pass through the biochar. The time for traveling the water from  $h_1$  to  $h_2$  was measured to find  $k$  in the formula.



- L: length of the cylinder
- A: biochar cross section area
- a: calibrated tube cross-sectional area
- t: elapsed time needed
- h1: point 1 of measuring (at the beginning of the test)
- h 2: point 2 of measuring (destinated point)

Figure 3.9 Measuring the coefficient of permeability of the biochar

Equation 3-2 is considered for designing filtration velocity (Darcy, 1856).

$$v = ki \quad (3-2)$$

In this Equation the filtration velocity ( $v$ ) is proportional to the hydraulic gradient ( $i$ ) and the coefficient of permeability ( $k$ ). A hydraulic gradient is a vector gradient between two or more hydraulic head measurements over the length of the flow path. A dimensionless hydraulic gradient can be calculated between two points with known head values by Equation 3-3:

$$i = \frac{dh}{dL} = \frac{h_2 - h_1}{length} \quad (3-3)$$

where:

$i$  is the hydraulic gradient (dimensionless),

$dh$  is the difference between two hydraulic heads (m)

$dL$  is the flow path length between the two piezometers (m)

The time of passing ( $T$ ) of effluent through the biochar column in EXP4 can be find by 3-4:

$$T = \frac{dL}{v} \quad (3-4)$$

$v'$  is the seepage and can be calculated by Equation 3-5

$$v' = \frac{\text{Darcy velocity } (v)}{\text{Porosity}} \quad (3-5)$$

### 3.10. Effective column operation conditions

It is important to determine the design parameters for the biochar column to scale up the system in a real WWTP. Major design factors for a column are bed capacity (BC), breakthrough time ( $T_b$ ), and exhaustion time ( $T_s$ ). These parameters can be found by creating the breakthrough curve for optimum removal conditions. Bed capacity (BC) is the area above the breakthrough curve, and this can be obtained by the below Equation (Bakly et al., 2019).

$$BC = G \int_0^{T_s} (C_0 - C) dt, \quad (3-6)$$

By integrating Equation 3-4 to a limit of  $T=T_s$  flowing Equation can be found:

$$BC = G(C_0 - C^*) T_s \quad (3-7)$$

Where  $G$  is the solution flowrate (L/min),  $C_0$  and  $C^*$  are the concentration of the pharmaceutical compounds in inlet and equilibrium concentration, respectively (mg/L).  $C^*$  is the concentration of the solution in equilibrium with the fresh adsorbent or concentration of the solution leaving the bed primarily (mg/L).  $T_s$  is the time required for complete bed exhaustion (min). Exhaustion time is a condition when the system reaches a stability situation, i.e., i) removal percentage is negligible, ii) operation is energy inefficient at this point, iii) significant percentage of the column bed would be saturated, iv) therefore would not contribute to SMX adsorption. The portion of the bed is termed as equivalent length of the unused bed (LUB), which can be found by Equation 3-8:

$$LUB = \frac{Z}{T_s} (T_s - T_b) \quad (3-8)$$

Where  $Z$  is the total bed height (cm), and  $T_b$  is the breakthrough time (min).  $T_b$  can be found from the breakthrough curve at  $C/C_0 = 0.2$  (Bakly et al., 2019).

### **3.11. Analytical approaches**

#### **3.11.1. Measurement of the VEN and SMX concentrations in the aqueous samples**

UV-vis spectrophotometer was used to determine the quantities of VEN and SMX in the aqueous samples (ThermoFischer, Evolution 201). The VEN's maximum absorbance wavelength was found to be 224 nm, which was consistent with the previous study (Karani and Pingale, 2009), and SMX maximum absorbance wavelength was determined to be 254 nm, which was according to previous research (Jahdi et al., 2020).

Beer-law Lambert's was used to create the calibration curve. According to Beer-law, there is a linear connection between the solute concentration and absorbance.

Lambert's blank sample was generated, and analyte concentrations ranging from 1 mg/ L to 30 mg/ L. Quartz cells with a route length of 1 cm were employed. Each concentration's absorbance was measured at its maximum absorption wavelength. Software (Thermo Scientific TM) interfaced with the device and automatically drew the absorbance chart against the concentration.

#### **3.11.2. Scanning electron microscopy (SEM)**

The surface morphology of biochar adsorbents before and after treatment was visualized using Scanning Electron Microscopy (SEM). A Philips XL30 microscope was used to record the SEM examination of the samples.

#### **3.11.3. Metal analysis in biochar**

To assess the heavy metal concentrations in biochar samples, acid digestion- based on the standard US EPA 3050B (US Environmental Protection Agency, 1996) was carried out. This procedure, which comprised repeated injections of nitric acid (HNO<sub>3</sub>) and hydrogen peroxide, digested 0.5 g (dry weight) of sludge (H<sub>2</sub>O<sub>2</sub>).

The final digested material was filtered using a 0.45 m syringe filter. The metal concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS) (Agilent Technologies 7700 Series ICP-MS).

#### 3.11.4. Anion and cation detection by ion chromatography

The ion chromatography method was used to analyze anions (chloride, bromide, nitrite, nitrate, phosphate, and sulfate) and cations (lithium, sodium, ammonium, calcium, magnesium) in the leachate samples from different column experiments and the WWTP effluent. This is Chromatography Metrohm 930 Compact IC Flex with external calibration methods. The used columns are Mtrosep A supp 5-150/4.0 and Metrosecp C4-150/4.0.

#### 3.11.5. Physicochemical parameters

Standard procedures were applied to analyze Chemical Oxygen demand (COD) and Total Suspended Solids (TSS) in aqueous samples. TNT821 vials (Hach procedure) were used for COD. TSS was measured using Standard Method 2540D-2015, ASTM D5907-13.

#### 3.11.6. Adsorption of pharmaceutical compounds from aqueous solutions

The amount of a pharmaceutical adsorbed per gram of adsorbent ( $q$ ) was calculated by using Equation 3-9:

$$qt = \frac{(C_0 - C_t) \times V}{m} \text{ (mg/g)} \quad (3-9)$$

Additionally, the removal efficiency was calculated by using Equation 3-10:

$$\%RE = 1 - \frac{(C_t)}{C_0} \quad (3-10)$$

Where  $qt$  (mg/g) is the mass of a pharmaceutical adsorbed at time  $t$ ;  $C_0$  is the initial pharmaceutical concentration (mg/L),  $C_t$  (mg/L) is the pharmaceutical concentration at time  $t$ ,  $V$  is the volume (L) of the adsorbate solution, and  $m$  (g) is the mass of dried carbon adsorbent.

### 3.12. Materials

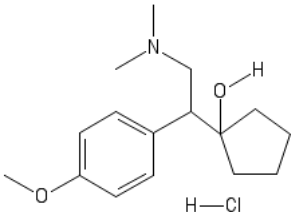
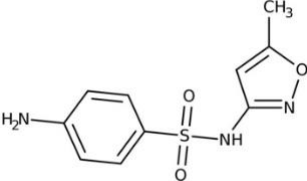
The following lab materials were used in this study: syringe filters (glass fiber/polyester, 45  $\mu$ m) and paper filter (45  $\mu$ m) from Sorbtech (USA), latex-free disposable syringes (60 mL and 10 mL), various bottles and amber glass jars (125mL), HDPE bottles.

Furthermore, the following substances were utilized: potassium hydroxide (KOH), hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium nitrate (KNO<sub>3</sub>), all from Fisher Scientific. Venlafaxine (VEN) hydrochloride standard (CAS# 99300-78-4, TCI America) and



Sulfamethoxazole (SMX, CAS# 723-46-6, Fisher Scientific). The chemical formula, structure, molecular weight, and water solubility of VEN and SMX substances are shown in Table 3.1.

Table 3.1 Physiochemical properties of VEN & SMX

Chemicals	Chemical formula	Structure	MW g/ mol	Sw mg/ L	Reference
Venlafaxine	$C_{17}H_{27}NO_2 \cdot HCl$		313.87	572000	(Zhu et al., 2022)
Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$		253.276	610	(Ninwiwek et al., 2019)

## **4. Results and discussion**

The study was conducted in three phases. During phase 1, filtration materials (biochar) were prepared, using three different Methods of preparation. In phase 2, batch tests were conducted to examine the biochar adsorption performance leading to the selection of the best method of biochar preparation. In phase 3, the prepared biochar materials were accommodated in the column to determine the best conditions for the adsorption/filtration process. Four column operation conditions with different volumes of biochar materials were investigated.

### **4.1. Batch tests**

#### **4.1.1. Effect of the preparation Method on adsorption**

Adsorption of two types of pharmaceuticals, namely VEN and SMX, were studied in batch test experiments to assess the effect of the preparation method on adsorption. A removal of 72.63 % for SMX, and 72.25 % for VEN observed by using biochar prepared with Method 1. However, their removal after using Method 2 was 79.13% and 79.63% for VEN and SMX, respectively (Figure 4.1), 9.6 % increase in adsorption was observed after using Method 2 of preparation.

Tsai et al. (2020) investigated enhancing the pore properties and adsorption performance of Cocoa Pod Husk (CPH)-derived biochar. In their study scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) and Fourier Transform Infrared spectroscopy (FTIR) were used to investigate the pore and chemical properties of the resulting biochar and their post-leaching biochar by acid washing. According to their findings, pores in biochar may be greatly generated during acid washing, resulting in a surface area increase from 101 to 342 m<sup>2</sup>/g.

According to present study crashing biochar in Method 2 before acid washing exposed the higher surface of the biochar to acid and made the reaction faster and easier.

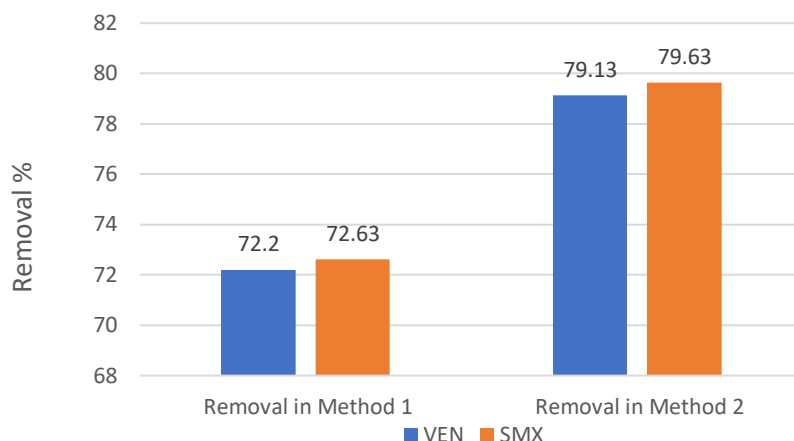


Figure 4.1 Removal VEN & SMX using biochar prepared according to Methods 1 & 2

#### 4.1.2. Effect of pH on adsorption

The pH of the solution plays a substantial role in the adsorption process. pH affects the adsorbent's chemical properties and the adsorbate's surface charge (Keerthan, 2020). According to the literature reviews, some chemicals, such as caffeine, exist in the neutral form at a point zero charge of 5.5. Above pH 5.5, they will be in the anionic form (Keerthan et al., 2020).

Variation of SMX adsorption and adsorption capacity of the biochar in different pH values is shown in Figure 4.2. It was revealed that the highest SMX adsorption occurred at lower pH values. By increasing pH, SMX adsorption decreases. In the pH range of 3 to 5, the SMX is in neutral form; therefore, the adsorption of SMX was the highest because the presence of SMX in leachate was near zero. At low pH values, the negatively charged surface of the biochar is protonated. The protonated biochar and neutral form of SMX may interact with each other.

These interactions are due to non-electrostatic forces, such as hydrogen bonding. At higher pH values (6–11), SMX<sup>-</sup> may interact with the positively charged surface of biochar. Under these conditions, the non-electrostatic interactions become less favorable, causing a decrease in the adsorption of SMX (Keerthan, 2020). The sorption of SMX was reduced as the pH was raised in general. SMX is an ionizable chemical whose distribution between organic and aqueous phases is determined by its degree of ionization. The degree of ionization is determined by the pH and pKa of the solution. The pKa of SMX is 1.25 and 5.29. (Wu et al.,

2013). Because changes influenced the sorption of SMX in solution pH, the electrostatic attraction might be one of the sorption processes implicated.

These results also showed that adjusting pH of biochar to neutral improve its adsorption efficiency. Thus, all preparation procedures included the use of acid.

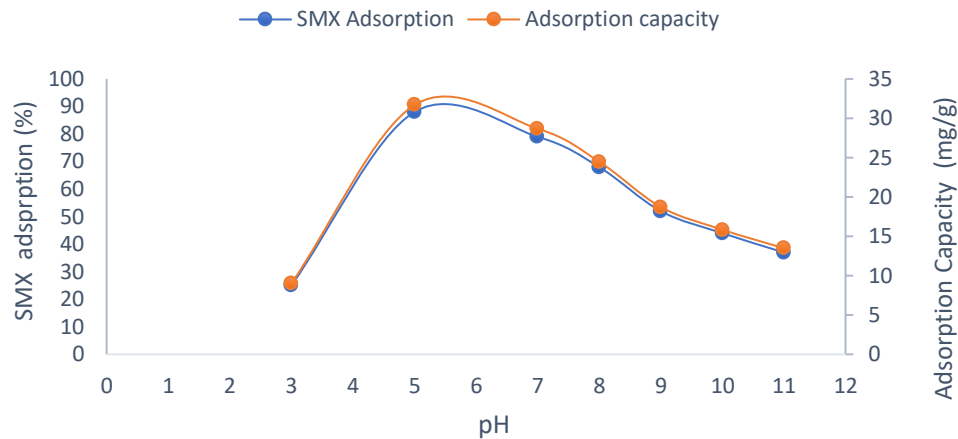


Figure 4.2 Effect of pH on SMX adsorption and adsorption capacity (batch test)

## 4.2. Column tests

Different column studies were conducted to evaluate the filtration behavior of prepared biochar samples and find the optimum operation contention. According to the batch test results, biochar was prepared using Method 2 (PBM2), applied in column experiments 1, 2, and 3, respectively (EXP1, EXP2, EXP3). Then, according to the column studies, biochar, prepared using Method 3, was installed in column experiment 4 (EXP4) to improve the adsorption. The description of the columns is shown in Figure 4.3.

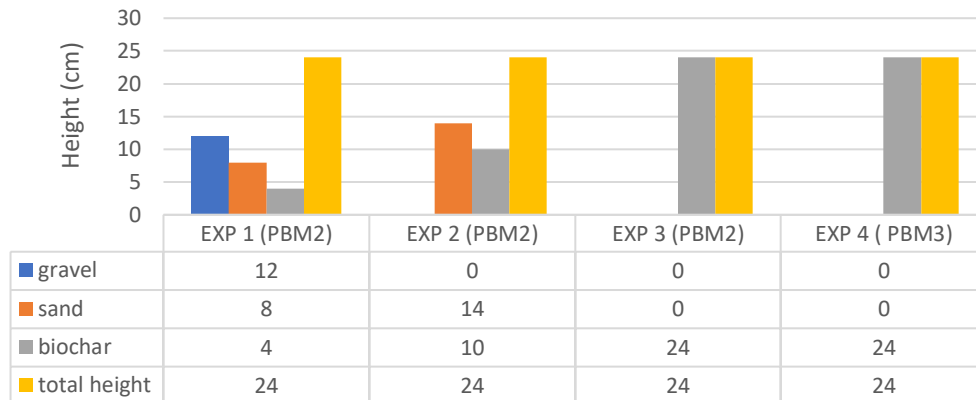


Figure 4.3 Configuration of column test experiments

#### 4.2.1. Hydraulic parameters of the filter

The hydraulic parameters of the column for the best condition (EXP4) containing the permeability of used biochar, velocity and time of passing were determined. The coefficient of permeability ( $k$ ) of prepared biochar with Method 3 and activated by CO<sub>2</sub> (PBM3-CO<sub>2</sub>) was determined using Equation 3-1. To find the permeability of the biochar according to the methodology described in chapter 3, biochar is accommodated in a cylinder; then, a calibrated tube is put above it to let effluent come and pass through the biochar. In this formula:  $l$  is the length of the cylinder of 4 cm, A: Biochar cross-section area of 19.846 cm<sup>2</sup>, a: inside cross-sectional area of 0.196 cm<sup>2</sup>, t: traveling time from point 1 to point 2 in the calibrated tube = 15s,  $h_1$  = height at point 1 equal to the height of 7cm above a reference level in the calibrated tube,  $h_2$  = height of 1cm above the reference level in the calibrated tube.

$$k = \frac{aL}{At} \ln \frac{h_1}{h_2} = \frac{(0.196 \text{ cm}^2)(4 \text{ cm})}{(19.846 \text{ cm}^2)(15 \text{ sec})} \ln \frac{7 \text{ cm}}{1 \text{ cm}} = 5.12 \times 10^{-3} \text{ cm/s}$$

$$k = 0.00512 \text{ cm/s}$$

Nirmal and Elsa investigated the biochar permeability they received similar results (Joy and Varghese, 2017).

In EXP 4, for the best condition according to Equation 3-2, the flow velocity ( $v$ ) is proportional to the coefficient of permeability ( $k$ ) and hydraulic gradient ( $i$ ).

Coefficient of permeability measured through permeability testing for biochar and showed to be 0.00512 cm/s, hydraulic gradient ( $i$ ) is calculated according to Equation 3-3. In this formula hydraulic gradient between two head values of the column in experiment 4 is calculated as below:

$$i = \frac{dh}{dL} = \frac{26}{24} = 1.08$$

$$dh = 2 \text{ cm (water)} + 24 \text{ cm (biochar)} = 26 \text{ cm}$$

$$dL = 24 \text{ cm (biochar)}$$

The velocity of the effluent in the column is calculated according to Equation 3-2 as below:

$$v = ki$$

$$v = 0.00512 \text{ cm/s} \times 1.08$$

$$v = 5.53 \times 10^{-3} \text{ cm/s}$$

$$v = 0.199 \text{ m/h}$$

time of passing (T) of the effluent through the biochar column in EXP4 can be found by Equation 3-4; in this formula velocity of the effluent through the column should be divided by the seepage, seepage in the column is calculated according to Equation 3-5 as below:

$$v' = \frac{\text{Darcy velocity } (v)}{\text{Porosity}} = \frac{5.53 \times 10^{-3}}{0.6} = 9.21 \times 10^{-3} \text{ cm/s}$$

$$T = \frac{dL}{v'} = \frac{24 \text{ cm}}{9.21 \times 10^{-3} \frac{\text{cm}}{\text{s}}} = 2603.97 \text{ s} = 43.39 \text{ min}$$

The time of passing for effluent through the biochar column in EXP4 were 45 min, which is consistent with the value of 43.39 min from the above calculation.

#### 4.2.2. Improvement of biochar properties by exposing to CO<sub>2</sub>

In order to decrease the usage of chemicals for biochar preparation and upgrade biochar efficiency, biochar was exposed to CO<sub>2</sub>, which is generated in abandoned amounts by WWTP facilities. To investigate the effect of CO<sub>2</sub> on biochar properties, CO<sub>2</sub> gas applied to crashed biochar samples with a different water ratio. To achieve an optimum condition, a series of tests, described in Tables 4.1 to 4.4 conducted. The objective of this procedure was to create carbonic acid which is the result of the kinetics of carbon dioxide's dissolution in water and subsequent chemical reactions. At room temperature (25 °C), dissolved carbon dioxide enters in reaction with water and carbonic acid is produced, from which hydrogen ions dissociate, resulting in increasing the acidity of the solution (Knoche, 1980; Mitchell et al., 2010) (Equation 4-1). In such way, biochar reached optimal pH for adsorption (Figure. 4.2). Carbonic acid can also enter in reaction with calcium hydroxide. If some minerals are dissolved from biochar (e.g., iron, copper, magnesium), carbonic acid might react to change initial structure of biochar. Subsequently, pH of biochar can reach neutral level and adsorptive surface area can improve.

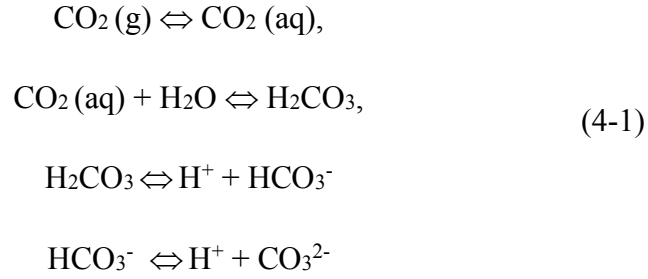


Table 4.1 Optimising CO<sub>2</sub> gas flow

Test	Biochar (g)	Water (mL)	Time min	CO <sub>2</sub> flow rate (L/min)	pH
1	250	250	30	1	8.5
2	250	250	30	1.5	7.6
3	250	250	30	2	7.2

Table 4.2 Optimizing biochar proportion

Test	Biochar (g)	Water (mL)	Time min	CO <sub>2</sub> flow rate (L/min)	pH
1	250	250	30	2	7.2
2	300	250	30	2	7.2
3	400	250	30	2	8.4

Table 4.3 Optimising water proportion

Test	Biochar (g)	Water (mL)	Time min	CO <sub>2</sub> flow rate (L/min)	pH
1	300	250	30	2	7.2
2	300	100	30	2	7.2
3	300	50	30	2	8.2

Table 4.4 Optimising time of exposure

Test	Biochar (g)	Water (mL)	Time min	CO <sub>2</sub> flow rate (L/min)	pH
1	300	100	30	2	7.2
<b>2</b>	<b>300</b>	<b>100</b>	<b>20</b>	<b>2</b>	<b>7.3</b>
3	300	100	10	2	8

According to the experiment results, the optimum condition for biochar preparation is ratio of biochar to water as 3:1 (by weight) and CO<sub>2</sub> flowrate of 2 L/min for 20 min if 300g of biochar was treated.

#### 4.2.3. Designing effective operation condition for column

Main designing factors for scaling up the column, containing bed capacity (BC), breakthrough time (T<sub>b</sub>), and exhaustion time (T<sub>s</sub>) calculated for different column experiments (Tables 4.5 to 4.8). Real effluent with a fixed concentration of 30 mg/l of SMX passed through the column in different flowrate of 25, 15, and 10 mL/min. The optimum condition for removing pharmaceutical compounds was determined for each experiment. The area above the breakthrough curve represents the bed capacity (BC). For optimum removal conditions, bed capacity (BC) is calculated by Equation 3-7.

$$BC = G(C_0 - C^*) T_s$$

Where G is the solution flowrate (L/min), C<sub>0</sub> and C\* are the concentration of the pharmaceutical compound in inlet and equilibrium concentration, respectively. C\* is the concentration of the solution in equilibrium with the fresh adsorbent or the concentration of the solution leaving the bed. T<sub>s</sub> is the time required for complete bed exhaustion (min). Exhaustion time occurs when the system has stabilized to the point that removal percentage is negligible, and operation is energy inefficient. In this study, the exhaustion point is selected to be C/C<sub>0</sub> = 0.9, where C is the concentration of pharmaceutical compound at any time (mg/L); at this stage, T<sub>s</sub> is considered as the corresponding time for column saturation. In this situation, a considerable portion of the column is saturated without profitable adsorption of a pharmaceutical compound. This portion is designated as the equivalent length of an unused bed (LUB), which is provided in Equation 3-8:

$$LUB = \frac{Z}{T_s} (T_s - T_b)$$

where Z is the total bed height (cm), and T<sub>b</sub> is the breakthrough time (min). T<sub>b</sub> can be found from the breakthrough curve at C/C<sub>0</sub> = 0.2 (Bakly et al., 2019).



Table 4.5 Design parameters for column EXP1

EXP1											
Adsorbent weight g	Ts min	Tb min	LUB cm	Total adsorption at Tb mg	qb mg/g	Total adsorption at Ts mg	qs mg/g	Z cm	flowrate L/min	C <sub>0</sub> mg/L	C* mg/L
200	150	12	3.68	8.55	0.04	106.88	0.53	4	0.025	30	1.5
200	270	20	3.70	8.64	0.04	116.64	0.58	4	0.015	30	1.2
200	440	32	3.71	9.31	0.05	128.04	0.64	4	0.010	30	0.9

Table 4.6 Design parameters for column EXP2

EXP2											
Adsorbent weight g	Ts min	Tb min	LUB cm	Total adsorption at Tb mg	qb mg/g	Total adsorption at Ts mg	qs mg/g	Z cm	flowrate L/min	C <sub>0</sub> mg/L	C* mg/L
500	250	42	8.32	29.61	0.06	176.25	0.35	10	0.025	30	1.8
500	580	87	8.50	37.82	0.08	252.13	0.50	10	0.015	30	1.02
500	1230	183	8.51	53.44	0.11	359.16	0.72	10	0.010	30	0.8

Table 4.7 Design parameters for column EXP3

EXP3											
Adsorbent weight g	Ts min	Tb min	LUB cm	Total adsorption at Tb mg	qb mg/g	Total adsorption at Ts mg	qs mg/g	Z cm	flowrate L/min	C <sub>0</sub> mg/L	C* mg/L
1200	980	298	16.70	212.33	0.18	698.25	0.58	24	0.025	30	1.5
1200	2100	589	17.27	256.22	0.21	913.50	0.76	24	0.015	30	1
1200	4240	1089	17.84	316.90	0.26	1233.84	1.03	24	0.010	30	0.9

Table 4.8 Design parameters for column EXP4

EXP 4											
Adsorbent weight g	Ts min	Tb min	LUB cm	Total adsorption at Tb mg	qb mg/g	Total adsorption at Ts mg	qs mg/g	Z cm	flowrate L/min	C <sub>0</sub> mg/L	C* mg/L
1200	1980	488	18.08	345.26	0.29	1400.85	1.17	24	0.025	30	1.7
1200	3820	928	18.17	403.40	0.34	1660.55	1.38	24	0.015	30	1.02
1200	6820	1428	18.97	416.98	0.35	1991.44	1.66	24	0.010	30	0.8

TS: time of saturation (min), Tb: break through time (min), LUB length of unused bed (cm), qb: adsorption capacity at breakthrough time (mg/g), qs : adsorption capacity at saturation time (mg/g), Z: height of biochar in the column (cm). C<sub>0</sub>: inlet concentration of SMX (mg/L), C\*: concentration at equilibrium (mg/g).

#### 4.2.4. Breakthrough and exhaustion time for column experiments

According to the experiments, the adsorption capacity will increase by decreasing the flow rate. The optimum flow rate was found to be 10 mL/min, according to the results of each experiment. The breakthrough curve derived from the column experiments is shown in Figure 4.4. The breakthrough time is considered the point where the effluent concentration (C<sub>t</sub>) over influent concentration (C<sub>0</sub>) is 0.2, and it was 32, 183, 1089, and 1428 minutes for experiments 1, 2, 3, and 4 respectively at a flow rate of 10 mL/min.

When the breakthrough time is reached before one hour, this might be due to the high initial concentration and inadequate bed depth, which contributed to an oversupply of ions, creating saturation of accessible sites (Maheshwari and Gupta, 2016). Inadequate bed depth widens the mass transfer zone and speeds up the breakthrough time (Ahmad and Hameed, 2010). Axial dispersion is the primary process of mass transfer at lower bed depths, according to Qaiser et al. (2009).

The saturation time or exhaustion time (T<sub>s</sub>) was calculated as the period when the effluent concentration reached 90 percent of influent concentration, and it was 440, 1230, 4240, and 6820 minutes for experiments 1, 2, 3, and 4, respectively. Insufficient bed depth may result in a short residence duration, preventing adsorbate from diffusing across the bed (Qaiser et al. 2009). According to the present study, the breakthrough time and exhaustion time have

increased by increasing the bed depth. Juela et al. (2022) reported the breakthrough curves demonstrating the predicted behavior as bed height increased; the curves showed a propensity to move to the right over time as bed height increased.

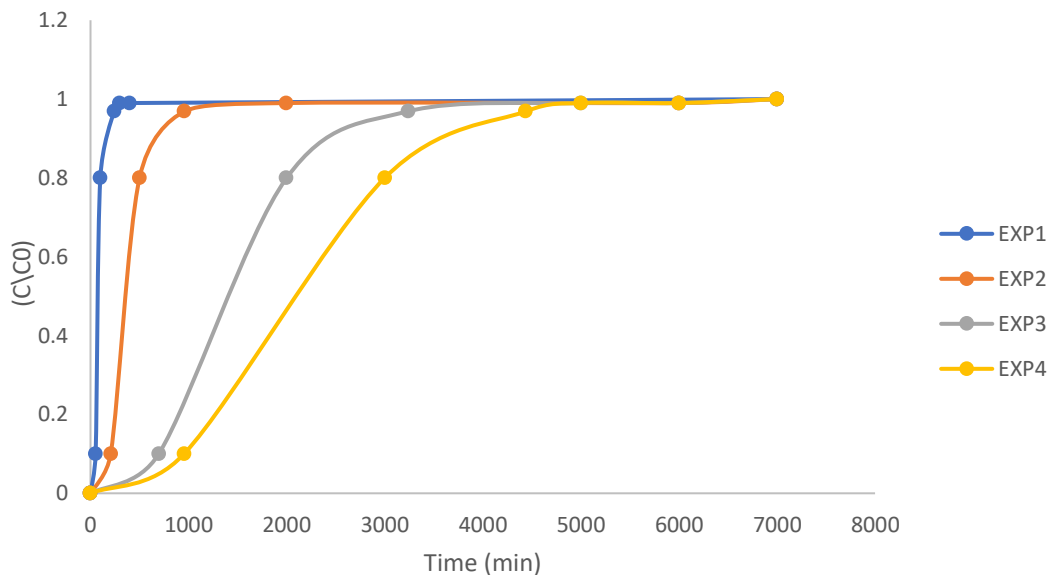


Figure 4.4 Break through curve for column experiments, EXP1 (Method 2 preparation, G:S:BCH= 12:8:4), EXP2 (Method 2, 0:14:10), EXP3 (Meth 2, 0:0:24), EXP4 (Meth 3, 0:0:24).

According to the results, the best condition for bed capacity occurred for the height of 24 cm and flow rate of 10 mL/min, especially in experiment 3 with 1.03 mg/g and experiment 4 (CO<sub>2</sub> exposed biochar) with 1.66 mg/g adsorption capacity. By increasing the bed height, adsorption capacity has been increased. In such a case, the adsorbate molecules have enough contact with the adsorbent within the column when the bed height (quantity of adsorbent increased). The availability of extra binding sites, which increases the adsorption area of the adsorbent, is credited with these results (Feizi et al., 2021).

Heidari et al. (2020) investigated the effect of biochar fixed-bed column in removing pharmaceuticals and heavy metals. In their study, the inlet concentration of venlafaxine was adjusted to be 30 mg/L; according to the results, the adsorption capacity at full bed exhaustion was 3.52 mg/g for venlafaxine removal. According to the present study, when the bed height is fixed at 24 cm, the adsorption capacity has been increased for the media exposed to the CO<sub>2</sub> in experiment 4.

#### 4.2.5. SMX removal in biochar column experiments

As can be seen in Figure 4.5, by increasing the biochar height from experiment 1 to 3, a significant percentage of the pollutant has been removed, this reduction in SMX has been meaningfully increased in experiment 4, where the biochar height is similar to the height in experiment 3, but the biochar filed in the column was activated with CO<sub>2</sub>. According to the studies, increasing the adsorbent height provides more time for the adsorbates to diffuse into the pores of the adsorbent particles. The flow rate and the initial concentration of the adsorbate are constant. (Marzbali and Esmaili, 2017).

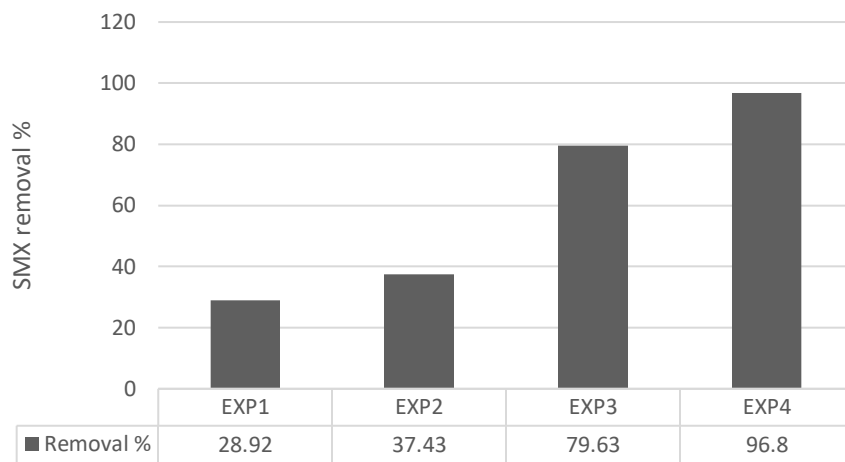


Figure 4.5 SMX removal in column experiments, EXP1 (Method 2 preparation, G:S: BC= 12:8:4), EXP2 (Method 2, 0:14:10), EXP3 (Method 2, 0:0:24), EXP4 (Method 3, 0:0:24).

#### 4.2.6. Metal removal in biochar column experiments

According to the results presented in Table 4.9, the metal removal has increased by increasing the volume of biochar (bed height) from experiments 1 to 3. Again, in experiment 4, there is an obvious increase in adsorption, where the height is similar to experiment 3 but Method 3 of the biochar preparation has been used. Sun et al. investigated the efficiency of food waste compost and wood waste biochar in removing metals from synthetic stormwater runoff in a bioretention system. Their results indicated that biochar was more recalcitrant and desirable in field-scale bioretention systems compared to the other bio-amended materials. Columns amended with biochar removed more than 50-70% of metals included in influent, whereas iron-oxide coated sand was much less effective. Enhanced metal removal by biochar owing to

the abundance of active sites (Sun et al., 2020)

Table 4.9 Metal removal by biochar in column experiments: EXP1 (Method 2 preparation, G:S: BCH= 12:8:4), EXP2 (Method 2, 0:14:10), EXP3 (Method 2, 0:0:24), EXP4 (Method 3, 0:0:24).

Experiments	EXP1	EXP2	EXP3	EXP 4
	( CO <sub>2</sub> activated biochar)			
Metals	Removal (%)			
<b>Mn</b>	ND	ND	80.5	69.9
<b>Zn</b>	ND	ND	48.1	53.2
<b>Pb</b>	ND	ND	50.5	28.7
<b>Cr</b>	ND	ND	6.4	20.2
<b>Co</b>	ND	ND	ND	9.4

#### 4.2.7. Chemical pollutants removal in biochar column experiments

According to the results presented in Table 4.10, column tests demonstrated satisfying removal of pollutants in the effluent. However, removing any contaminants can be affected by another (J.Li et al., 2019). According to the study conducted by J.Li et al. (2019) phosphate removal by sludge-base biochar, showed high efficiency, however, by increasing the pH, phosphate removal effectiveness drops (57.5% at pH = 3 and 36% at pH =12).

In addition, according to their results, the presence of SO<sub>4</sub><sup>-2</sup> and HCO<sub>3</sub><sup>-</sup> could negatively affect phosphate removal (J. Li et al., 2019). Thao et al. (2021) examined the adsorption of ammonium, nitrite, and nitrate onto rice husk biochar. According to their results, biochar can be used for nitrogen removal because its adsorption capacity towards ammonium, nitrite, and nitrate ranges from 0.10-0.24 mg/g, which adequately satisfies water quality control (Thao et al., 2021).

Table 4.10 Pollutant removal by column experiments in %: EXP1 (Method 2 preparation, G:S: BCH= 12:8:4), EXP2 (Method 2, 0:14:10), EXP3 (Method 2, 0:0:24), EXP4 (Method 3, 0:0:24).

Experiments	EXP1	EXP2	EXP3	EXP4
Item	Removal (%)			
Chloride	6.78	9.41	15.53	22.42
Nitrit	5.23	8.96	12.41	23.36
Nitrate	9.46	11.27	17.42	30.29
Ammonia	7.45	12.34	21.4	34.5
Bromide	16.7	38.48	68.5	99.5
Phosphate	9.33	11.45	12.5	27.12
Sulfate	7.48	9.8	14.23	22
Sodium	3.5	7.45	11.9	14.96
Calcium	7.43	12.11	18.9	36.94
Magnesium	13.8	27.5	42.9	64.56

#### 4.2.8. COD, TSS and turbidity removal in biochar column experiments

According to the results presented in table 4.11, biochar was also valuable for the simultaneous removal of COD, TSS, and turbidity. As the results show, more removal has occurred by increasing the volume (height) of biochar. Furthermore, experiment 4, using biochar activated with CO<sub>2</sub>, showed better results than experiment 3, using the same volume (24 cm height).

Kurshid et al. (2021) studied adsorptive removal of COD from produced water using tea waste biochar, where biochar was prepared by modifying tea waste with single (pre-pyrolysis) and combined (pre and post pyrolysis) treatments using phosphoric acid and hydrogen peroxide solutions. Their results showed a noticeable COD reduction,  $89.35 \pm 0.5\%$  and  $95.5 \pm 0.5\%$  for single and combined modified biochar, respectively. The study offers a successful approach toward a high level of COD removal from WWTP. Qaisrani et al. (2021) investigated the treatment of palm oil mill effluent using activated biochar from a gasifier's residue. Their results indicated the following reductions: COD 79.1%, BOD 85.62%, color 94.12%, TDS 82%, TSS 78.53%, and turbidity 96%.

Table 4.11 COD, TSS and turbidity removal in column experiments, EXP1 (Method 2 preparation, G:S:BCH= 12:8:4), EXP2 (Method 2, 0:14:10), EXP3 (Method 2, 0:0:24), EXP4 (Method 3, 0:0:24).

Removal of elemnts %	EXP1	EXP2	EXP3	EXP 4 ( CO <sub>2</sub> activated biochar)
<b>COD</b>	39	43	52	69
<b>TSS</b>	29	33	48	56.6
<b>Turbidity</b>	28	33	42	68.75

### 4.3. Biochar tests

#### 4.3.1. Effect of CO<sub>2</sub> application on heavy metal components of the biochar

According to the results, after exposing biochar to CO<sub>2</sub>, the metal content has been reduced in biochar. This shows that CO<sub>2</sub> has a positive effect on metal removal from biochar (Tab. 4.12). T. Lu et al. (2016) investigated the characteristic of heavy metals (Pb, Zn, Cu, Cd, Cr, Ni and As) in biochar derived from sewage sludge at different pyrolysis temperatures, their findings revealed that the heavy metal concentrations in biochar were greater than in sludge and that heavy metal enrichment in biochar increased with pyrolysis temperature.

The concentration of Pb, Zn, Ni, Cd, As, Cu, Cr in their study have been reported as 3740, 735, 72.4, 169, 26, 172 and, 100 mg/kg, respectively. Although the influence of pyrolysis temperature on chemical speciation distribution, leaching toxicity, and bio-available heavy metal concentrations in biochar was inconclusive, some metals (Al, Fe, Mn) in biochar might pose a reduced risk of soil and groundwater pollution than sewage sludge (T. Lu et al., 2016). In the present study, CO<sub>2</sub>, used in biochar preparation, has a significant effect on heavy metal reduction in the biochar.

Table 4.12 Heavy metal reduction in biochar after activation by CO<sub>2</sub>

Heavy metals in biochar (mg/kg)	BCH-NO CO <sub>2</sub>	BCH-CO <sub>2</sub>	Reduction %
Al	41994.81	36241.23	13.70
Cr	9.65	7.16	25.78
Mn	268.39	260.61	2.90
Fe	6341.12	2163.04	65.89
Co	2.24	2.10	6.17
Ni	25.89	28.83	No reduction
Cu	14.13	0.91	93.57
Zn	374.16	183.02	51.09
As	0.32	0.19	39.68
Cd	0.07	0.06	6.96
Sb	0.05	0.08	No reduction
Pb	0.81	0.37	54.56

#### 4.4. Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDX), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

In order to visualize the surface morphology of the biochar at each step of preparation, before and after adsorption (when the biochar becomes exhausted), scanning electron microscopy (SEM) analysis was applied. Then, for defining the atomic percentage of different elements in the biochar samples, energy dispersive X-ray spectroscopy was used. All analyses have been accomplished with a Philips XL-30 microscope.

##### 4.4.1. Scanning biochar before treatment

The preparation method significantly impacts biochar properties; according to J. Zhang et al. (2020), deashing biochar with hydrochloric or hydrofluoric acid improves the pore characteristics of sludge-based biochar and promotes the activating impact of potassium acetate thereafter. Figure 4.6 shows SEM images of biochar before treatment, where Figure 4.6 (a) is the biochar prepared with Method 1. As can be seen, the biochar surface is still uneven and dispersed, with some regions displaying granular morphology and others showing a



fragmented structure. Such structure might be due to minerals in the sludge decomposed into the granular matrix, which has not been removed entirely through washing and then adhering to the biochar's surface.

Figure 4.6 (b) is biochar prepared with Method 2. As can be seen, many granular materials vanished, revealing a cupped structure with numerous pore structures, which most likely emerged. Due to the HCl washing, many inorganic minerals that had previously accumulated on the surface or in the biochar pores have been removed. The surface morphology of biochar after washing with Method 2 altered dramatically. This means that hydrofluoric acid, through Method 2 of washing, not only interacts with more inorganic minerals and removes more materials from the pores and surface but also etches the biochar's surface and generates a better lamellar and pores structure.

Biochar prepared with Method 3 and activated by CO<sub>2</sub> (Figure 4.6 (c)) reveals that initial particles on the surface of biochar are smaller after activation, and the flat material tends to split into smaller structures, exposing more pore structures and a tiny amount of flake structures. This might be due to the CO<sub>2</sub> reaction with granular and flattened compounds, which increases carbon available in the activated biochar. As can be seen, activated biochar demonstrated a spherical structure.

According to (Tran et al., 2020), spherical biochar has established a more significant specific surface area than the other type of biochar, as well as a substantial total pore volume. By improving the Method of preparation, the carbon atomic percentage has been increased. According to Figure 4.6 (a), the carbon atomic percentage is 60%, while this amount will be increased to 64% in Method 2 of washing in Figure 4.6 (b). For activated biochar, carbon atomic percentage has been increased significantly to 80%, which shows the impact of CO<sub>2</sub> on the carbon percentage after activation.

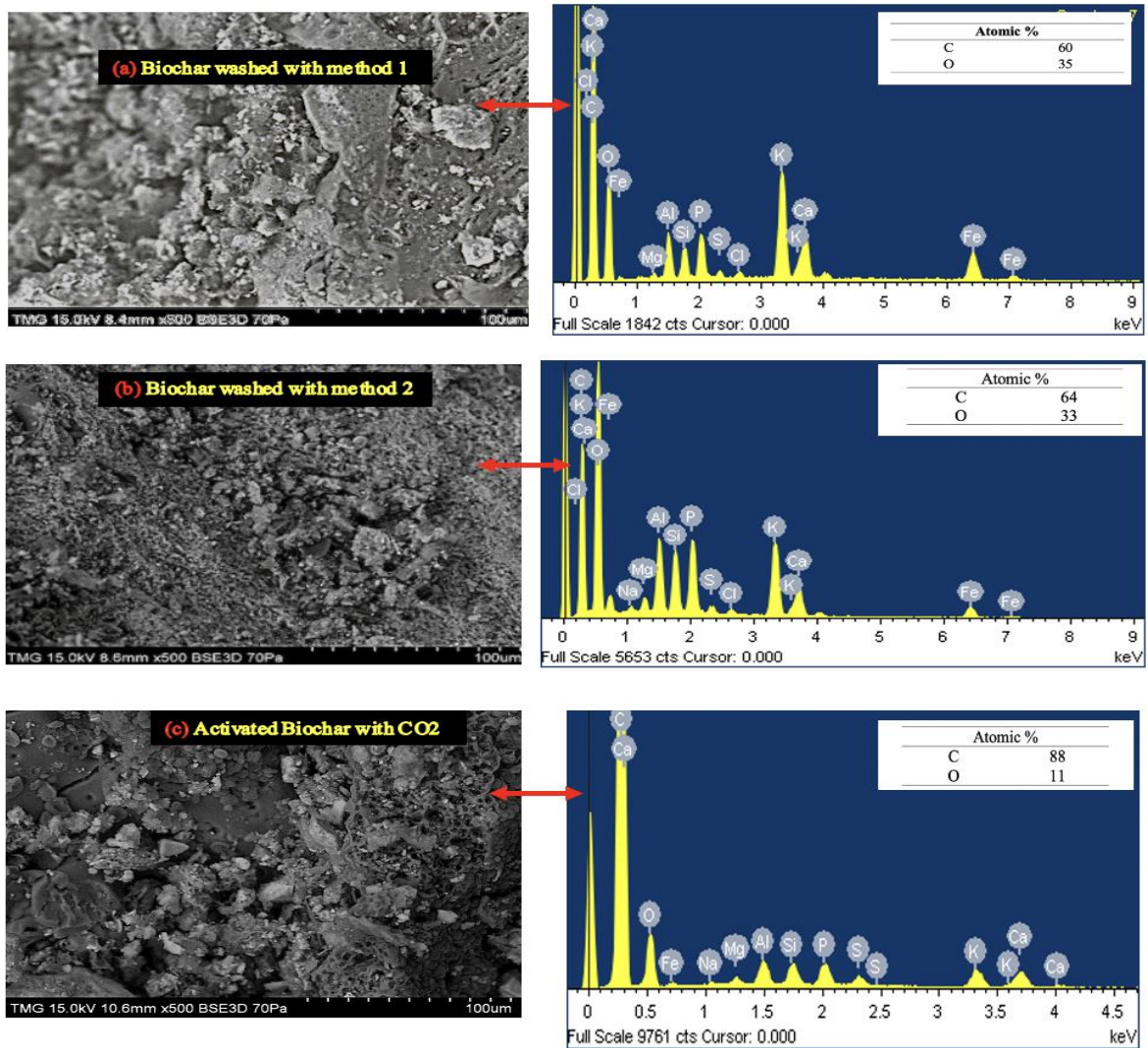


Figure 4.6 (a) Biochar washed with Method 1, (b) Biochar washed with Method 2. (c) Activated biochar with CO<sub>2</sub>

#### 4.4.2. Scanning biochar after treatment

To investigate the contribution of different sections of the column's material in the filtration, each section of the column was scanned through Scanning Electron Microscopy (SEM) after exhaustion. To this end 24 cm of total biochar column height of the best performance of the column filtration (EXP4) was divided into six layers named S1 to S6 of 4cm each. Then each section was scanned through SEM separately. The results for Scanning Electron Microscopy for S1to S6 have been presented in in Figure 4.7. As can be seen the bigger particles are precipitated in the top layers.

The same situation can be seen in the S2 zone, where still big particles are clogging the porous

media. In a study by Wang et al. (2022), chlorinated secondary effluent injected into saturated porous media which was composed of high-purity quartz sands. The column experiment was carried out and modeled using a numerical model that was designed to anticipate the progression of physical clogging. Certain typical inorganic and organic markers were measured at different periods and in different column sections. According to their study, organic floc particles were mostly preserved in the first 3 cm of the column (Wang et al., 2022).

By entering the S3 zone, as more big particles have been precipitated in the upper layers, more void sections are apparent in S3 zone. By entering S4, fine particles saturate the media. In S5, the particle size becomes smaller until the finest particles are displaced in S6.

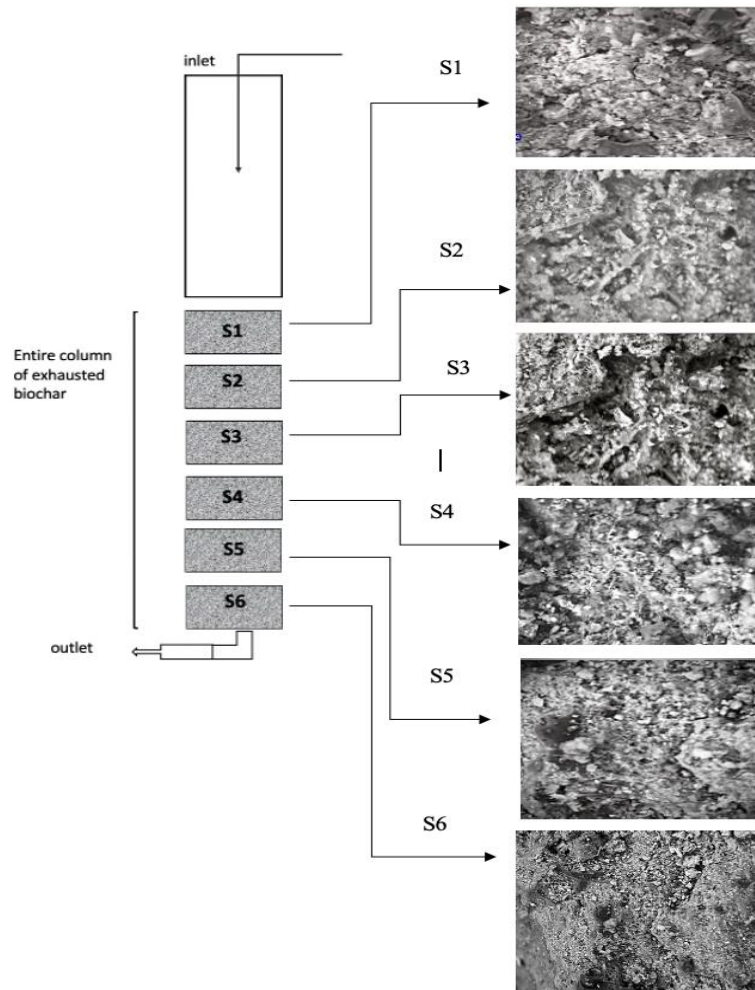


Figure 4.7 Different biochar column layer scanning after treatment

Inductively Coupled Plasma Mass Spectrometry (ICPM) analyses results showed that 92-97 % of metals settle in the last layer (S6), except Mn, with 60 % precipitation in the upper layers. The results have been presented in Table 4.13.

Physical adsorption, ion exchange, electrostatic adsorption, precipitation, complexation, and reduction are all essential adsorption processes according to extant studies; however, biochar's heavy metal adsorption activity is mostly determined by its specific surface area, the number of surface-active functional groups, cation exchange capacity, and acidic groups have been introduced as the main factors for electrostatic attraction and surface complexation processes for metal removal. The adsorption of heavy metals by biochar, on the other hand, is not due to a single process but rather to a mixture of many processes (Sun et al., 2020).

Lu et al. (2019) investigated the mechanism of  $Pb^{2+}$  adsorption by sludge biochar and discovered that ion exchange and surface complexation of functional groups were involved in addition to surface precipitation. According to their study approximately 38.2–42.3 % of  $Pb^{2+}$  was removed from the surface of biochar by complexation with organic functional groups (single bond OH, single bond COOH), whereas 57.7–61.8 % of  $Pb^{2+}$  was adsorbed by minerals in the biochar (H. Lu et al., 2012).

Table 4.13 Heavy metals removal in different layers of the biochar column

Metals (mg/kg)	BCH-CO <sub>2</sub> after treatment: layer 1-5	BCH-CO <sub>2</sub> after treatment: layer 6	Total layers
Al	843.60	27276.43	28120.04
Cr	0.57	6.59	7.17
Mn	179.41	117.95	297.36
Fe	32.43	1048.50	1080.93
Co	0.21	2.36	2.56
Ni	0.74	8.56	9.30
Cu	0.77	8.84	9.61
Zn	18.96	218.08	237.05
As	0.04	0.45	0.49
Cd	0.00	0.04	0.04
Sb	0.00	0.04	0.04
Pb	0.04	0.41	0.44

## 5. Conclusion and future work

General conclusions from the research outcomes, contribution and future work are presented in Chapter 5.

### 5.1. Conclusions

- 1) Three methods were tested for preparing adsorbing materials, and the adsorption performance of each material was investigated. Method 3 has been proven to be the best method for biochar preparation to remove pharmaceutical compounds (SMX) from real wastewater treatment plant's effluent with 1.66 mg/g adsorption capacity and 96.8 % removal efficiency.
- 2) Using biochar as an adsorbent produced from wasted material is a sustainable approach for removing emerging micropollutants from WWTP effluent. Method 3 used CO<sub>2</sub> (usually generated by treatment facilities) and biosolids locally produced by the same facilities. If WWTP can conduct pyrolysis on-site, the entire process of biochar production and filter construction can be done in-situ. Such approach demonstrates new sustainable WWTP management. The results showed that using CO<sub>2</sub> as an activator can increase the adsorption capacity of SMX from 1.03 mg/g to 1.66 mg/g and removal efficiency from 79.63% to 96.8 %.
- 3) According to the results, the new approach for biochar activation is an effective way to improve the quality of a wastewater treatment plant effluents in the province of Quebec (Canada) to protect water resources (e.g., water quality of the St. Lawrence River) against pharmaceuticals in addition to metals, organic and inorganic pollutants.
- 4) Based on the column experiments, major design factors for an efficient removal of pharmaceuticals were bed capacity (BC), breakthrough time (T<sub>b</sub>), and exhaustion time (T<sub>S</sub>), which were determined for scaling up the system.
- 5) The total biochar column of 24 cm was divided into six horizontal sections of 4cm. Then, each section was scanned with SEM, which permitted to find possible displacement of fine particles within the column. Thus, bigger particles remained at the top layers. Third section (S3 zone) contained bigger particles, while more voids were seen in lower layers. The number of fine particles increased toward lower sections until S6, showing displacement of fine particles during the filtration process. It is expected that fine particles, having higher surface area, can adsorb more

pollutants of concern. Considering all above, it could be speculated that the lower part of the column only should be backwashed or replaced with a new biochar material.

6) The ICPM analysis also showed that 92-97% of metals were adsorbed in the last section, except Mn, having 60% of precipitation in the upper section of the column. Physical adsorption, ion exchange, electrostatic adsorption, precipitation, complexation, and reduction are all essential adsorption processes according to extend studies. It is assumed that this biochar's heavy metal adsorption activity is mostly determined by adsorbent-specific surface area, the number of surface-active functional groups, and cation exchange capacity.

7) Method 3 introduced acid functional groups which contributes to electrostatic interactions. It is not due to a single process but a mixture of many.

8) According to the findings, metal content in biochar was decreased following exposure to CO<sub>2</sub>. This demonstrates that CO<sub>2</sub> has a beneficial influence on removing metals from biochar.

9) Overall, waste-based biochar is an adequate material for a filtration/adsorption facility dedicated to upgrading the quality of WWTP effluent before its discharge to the environment (e.g., St Lawrence River)

## **5.2. Contribution**

The thesis brought the following contributions:

1) Formulation of biochar based on wasted materials such as biosolids from WWTP, woodchips from the forest industry, and CO<sub>2</sub> generated in WWTP which was a unique, and sustainable approach to the production of filtration/adsorption materials.

2) Defining a method of upgrading biochar material produced by pyrolysis at full scale, characterized by ununiform mixing, different temperature distribution, and ununiform granulation.

3) Designing and optimizing a filtration/adsorption unit for the removal of micropollutants from WWTP effluents.

### **5.3 Future work**

Future work concerning waste-based biochar should focus on the following activities:

- 1) To demonstrate waste-base biochar efficiency in removing micropollutants in a full scale, it is necessary to test biochar using a pilot-scale installation in a real wastewater treatment plant. Thus, pilot scale facilities must be built based on this thesis outcomes.
- 2) To conduct electrochemical removal of metals adsorbed to biochar since they would permit recycling of both metals and biochar. According to the present research, metals are adsorbed to the fine fraction precipitate (the last filtration column segment).
- 3) To improve the sustainability of the system, biochar regeneration is an option that can be considered in the future.
- 4) To study the recovery of heavy metals from leached after washing biochar exposed to CO<sub>2</sub>.

## Appendix

### Particles distribution of materials filling the filtration columns in EXP 1 - 4

**Table A-1: Granular distribution of gravel**

Sieve No:	Sieve size:	Mass remained on each sieve (g)	Percent remained %	Percent cumulative %	Percent passed %
# 16	1.88 mm	1.02	1.02	1.02	98.98
# 30	600 $\mu\text{m}$	14.36	14.36	15.38	84.62
#50	300 $\mu\text{m}$	39.85	39.85	55.23	44.77
# 140	105 $\mu\text{m}$	36.55	36.55	91.78	8.22
# 200	75 $\mu\text{m}$	2	2	93.78	6.22

**Table A-2: Granular distribution of sand**

Sieve No:	Sieve size:	Mass remained on each sieve (g)	Percent remained %	Percent cumulative %	Percent passed %
# 8	2.38 mm	1.18	1.18	1.18	98.82
# 16	1.88 mm	55.13	55.13	56.31	43.69
# 30	600 $\mu\text{m}$	39.65	37.65	93.96	6.04
#50	300 $\mu\text{m}$	4.04	4.84	98.8	1.2



**Table A-3: Granular distribution of Biochar**

Sieve No:	Sieve size:	Mass remained on each sieve (g)	Percent remained %	Percent cumulative %	Percent passed %
# 16	1.88 mm	1.08	1.08	1.08	98.92
# 30	600 μm	24	24	25.08	74.92
#50	300 μm	18.56	18.56	43.64	56.36
# 140	105 μm	23.18	23.18	66.82	33.18
# 200	75 μm	7.48	7.48	74.3	25.7
# 325	45 μm	5.21	5.21	79.51	20.49

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