

Sustainable management of feedlot and agricultural runoff through bio-inspired bioreactor-constructed wetland configuration for high-quality reuse

by

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B.S., Federal University of Santa Maria, 2016

M.S., Federal University of Santa Maria, 2019

AN ABSTRACT OF A DISSERTATION

submitted in partial fulfillment of the requirements for the degree

DOCTOR OF PHILOSOPHY

Department of Biological and Agricultural Engineering
Carl R. Ice College of Engineering

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Abstract

Pollution from animal wastes is a threat to water resources. Animal agriculture generates substantial amounts of manure, typically collected and stored in wastewater lagoons on farms. Insufficient treatment and disposal of animal manure results in potential runoff and leaching of waste into surface and groundwater, causing environmental damage (e.g., algal blooms and fish kills) and contaminating drinking water in many rural areas. As global concerns regarding water security and environmental pollution continue to rise, new economic, sustainable solutions for runoff management and wastewater treatment are crucial. The ultimate goal of this research is to assess the efficiency of an innovative configuration of anaerobic membrane bioreactor (AnMBR) technology and constructed wetlands (CWs) systems to provide a sustainable, resilient management system for agricultural wastewaters. Additionally, this dissertation explores the broader issue within ecological engineering by evaluating the impact of using different terms on the field's advancement and communication through a bibliometric analysis. Moreover, this study investigated the capacity of eastern red cedar biochar to decrease the concentrations of target antibiotics that have been extensively used in the swine industry, such as tetracycline, oxytetracycline, chlortetracycline, sulfadiazine, and sulfamethazine. Finally, preliminary CW designs were evaluated using HYDRUS CW2D to better assess system variability and function.

A bibliometric analysis was performed using the bibliometrix package in RStudio on environmental engineering, ecological engineering, nature-based solutions, engineering with nature, constructed wetlands, green engineering, and ecological systems. The results showed that these terms developed over different periods with a recent increase in the scientific literature. Scientific production in environmental engineering and ecological systems started in the early 1960s, gaining force in the 1990s and reaching a peak in 2020 with 4779 and 1398 publications,

respectively. The growth of ecological engineering is stagnant with first publications in 1971 and reaching a peak in 2018 with 145 publications. Nature-based solutions is becoming more popular with the first publication in 2009 and thriving in 2020 with 323 publications. Engineering with nature, on the other hand, was dated in 2001, reaching a peak of 5 in 2018. Constructed wetlands and green engineering started in 1985 and 1991, reaching a peak in 2020 with 818 and 55 publications, respectively. The term constructed wetlands was chosen as part of the ecological engineering field. However, the most substantial connection appears to be with environmental engineering. Environmental engineering remains the predominant area, with nature-based solutions gaining popularity instead of ecological engineering.

To remove antibiotics from swine wastewater, eastern red cedar biochar was produced by pyrolysis from eastern red cedar at 450 °C. The sorption tests were performed by mixing biochar and a solution containing each antibiotic in 100, 300, 600, and 900 µg L⁻¹ concentrations. The results indicate that red cedar biochar was able to effectively remove up to 99.93% of tetracycline, 96.23% of oxytetracycline, 98.28% of chlortetracycline, 76.4% of sulfadiazine, and 78.6% of sulfamethazine at the lowest concentrations. The removal efficiency at higher concentrations declined up to 83.52%, 47.23%, 64.16%, 69.8%, and 58.4% for tetracycline, oxytetracycline, chlortetracycline, sulfadiazine, and sulfamethazine, respectively. The adsorption capacity and mechanisms were significantly influenced by each antibiotic's chemical properties and the biochar's surface properties. Overall, the results highlighted the potential utilization of eastern red cedar biochar as filter media in CWs systems.

Numerical simulations were conducted to assess the capacity of CWs to remove nutrients from AnMBR permeate varying NH₄⁺, P, and chemical oxygen demand (COD) concentrations and temperature conditions (10, 20, 30, and 40 °C). The simulations were conducted using HYDRUS

software with the CW2D module. The results supported the assumption that the given CWs design can be an efficient polishing step for AnMBR permeate, removing more than 90% of NH_4^+ and P, further confirmed with experimental measurements. The effectiveness of this design relies on the natural processes for nutrient removal that can be optimized by altering nutrient and COD loading rates from the AnMBR system. When AnMBR systems face unexpected failures or technical issues, the integration of CWs provides a reliable contingency plan, ensuring a practical and resilient wastewater treatment process. The findings from this research offer significant promise for developing cost-effective and environmentally friendly solutions for the treatment and reuse of agricultural runoff, contributing to the broader goals of sustainable water management and agricultural practices.

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Dedication

I dedicate this dissertation to my family – To my parents, Gildo and Maria, brother Jovani, and husband Carlos, whose unwavering support and encouragement have been the driving force behind this academic journey.

Chapter 1 - Introduction

The world livestock production has shifted towards larger and more extensive farms over time, driven by the industrialization of the food system and economic growth (Lowder et al., 2019). The concentrated animal feeding operation (CAFO) system allows the growth of thousands of animals on strict diets, where animals are fed with high nutrient diets, including nitrogen-rich foods (Ghaly and Ramakrishnan, 2015). In the U.S., CAFOs are estimated to produce over 40% of the country's livestock, with extensive facilities raising more than 125,000 broiler chickens or 2,500 pigs each (Copeland, 2010; USEPA, 2011; Handan-Nader and Ho, 2019). Animal agriculture results in the production of large amounts of manure. According to the U.S. Census data and USDA livestock reports, it can be estimated that animals generate somewhere between 3 and 20 times the amount of manure annually compared to humans, as much as 1.2 to 1.37 billion tons (wet weight) (American Society for Microbiology, 1998; USEPA, 2003; USEPA, 2004; USEPA 2005).

Large volumes of wastewater and stormwater runoff can be generated at CAFOs, typically collected and stored in farm wastewater lagoons. CAFO lagoons function as holding reservoirs or anaerobic reactors, and waste effluent usually receives no further treatment before land application (Hutchins et al., 2007). Additionally, these lagoons are prone to leakage, contributing to the pollution of freshwater sources (Zahoor and Mushtag, 2023). Kansas is not one of the country's top CAFO producing states, however, remediation of agricultural runoff under CAFOs in Kansas has been projected to cost taxpayers \$56 million. Based on this data, a rough estimate of the total cost of soil remediation under U.S. CAFOs could approach \$4.1 billion (Gurian-Sherman, 2008). Therefore, suitable animal waste and agricultural runoff management is a severe issue for the U.S. administration and scientific community (Kumwimba et al., 2023).

Swine manure accounts for about 40-60% of livestock wastewater worldwide and contains high concentrations of potential water contaminants, such as organic matter, nitrogen, phosphorus, pathogens, trace elements (Pb, Cu, Zn, Cr, and Hg), and other compounds of concern (Zhou et al., 2015; Wang et al., 2016). Swine wastewater contains approximately 10 times higher levels of $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ in comparison to municipal wastewater (Vanotti et al., 2017; Zheng et al., 2018; Cao et al., 2019). Furthermore, swine facilities have been identified as a significant source of natural hormones and antibiotics in the environment (Kolodziej et al., 2004; Hutchins et al., 2007; Bradford et al., 2008; Zheng et al., 2008; Zheng et al., 2012; Zheng et al., 2013). In the last decades, worldwide utilization of antibiotics for both humans and animals has been on the climb. Globally, the consumption of antibiotics in animal feeds increased by 9% from 2017 to 2018 (Food and Drug Administration, 2019). Currently, traditional wastewater treatment technologies for swine wastewater, such as anaerobic digestion, are not able to meet water quality requirements for reuse purposes (Li et al., 2019). Thus, there is a critical need to select a treatment technology that is highly efficient and has a reasonable cost of operation for application in rural areas (Liu et al., 2013).

Environmental technologies, such as the anaerobic membrane bioreactor (AnMBR), have been attracting interest due to its ability to retain solid biomass of the waste and microorganisms within the reactor by integrating anaerobic biodegradation and membrane filtration (Su et al., 2019). This technology allows the solid biomass to be maintained in the digester while the liquid phase passes at a higher rate. AnMBR has demonstrated remarkable efficacy in removing pollutants such as antibiotics and organic materials while recovering energy with biogas production and digestate reuse (Pu et al., 2022). Moreover, the AnMBR system offers the potential for mobilizing nutrients for subsequent controlled capture of nitrogen (as ammonium) and

phosphorus (as orthophosphate) using techniques such as coagulation, flocculation, chemical precipitation, and ion exchange (Kannan and Parameswaran, 2021).

Alternatively, ecological wastewater treatment technologies have been developed to integrate human society with the environment, offering mutual benefits, and they utilize the natural microbial and physicochemical processes of terrestrial and aquatic plants to treat wastewater (Mitsch and Jørgensen, 1989; Shao et al., 2013; Su et al., 2019). As a typical ecological technology, constructed wetlands systems (CWs) have many advantages, including low costs, simple operation and maintenance, lower pollution production, and several ecosystem service benefits (Shao et al., 2013). CWs can transform and remove pollutants (organics, nutrients, trace elements, etc.) through physical, biological, and chemical processes. Furthermore, the main characteristics of CWs (i.e., the presence of water and vegetation) make them suitable for creating a new ecological habitat or restoring a degraded ecosystem by attracting wildlife species, especially birds, and establishing a green area. These systems can also be utilized as a source of food and fiber and as public recreation and education sites (Knight, 1997; Sundaravadiel and Vigneswaran, 2001; Stefanakis et al., 2014; Stefanakis, 2019).

Constructed wetlands have been used and studied for several decades to treat urban sewage and several kinds of industrial wastewater (Vymazal, 2007; Reyes-Contreras et al., 2012). These systems have demonstrated their efficacy in removing various compounds, including emerging pollutants such as antibiotics (Matamoros et al., 2005; Conkle et al., 2008; Park et al., 2009; Reyes-Contreras et al., 2012). The coexistence of several micro-environments in CWs allows for a variety of microbiological communities, which might offer different metabolic pathways to degrade antibiotics (Hijosa-Valsero et al., 2010). CWs are attractive because they show a high capacity to remove organic micropollutants, consuming little energy and restoring the ecological function of

natural systems. In addition, CWs are proven to be efficient in eliminating biochemical oxygen demand, total suspended solids, chemical oxygen demand, total nitrogen, and total phosphorus (Wang et al., 2019). In this context, integrating CWs as a final polishing step in conjunction with advanced systems such as the AnMBR appears as a promising and sustainable approach for treating swine wastewater and agricultural runoff, improving wastewater quality while enhancing ecosystem services. The combination of environmental technologies with nature-based solutions demonstrates the potential to address the pressing challenges of wastewater treatment and resource recovery in CAFOs in an eco-friendly and economically viable manner. Thus, research is needed to understand this synergy and the removal of target compounds from swine wastewater. With this understanding, systems can be tailored and optimized for the efficient treatment of each specific pollutant.

1.1. Constructed wetlands approach in environmental and ecological engineering

Ecological engineering is defined as “the design of sustainable ecosystems that integrate human society with its natural environment for the benefit of both” (Mitsch and Jorgensen, 2003). The goals of ecological engineering are the restoration of ecosystems that have been substantially disturbed by human activities, such as environmental pollution or land disturbance, and the development of new sustainable ecosystems that have both human and ecological value (Mitsch and Jørgensen, 2003). Ecological engineering has evolved as a prominent field with global significance, particularly in the context where resources are dramatically diminished (Mitsch, 2012; Tien et al., 2021).

Otherwise, the American Academy of Environmental Engineers defines environmental engineering as the branch of engineering concerned with applying scientific and engineering

principles for protecting human populations and both local and global environments from potentially deleterious effects of natural and human activities and improving environmental quality. The main goal of environmental engineers is to restore, protect, improve, and provide (Šalić and Zelić, 2018). Environmental engineering is an extension of the engineering process that considers the environment in many relevant aspects, requiring models to be constructed of the action to be undertaken, considering safety factors only at the anthropomorphic level, not at the level of the safety of the ecosystem. This fact puts environmental engineering in a different class from ecological engineering (Allen et al., 2003).

Constructed wetlands are treatment systems that use natural processes involving wetland vegetation, soils, and microbial assemblages to improve water quality, and assist in treatment of an effluent or other water source (USEPA, 2021). CWs functioning will be affected by its components (plants, microorganism communities, and substrate composition) as well as design. Several physical, chemical, and biological mechanisms contribute to eliminating the pollutants in these systems. Among the most dominant processes, there are two biological (biodegradation and phytoremediation) and two physical (photodegradation and sorption) processes (Santos et al., 2019). Wetlands have been identified as one of the most productive ecosystem types. Through photosynthesis, they can actively sequester and accumulate carbon as plant biomass or organic matter in soil (Salimi et al., 2021). Within ecological engineering, CWs have proven to be a green, low-cost, and efficient means of treating polluted water. In this way, the ecosystem services provided by these systems are manifold, including provisioning (water, timber, genetic resources); regulating (air and water quality regulation and purification, pollination); habitat conditioning (nutrient cycling, primary productivity); and cultural services (aesthetics, ecotourism) (Mitsch et al., 2015; Ansari et al., 2016).

In the literature, the use of environmental engineering or ecological engineering approaches sometimes differ and sometimes overlap when connected to CWs. For instance, Miksch et al. (2015) address CWs as a novel environmental engineering technology. According to these authors, CWs are man-made systems, considered to be an alternative to more technically advanced wastewater treatment technologies, envisaged to pursue wastewater treatment intensification (Miksch et al., 2015). On the other hand, García et al. (2020) refer to CWs in the context of the ecological engineering approach, mentioning that generally the remediation of agricultural runoff cannot be conducted with environmental engineering solutions, and, thus, ecological engineering approaches such as CWs are much more suitable.

The frequent connection between environmental engineering and CWs is also noted when environmental engineering addresses the problem, and CWs are seen as the solution. Obarska-Pempkowiak et al. (2015) studied the removal of nitrogen compounds from landfill leachate in pilot CWs. According to the authors, leachate treatment is one of the most challenging and up-to-date problems of environmental engineering, and CWs systems can be an effective treatment (Obarska-Pempkowiak et al., 2015). Papadopoulos et al. (2012) state that organic micropollutants are an environmental engineering challenge CWs encounter. Another example would be the research conducted by Jain et al. (2020), where the authors reviewed the use of CWs to treat wastewater from petroleum refinery and petrochemical plant. These are the major contributors to toxic and recalcitrant organic polluted water, which is a significant concern in the field of environmental engineering (Jain et al., 2020).

One interesting overlap is in the work published by Revell and Anda (2014). They recognize CWs based on ecological design principles, although at the same time, they consider them to be part of the environmental engineering field (Revell and Anda, 2014). Zhang et al. (2021)

claim that CWs were introduced in China in 1987 and used in environmental engineering for over 30 years. According to Zhang et al. (2021), to date, CWs are still a research hotspot in the field of environmental engineering.

On the other hand, Zhang et al. (2009) emphasize CWs systems for wastewater treatment as one of the most important applications in ecological engineering, resulting in the beneficial conservation of natural resources with low capital costs and energy consumption, as well as minimum operation and maintenance expenditures. Ghermandi (2016) mentioned that CWs are natural treatment systems with extensive review of the recreational and educational benefits, and all the benefits are among the characteristics that make ecological engineering (also known as “natural”) unique in the panorama of water and wastewater treatment technologies.

Constructed wetlands are extensively used as an ecological and environmentally friendly wastewater treatment under the ecological engineering technology approach because of the synergistic effects of soil, macrophytes, and microorganisms on the physical, chemical, and biological processes in the system (Wang et al., 2018; Shiao et al., 2022). Chen et al. (2018) state that using CWs as part of ecological engineering technology removes particulates and dissolved contaminants from water. They have various crucial functions that contribute significantly to the sustainability of the Earth, such as water purification, torrent prevention, prevention of saltwater intrusion, and the breeding of natural resources (Chen et al., 2018).

According to Turon et al. (2007), the term ecological engineering implies restoring, creating, and maintaining sustainable ecosystems that have value for both humans and nature. Different knowledge sources (literature and databases), expertise (chemistry and biology of the processes, ecological and environmental engineering, etc.), and points of view (different

stakeholders) provide connections between CWs and environmental or ecological engineering (Turon et al., 2007).

Constructed wetlands play a crucial role in ecological conservation and environmental quality improvement, which may be the leading cause of overlap between the terms. The wetland literature has focused primarily on physical construction and the hydrologic characteristics of wetland function (Chang et al., 2013). Thus, when the focus is to highlight the use of CWs as part of a complex wastewater treatment system, such as an alternative to more technically advanced wastewater treatment technologies, or address environmental engineering pollution problems, the link is between CWs and environmental engineering. However, when focusing on ecosystem functions, ecological conservation, economic benefits, biological diversity, and CWs as a physical environment, the stronger connection is between CWs and ecological engineering.

1.2. Transformation and removal of target compounds from swine wastewater in constructed wetlands

1.2.1. Nitrogen

In CWs, the transformation and removal of nitrogen are accomplished by biological and physicochemical pathways. Biological pathways include ammonification, nitrification, denitrification, biomass assimilation, dissimilatory nitrate reduction, and plant uptake. Physicochemical routes include ammonia volatilization and adsorption (Saeed and Sun, 2012). If the incoming wastewater is rich in organic nitrogen, ammonification initiates the first step of nitrogen transformation in CWs systems. Ammonification is an energy-releasing, complex biochemical process where the amino acids are subjected to oxidative deamination, producing ammonia (NH₃) (Saeed and Sun, 2012). However, ammonia is one of the primary forms of nitrogen

pollution entering CWs, and 90% of the CWs are used to treat wastewater containing ammonia (Tang et al., 2020). Ammonia oxidation is the rate-limiting step in nitrogen removal (Jia et al., 2021). It is widely acknowledged that nitrification/denitrification is a primary pathway for N removal in CWs (Wu et al., 2015; Zhou et al., 2018; Liu et al., 2019a).

In the traditional nitrification-denitrification process dominated by microorganisms, ammonia is first oxidized to nitrite and then to nitrate, and nitrate is next reduced to N_2O or N_2 step by step, leaving the CWs system. Two key types of microorganisms are responsible for ammonia oxidation: ammonia-oxidizing archaea (AOA) and ammonia-oxidizing bacteria (AOB) (Tang et al., 2020). Thus, $\text{NH}_4^+\text{-N}$ is converted to $\text{NO}_2^-\text{-N}$ and then to $\text{NO}_3^-\text{-N}$ in aerobic conditions by *Nitrosomonas* and *Nitrobacter*. Finally, the elimination of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ in CWs takes place through its assimilation in the tissues of plants by absorption through the radical zone. However, the elimination of $\text{NO}_3^-\text{-N}$ occurs mainly through denitrification (Nakase et al., 2019). Denitrification consists of four reduction steps. In the initial step, NO_3^- is reduced to NO_2^- by nitrate reductase. Subsequently, NO_2^- is reduced to nitric oxide (NO) by nitrite reductase, after which NO is reduced to nitrous oxide (N_2O) by nitric oxide reductase. At last, N_2O is reduced to N_2 by nitrous oxide reductase (Li et al., 2019a).

As mentioned above, high nitrification efficiency of ammonia is the first step of total nitrogen removal. However, the presence of dissolved oxygen (DO) to oxidize ammonia to nitrite and then to nitrate cannot significantly improve the total nitrogen removal rate. One direct reason is that high DO inhibits the anoxic bacterial denitrification process. Since the optimal conditions for nitrification and denitrification are not the same, how to strengthen the denitrification after ammonia oxidation should be considered next because denitrifying bacteria are generally

heterotrophic bacteria, conversing nitrate (NO_3^- -N) or nitrite (NO_2^- -N) into nitrogen gas (N_2) (Zhuang et al., 2019).

Biomass assimilation proceeds through the incorporation of NH_4^+ -N in the heterotrophic biomass to fulfill nutrient requirements. Dissimilatory nitrate reduction, which includes reduction of NO_2^- -N and NO_3^- -N to NH_4^+ -N, is generally observed in carbon-rich environments and nitrate-limited conditions. The bacterial population responsible for such transformation belongs to the facultative/strictly anaerobic group (Saeed and Sun, 2012).

The presence of macrophytes is essential for wetlands in terms of improving nitrogen removal performances because they provide surfaces and oxygen for the growth of microorganisms in the rhizosphere, thereby enhancing nitrification, and provide carbon from root exudates (due to photosynthetically fixed carbon within a range of 5–25%), optimizing organics removal and denitrification process. Nitrogen uptake by plants differs according to the system configurations, loading ranges, wastewater types, and environmental conditions. The contribution of plants in nitrogen removal has been reported within the range of 0.5–40.0% of the total nitrogen removal (Saeed and Sun, 2012).

Ammonia volatilization is a physical removal process where volatile ammonia gas can be removed through mass transfer from the water surface to the atmosphere. At $\text{pH} > 8$, ammonium is transformed into ammonia and might be volatilized or sequestered on the substrates by ion exchange (Nakase et al., 2019).

Substrate is an essential component of CWs. The primary nitrogen removal mainly takes place in the substrate via microbial processes. Biochar, for example, is a carbon-rich biomass pyrolysis material that can provide abundant reactive sites for microbes owing to its large specific surface area and highly porous structure (Li et al., 2019b). Li et al. (2019b) showed that introducing

biochar remarkably intensified oxygen diffusion and nitrogen removal, suggesting that the biochar contributed to oxygen sequestration and transfer while enhancing adsorption and biofilm attachment ability. The adsorption phenomenon in CWs is governed by specific media promoting cation exchange between media components and NH_4^+ ions in the water (Saeed and Sun, 2012).

Nitrogen removal in CWs is also related to the bioavailability of organic carbon (C), which acts as the C substrate during the complete denitrification of nitrate. Studies have shown that low C:N ratios result in unbalanced and simultaneous nitrification and denitrification due to C deficits, leading to suboptimal N removal rates (Li et al., 2019c). Zhao et al. (2010) evaluated the effects of three influent C:N ratios on TN removal in vertical subsurface flow CWs and reported that high total nitrogen removal efficiencies were only achieved when influent chemical oxygen demand (COD):N ratios were in the range of 2.5:5. Li et al. (2019c) obtained highest N removal efficiency and lowest N_2O emissions at a C:N ratio of 5:1. Although high C:N ratio conditions theoretically result in more optimal denitrification rates, and thus more efficient N removal, the depletion of DO associated with the rapid consumption of available O_2 during the biodegradation of excess organic matter will inevitably limit nitrification efficiency (Zhu et al., 2014; Li et al., 2019c).

1.2.2. Phosphorus

The phosphorus removal mechanisms in CWs mainly include substrate adsorption, chemical precipitation, and plant uptake. The removed phosphorus via substrate adsorption has been described to account for 36.2% - 87.5% of total phosphorus, while the removed phosphorus through plant uptake and microbial assimilation only accounted for 1.3% - 26.4% of total phosphorus (Wu et al., 2021). Phosphorus removal efficiency can be directly influenced by

material granulometry, specific area, contents of Fe, Al, Mg, and Ca from substrates, and the amount of organic matter (Dai and Hu, 2017).

Biological phosphorus removal is very low since uptake by microbiota is only temporary and uptake by macrophytes can be considered as a “removal” mechanism only in case that macrophytes are harvested. If macrophytes are not harvested, phosphorus is released back into the water during the decomposition of the biomass, and only a small amount of phosphorus is not released and becomes recalcitrant (Bakhshoodeh et al., 2020).

Unlike denitrification, in which nitrite and nitrate are mainly converted into harmless nitrogen gas that escapes from the wetland, microbial phosphorus removal exhibits no similar sink. Bacteria can only take up and store P, which is a partly reversible removal mechanism. The continuous cycle of growth, die-off, and decay releases most of the initially assimilated phosphorus, and only some refractory fractions become a permanent sink for P. Consequently, once the CWs start-up phase has been completed, net microbial P removal is generally very low. Different water regimes and, therefore, different oxygenation conditions could stimulate phosphate-accumulating organisms (PAOs), such as *Candidatus_Accumulibacter* and *Pseudomonas*, confirming that microbial P consumption is higher in aerobic regions of the rhizosphere, whereas P mineralization is predominant in the anaerobic regions (Garcia et al., 2010).

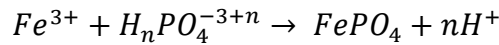
Macrophytes generally have a lower capacity for absorbing P than N because, under anaerobic conditions, insoluble phosphates are precipitated by Fe, Ca, and Al ions. Besides, phosphates can be sorbed by organic peats, clay and by Fe and Al oxides. Likewise, it is important to mention that phosphorus can be linked to organic matter through assimilation and accumulation

in bacteria, algae, and macrophytes (Dell’Osbel et al., 2020). In oxidized conditions, P binding is mainly based on the ligand-exchange process on the Fe-OH₂⁺ and Fe-OH sites (Ji et al., 2022).

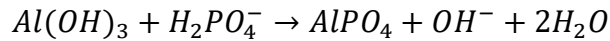
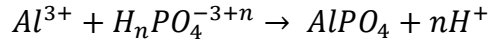
The water pH is another factor that influences phosphorous removal. According to Cheng et al. (2018), the reduction of P reached 71.5% in pH 5. When pH was increased to values between 5 and 7, the adsorption capacity reached up to 0.5 mg of P/g substrate, and at pH 7, the removal efficiency increased to 95.6%. With pH values ranging between 7 and 11, phosphorous removal rates slightly increased, reaching 99.4% (Dell’Osbel et al., 2020).

The precipitation equation of phosphate under the influence of pH and substrates can be expressed as (Ji et al., 2022):

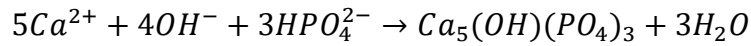
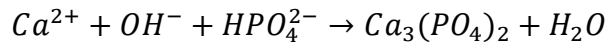
Iron-containing substrates (in acidic environment):



Aluminum-containing substrates (in neutral environment):



Calcium-containing substrates (in alkaline environment):



Phosphorus adsorption efficiency depends on sorbent characteristics, such as particle size and surface functional groups. Therefore, the filter media play an essential role in P removal in CWs. Recently, biochar has received more attention as an alternative filter media for P removal due to its low cost, wide availability, and low environmental effect. Phosphate removal by biochar could be achieved by (a) electrostatic attraction of negatively charged phosphate ion with

positively charged biochar surface, (b) ion exchange, or (c) co-precipitation with Ca^{2+} and Mg^{2+} on the biochar surface (Shahraki and Mao, 2021).

1.2.3. Antibiotics

Biodegradation, substrate adsorption and plant uptake are reported to be the main mechanisms in reducing antibiotics in CWs. Biodegradation involves the transformation of complex compounds into simpler breakdown molecules through catalytic metabolic degradation. Microorganisms are the main drivers of antibiotic biodegradation in the CWs using antibiotics as carbon sources or electron donor/acceptor and inducing the expression of relevant enzymes. Antibiotic biodegradation occurs in aerobic and anaerobic conditions facilitated by aerobic and anaerobic bacteria, facultative bacteria, heterotrophic bacteria, autotrophic bacteria, actinomycetes, and fungi (Ohore et al., 2022).

Sorption can be considered as the main removal mechanism for compounds with mid-low biodegradation rates, such as tetracycline (Liu et al., 2019b). The adsorption process in CWs is highly complex. Various adsorption mechanisms, such as hydrophobic partitioning, electrostatic interaction, cation exchange, hydrogen bonding, surface complexation, and cation bridging, are involved in this process (Lv et al., 2022). Dan et al. (2021) found that hydrogen bonding and metal complexation are the predominant mechanisms responsible for the sorption of antibiotics to the CWs substrate. The complex formation with metal ions on the substrate surface, such as Ca^{2+} , Mg^{2+} , Fe^{3+} or Al^{3+} , may play a significant role in the adsorption of antibiotics, owing to their polar/ion functional groups. Both the mineral and organic matter in wetland substrates can be the main adsorption carriers (Alfonso-Muniozguren et al., 2021).

Wetland macrophytes play indispensable roles in effectively removing antibiotics. The effects of plants on antibiotic removal are associated with the direct uptake (i.e., root accumulation)

and degradation of antibiotics, as well as the rhizosphere effect relative to the release of root exudates. Once they enter roots, antibiotics can potentially translocate to different organs of plants. Antibiotics reaching the vascular tissue can be transported to the aboveground tissues of plants via the xylem or phloem, and they may end up in leaves if transported by the xylem. Antibiotics in plants may be transformed, biodegraded, and sequestered by plant metabolic processes (Lv et al., 2022).

1.3. Dissertation objectives

The main objectives of the proposed research are to achieve holistic treatment of swine wastewater by effectively removing antibiotics and nutrients and to investigate performance and mechanisms when coupling environmental and ecological technologies, contributing to sustainable wastewater management practices. This combined capability will be transformative, because it allows to reduce the impacts caused by the presence of wastewater contaminants paired with a design adapted to receive variability of inputs, providing more flexibility and resilience to the system. Finally, the ability to link the advantages of AnMBR and CWs system can generate an effluent with high quality, fitting in with the discharge water quality parameters. The chapters of this dissertation are structured in ascending order based on the scope of each individual project. Each chapter provides individual understanding to support human and environmental needs and mitigate the adverse impacts of livestock production. The specific objectives are:

1. Conduct a bibliometric analysis of the terms ecological engineering, environmental engineering, nature-based solutions, engineering with nature, constructed wetlands, green engineering, and ecological systems to understand better the impact that the

use of different terms has on the acceptance and perception of the terms and to evaluate the connections and/or differences amongst the terms.

2. Investigate the capacity of eastern red cedar biochar to remove tetracycline and sulfonamide antibiotics and evaluate the adsorption mechanism of these antibiotics at different concentrations.
3. Design and simulate the performance of CWs systems as a polishing step for AnMBR using HYDRUS software with the CW2D module to investigate the degradation of target pollutants from swine wastewater and the effect of runoff discharges with different concentrations of chemical oxygen demand (COD), NH_4^+ and P.

These objectives will be aimed at evaluating the following hypotheses:

1. Test if using different terms referring to ecological engineering systems would weaken the ability to improve science and communicate the progress that has been done in this subject.
2. Determine if economically and environmentally friendly biochar can effectively remove the most consumed antibiotics in the swine industry from water, yielding a pollutant removal source that could be effectively used for practical purposes such as within a CWs configuration.
3. CWs can effectively remove nutrients from AnMBR effluent. A design adapted to receive different runoff inputs can provide flexibility and resilience to handle seasonal flow rate variability.

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Chapter 2 - Ecological engineering: Evolution and impact of different terms by a bibliometric analysis

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2.1. Introduction

We are living in an unprecedented time – a global population that exceeds 7.7 billion people is growing at approximately 1% per year (Sadiqa et al., 2022) and projected to reach 10 billion people by around 2050 (Tallard et al., 2022), which is expected to exacerbate risks to both people and the planet since population growth and increased food production increase environmental risks and degradation, including the increased emission of greenhouse gases (GHGs) (Sadiqa et al., 2022; Tallard et al., 2022); unparalleled climate change driven by increased GHGs (Shaftel et al., 2019) fueling new weather patterns and increasing the frequency and severity of disasters such as droughts (Mukherjee et al., 2018), extreme rainfall (Westra et al., 2014), wildfires (Jones et al., 2020), and hurricanes (Alam et al., 2020; Bevere et al., 2019; Coffetti et al., 2022). Since the early 20th century, human activities, specifically the combustion of fossil fuels, have been the primary driver behind the observed changes in Earth's climate. These changes manifest as long-term alterations in the average weather patterns that define Earth's local, regional, and global climates. The burning of fossil fuels leads to the emission of greenhouse gases in the atmosphere, resulting in a rise in Earth's average surface temperature (Shaftel et al., 2019).

At present, significant segments of the scientific community are raising alarms about the elevated dangers associated with shifts in global land processes. These changes have led to

substantial disruptions in biochemical flows, biosphere dynamics, and climate systems, consequently causing unforeseen and perilous ramifications for both the natural environment and human life (Vitousek, 1994; Steffen et al., 2015; Varela-Losada et al., 2021). The United Nations (UN) estimates that 20% of the Earth's total land area has been degraded just between 2000 and 2015. The well-being of 3.2 billion individuals is at risk due to the deterioration of both land-based and aquatic ecosystems (United Nations, 2020; Peña et al., 2022).

Furthermore, we are currently experiencing the “Fourth Industrial Revolution” (4IR), a remarkable technological revolution with exponential rates of technology transformation which in its scale, scope, and complexity, will be unlike anything humankind has experienced before (Oosthuizen, 2016). While the exponential curves of GHGs, temperature rise, sea-level increase, and global population growth are all coming together to impose unprecedented stresses on our ecosystems, political systems, and economies that typically only react in linear ways (Gleick, 2010), leveraging the 4IR for data collection, management, and assessment to generate solutions for food security, sustainable resource management, and health is critical.

The awareness that an “environmental crisis” was taking place emerged in the early 1960s with a series of environmental catastrophes. In 1963, approximately 400 New Yorkers had lost their lives due to smog, while the oxygen levels in Lake Erie had declined that the center of the lake sustained almost no precious life (Rothman, 2017). The 1960s witnessed a significant surge in oil pollution (Hartig, 2019). In 1969, an oil spill in California's coastal waters resulted in a slimy coating spreading across an area of 400 square miles and killed hundreds of birds (Rothman, 2017). In the same year, Cuyahoga River bursts into flames 5 stories high from oil and chemical pollution, capturing national attention and defining the moment for the new environmental movement (Blum et al., 2017). Given the combination of such catastrophic events in the early 1970s, pollution has

reached a severity that was impossible to be undeniable, and science had become advanced enough to provide a clearer understanding of the causes (Rothman, 2017).

Therefore, growing public awareness and concern for controlling pollution led to the creation of the Environmental Protection Agency (EPA), the National Oceanic and Atmospheric Administration (NOAA), and helped to the creation of federal laws such as the Clean Water Act, Pesticide Control Act (which banned DDT), Marine Mammal Protection Act, Endangered Species Act, and the Safe Water Drinking Act (USEPA, 2022). To mitigate the adverse impacts associated with human activities and to support human and environmental needs, the field of environmental engineering has emerged since then and achieved remarkable successes over the past several decades. However, the solutions of the past will not be sufficient to address the problems of the future (Grasso et al., 2019).

Many organizations, including the US Army Corps of Engineers (USACE), International Union for the Conservation of Nature (IUCN) and the U.S. Environmental Protection Agency (USEPA), are exploring new approaches to achieve agency goals in response to present-day realities and evolving policy with the practice of incorporating nature-based approaches (Nesshöver et al., 2017; Kurth et al., 2020). The only way to face these problems is to develop more sustainable practices informed by ecological knowledge and aimed at protecting and restoring ecological systems, modifying ecological systems to increase the quality, quantity and sustainability of the services they provide, or constructing new ecological systems that offer services that would otherwise be offered through traditional engineering methods relying on non-renewable resources (Barot et al., 2012).

The challenge is to avoid adopting standardized solutions and to search for niche solutions that adapt to different situations. To build a strong field of sustainable science and move beyond

panaceas, one needs is to build on the work of scholars who have undertaken careful, well-documented, and theoretically sound studies of ecological systems, socioeconomic systems, and linked social-ecological systems (Ostrom, 2007). Terms such as Ecological engineering (ECO), Environmental engineering (ENV), Nature based solutions (NBS), Engineering with nature (EWN), Constructed wetlands (CWs), Green engineering (GE), and Ecological systems (ES) are all related to the concept of sustainable development, reflecting similar conceptualization, with CWs being one example of the other remaining terms. In the present world, the goal of sustainability will not be attractive if it is not exceedingly advantageous. Sustainability implies a three-fold added-value itself, economic, social, and environmental profit, 'all in one' and only few companies had promoted sustainable products, processes, and production systems if they do not visualize a clear benefit at the same time (García-Serna et al., 2007).

We believe that the creation and use of different terms resulting from attempts to find the most advantageous term politically, environmentally, and economically may have impacted the overall success of these initiatives, since it is difficult to search for a specific solution if there is an inconsistent use of terms. Although these terms represent and express the same idea of a sustainable ecosystem design, the hypothesis of this study is to test if the use of different terms referring to ecological engineering systems would weaken the ability to improve science and communicate the progress that has been done in this subject.

Perhaps the more important question is whether either paradigm will be the right approach as we enter an age of more environmental issues now complicated by climatic shifts, more populated and more dense urban complexes, and a good possibility that we are running out of conventional energy resources that we have depended on (Mitsch, 2014). Thus, the goal of this research is to conduct a bibliometric analysis of the terms ECO, ENV, NBS, EWN, CWs, GE, and

ES to better understand the impact that the use of different terms has on the acceptance and perception of the terms and to evaluate the connections and/or differences amongst the terms.

2.2. Ecological engineering, related terms and concepts

The 1960s emerged as a pivotal era for the acceleration of environmental discourse across nations. This aligns with historical evidence that highlights the proliferation of the transnational environmental movement (Horvath, 2019; Kanger et al., 2022). Subsequently, there has been a growing adoption and utilization of concepts associated with environmental sciences, primarily driven by concerns regarding climate change and environmental deterioration resulting from human activities. It is worth noting that the concerns about a new ice age in the 1970s turned out to be a misguided path in the advancement of climate science (Gleditsch, 2021).

The popular demand for federal guidance in addressing the pollution problem stimulated the presidential effort to create the EPA in 1970. This initiative granted the EPA a comprehensive set of statutory mandates and authority, effectively centralizing the fundamental tasks of pollution and toxic chemical control. Moreover, these mandates primarily emphasized regulatory functions rather than encompassing broader and more holistic management responsibilities (Andrews, 2010). Since that time, significant progress has been made in environmental protection, product design, and occupational safety, driven by specific legislative measures. As a result, we have witnessed cleaner air and water, reduced pollution levels, and the restoration of numerous waste sites (Fiksel et al., 2009).

In 1972, the United Nations Conference on the Human Environment (UNHCE) in Stockholm brought together global leaders and scientists to address growing international environmental issues, including trans-boundary air and water pollution. This conference marked

the initial occurrence of a large-scale environmental meeting. Later, in 1987, the World Commission on Environment and Development introduced the term ‘sustainable development’ to bring the concepts of environment and development together, which had been lacking during the conference in Stockholm (Seyfang, 2003).

In 1988, the establishment of the Intergovernmental Panel on Climate Change (IPCC) was a combined effort by the World Meteorological Organization and the United Nations Environment Programme. The primary objective of the IPCC was to assess the rate of climate change, its causes and effects, and the potential for both mitigation and adaptation. Rather than conducting independent research, the Panel aggregates and synthesizes information from relevant scientific literature, with a preference for peer-reviewed publications. Additionally, the IPCC evaluates the probability of physical and societal consequences of global warming (Gleditsch, 2021). Over the past few decades, public concern has focused on the prospects of climate change, collecting a much more solid basis in scientific evidence. A crucial element is the growing realization that the current warming is caused by human activities, particularly the release of greenhouse gases (Gleditsch, 2021).

With the increase of environmental concerns, policymakers have been exploring various approaches to address the problems related to natural resource use. This includes how to protect lands of exceptional amenity value, how to promote efficient water use, pricing, and transfer, how to mitigate air, water, and land pollution, and how to maintain habitats for endangered species while managing competing demands for production and recreation (Libecap, 1992). As part of the arsenal of options developed to mitigate environmental challenges, the concepts of ECO, ENV, NBS, EWN, CWs, GE, and ES have emerged as crucial solutions to ensure a high quality of life for future generations.

Ecological engineering (ECO) can be defined as the deliberate design of sustainable ecosystems that integrate human society with the natural environment, resulting in mutual benefits (Mitsch and Jorgensen, 2003). ECO represents an extension of process-based restoration and emphasizes the application of engineering principles to natural systems, aiming to recover or replace lost biophysical processes (Palmer et al., 2014). The primary objectives of ECO are the restoration of ecosystems that have experienced significant disturbances caused by human activities, such as pollution or land disturbance, as well as the creation of new sustainable ecosystems that have both human and ecological value (Mitsch and Jørgensen, 2003). Over time, ECO has emerged as a prominent field of study with global relevance, particularly in the context where resources are severely limited (Mitsch, 2012; Tien et al., 2021).

According to the American Academy of Environmental Engineers, Environmental engineering (ENV) can be defined as a branch of engineering that focuses on the application of scientific and engineering principles to protect human populations and both local and global environments from potential harm caused by natural and human activities. The main goal of environmental engineers is to restore, protect, improve, and enhance environmental quality (Šalić and Zelić, 2018). ENV represents an extension of the engineering process that considers various relevant environmental aspects, requiring the construction of models for planned actions while considering safety factors only at the anthropomorphic level, rather than ecosystem safety. This fact places ENV in a different category compared to ECO (Allen et al., 2003).

Nature-based solutions (NBS) are actions aimed at protecting, managing, and restoring ecosystems in a sustainable manner to effectively address societal challenges such as climate change, food security, and natural disasters. These solutions are designed to be adaptive and beneficial to both human well-being and biodiversity, as defined by the International Union for

Conservation of Nature (IUCN) (Cohen-Shacham et al., 2016; Grace et al., 2021). The concept of NBS is still evolving and in the process of being framed (Cohen-Shacham et al., 2016). According to Grace et al. (2021), there is a recognized need to enhance our understanding of the NBS concept by addressing specific knowledge gaps related to implementation, as well as improving information dissemination and accessibility across society and policy contexts.

The concept of Engineering with Nature (EWN) is an initiative of the US Army Corps of Engineers (USACE) aimed at exploring, demonstrating, and supporting the design of projects that meet engineering and mission objectives but also prioritize environmental benefits and long-term sustainability (Kurth et al., 2020). The USACE (2015) defines EWN as the intentional alignment of natural and engineering processes to deliver economic, environmental, and social advantages efficiently and sustainably through collaborative processes (USACE, 2015). EWN concepts includes the application of scientific and engineering principles to achieve operational efficiencies that support the sustainable delivery of project benefits and the use of natural processes to maximize environmental benefits while enhancing the quality of the project. Consequently, EWN aligns with the broader context of ECO by developing engineering practices that prioritize human welfare while protecting and enhancing environmental goods and services (Mitsch, 1993; Mitsch, 2012; Bergen et al., 2001; Mitsch and Jørgensen, 2004; Berkowitz et al., 2016).

Constructed wetlands (CWs) are engineered treatment systems that use natural processes involving wetland vegetation, soils, and microbial communities to enhance water quality, assisting in the treatment of wastewater or other water sources (USEPA, 2021). Within the framework of ECO, CWs have demonstrated to be a green, low cost, and efficient solution for treating polluted water. In this way, the ecosystem services provided by wetlands are manifold, including the provision of essential resources such as water, timber, and genetic materials; regulation of air and

water quality purification; pollination, nutrient cycling, and primary productivity as habitat conditioning; and cultural services such as aesthetic value ecotourism (Mitsch et al., 2015; Ansari et al., 2016).

The USEPA (2021) defines Green engineering (GE) as the design, commercialization, and use of processes and products to decrease pollution, foster sustainability, and mitigate risks to both human health and the environment, all while ensuring economic viability and efficiency. GE focuses on how to achieve scientific and technological advancements, while providing a framework for scientists and engineers to follow when designing materials, products, processes, and systems that are environmentally friendly and benign to human health (Anastas and Zimmerman, 2003).

Ecological systems (ES), also referred to as "ecosystems," according to Van Dyne (2012), are defined as biological systems consisting of all the organisms present in a specific physical environment, interacting with it and each other. The term can also be extended to describe complex systems that resemble such biological systems (Oxford English Dictionary, 2017; Tsujimoto et al., 2018). However, Tsujimoto et al. (2018) discovered that the definition of ES lacks clarity, and they identified four major streams of ecosystem research and each stream has a different theoretical foundation. In this study, the concept of ecological system engineering will be considered for the keyword "Ecological system". Ecological system engineering refers to the pervasive process through which species modify their abiotic environment that often has consequences for populations, communities, ecosystem functioning, and landscape structure (Jones et al., 1994; Jones et al., 1997; Wright et al., 2002; Wright and Jones et al., 2004; Byers et al., 2006). This is because the ecological system engineer concept can contribute to ecological applications such as ecosystem restoration and invasive species management (Byers et al., 2006).

2.3. Methodology

Bibliometric analysis refers to a statistical assessment of published articles or books and it is an effective method to measure the influence of publications within the scientific community (Schubert et al., 1989; Moya-Anegón et al., 2007; Iftikhar et al., 2019). This analytical approach plays a crucial role in gaining a comprehensive understanding of specific research areas. Stakeholders interested in a particular field of research or journal find these analyses highly valuable to identify trends and relevant issues. Moreover, these studies can offer clear research agendas or guidelines for future development based on the current trajectory of a given research field or journal (Farrukh et al., 2020). A thorough database search of Web of Science and Scopus was conducted to retrieve and analyze all published articles with the terms ECO, ENV, NBS, EWN, CWs, GE, and ES. These databases were selected because they are two of the most popular databases used by researchers, scholars, and academic institutions to access scholarly literature and bibliographic information. Data were selected based on titles, abstracts, and keywords of the published articles (Cadore et al., 2020).

In the first step of the bibliometric research, the articles were selected using each term as keywords. Table 2.1 shows the number of publications obtained for each term searched in Web of Science and Scopus. The first keyword entered was “ecological engineering”, obtaining 924 results and 2,140 results from Web of Science and Scopus, respectively. Further, “environmental engineering” with 31,209 results from Web of Science and 45,430 results from Scopus, “nature based solutions” obtaining 637 results from Web of Science and 894 results from Scopus, “engineering with nature” obtaining 9 results from Web of Science and 19 results from Scopus, “constructed wetlands” obtaining 6,835 results from Web of Science and 10,019 results from Scopus, “green engineering” obtaining 291 results from Web of Science and 612 results from

Scopus, and finally “ecological systems” obtaining 8,769 results and 16,696 results from Web of Science and Scopus, respectively (Table 2.1). The results are higher for Scopus as Scopus has a higher number of journals (21,950) compared to Web of Science (13,100) (Iowa State University, 2022).

Table 2.1. Keywords search result from Web of Science and Scopus in 2021.

	Results from Web of Science	Results from Scopus
Ecological engineering	924	2,140
Environmental engineering	31,209	45,430
Nature based solutions	637	894
Engineering with Nature	9	19
Constructed wetlands	6,835	10,019
Green engineering	291	612
Ecological systems	8,769	16,696

The full records of the publications were exported in BibTex format and imported into the software RStudio through the Bibliometrix package with the Biblioshiny interface (RStudio Team, 2021). Data on the annual scientific production, average citations per year, most relevant sources, country scientific production, most cited countries with total citations and average citations per year, Word Clouds with 50 words, and Co-occurrence map were obtained for each term. However, some results are not presented for ENV using the data from Scopus due to a software limitation related to the maximum of publications allowed to be uploaded and analyzed.

2.4. Bibliometric analysis of literature: Results and discussion

2.4.1. Trends in the number of publications and citations

A thorough database search of Web of Science and Scopus was conducted to retrieve all published articles containing the terms from 1945 to 2021. The results showed that these terms developed over different periods of time with an increase in the scientific literature in the last years (Figure 2.1). Scientific production in ENV and ES began in the early 1960s, being tied to the idea that an “environmental crisis” was emerging marked through a series of environmental disasters, e. g., the smog event in New York, oil spill in California, and the Cuyahoga River fire. Both ENV and ES terms gained force around the 1990s, which can be the result of growing public awareness and concern for controlling pollution since it overlapped with amendments to the Clean Water Act in 1987. The Clean Water Act addressed nonpoint source pollution (runoff from farm lands, forests, construction sites, and urban areas), estimated to represent more than 50% of the nation’s remaining water pollution problems (Copeland, 2016) and with the largest oil spill in human history resulting from the Gulf War in 1991 (Hussain and Gondal, 2008). ES reached a peak in 2019 with 1398 publications per year and ENV thrived even more in 2020 with 4779 publications per year. Similarly, CWs and GE started in 1985 and 1991, and reached a peak in 2020 with 818 and 55 publications, respectively.

New engineering approaches started at different times, ECO began in 1971, coinciding with the period that EPA and federal laws such as the Clean Water Act were created. This term reached a peak in 2018 with 145 publications. NBS had the first publication in 2009 and was thriving in 2020 with 323 publications, indicating a potential shift in how solutions are categorized and implemented. EWN, on the other hand, started in 2001 and reached a peak of 5 in 2018. Thus,

considering the latest publications, ENV remains the predominant area with NBS gaining popularity in lieu of ECO.

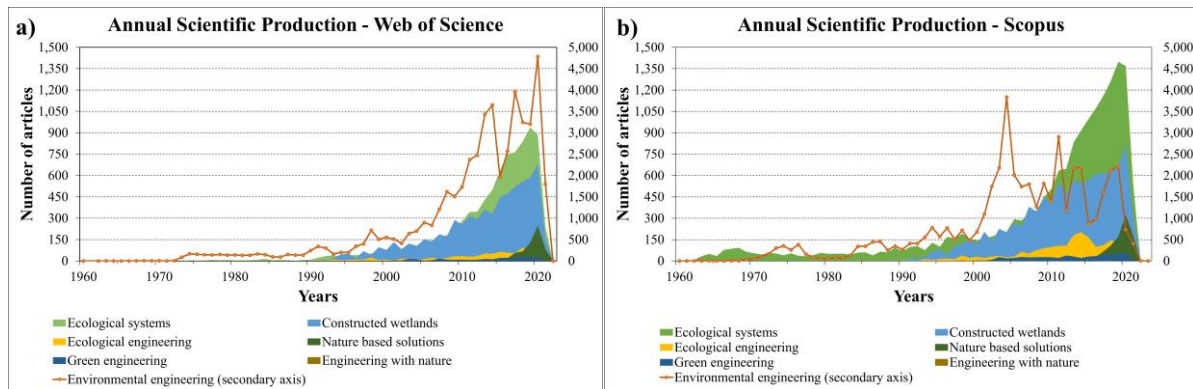


Figure 2.1. Number of publications by years on (a) Web of Science and (b) Scopus.

The article written by Olson (1963), with the term ES, has the highest average number of citations per year compared to the other terms (Figure 2.2a). This paper is related to energy storage and balance of producers and decomposers in ES using mathematical models for litter production and decay in evergreen and deciduous forests, which is the main route of nutrient return to the soil (Olson, 1963).

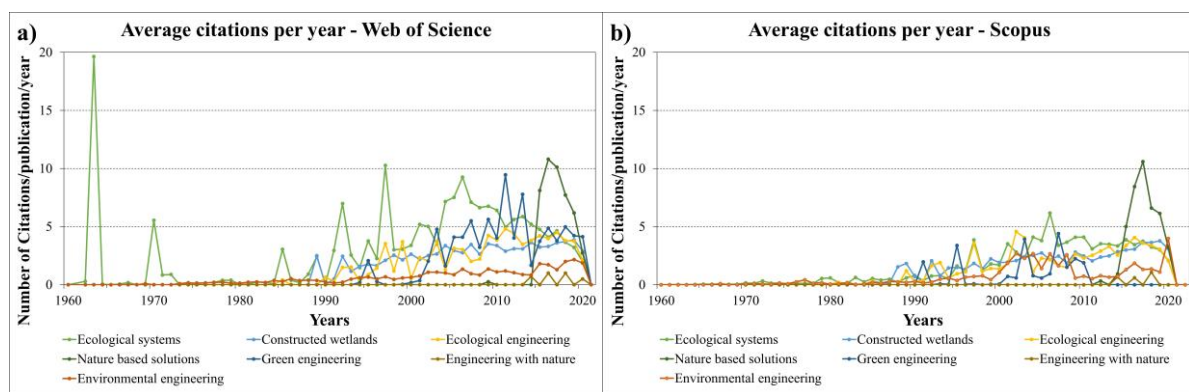


Figure 2.2. Number of citations per year for each term on (a) Web of Science and (b) Scopus.

As with many modern concepts, the concept of ECO is one that at first appears attractive, consensual, and intuitive, marrying engineering methods with the expertise of the ecological scientist under the banner of increasing respect for nature. Furthermore, it is a concept that is gaining force, both as an international academic discipline (Xu and Li, 2012; Dale et al., 2021) and among scientific discourse (Mihai et al., 2021; Ounanian et al., 2018). The term ECO was coined by Howard T. Odum in the 1960s and has since been used in the North America, Europe, and China (Mitsch and Jørgensen, 2003). According to Odum (1989), ECO can be defined as "the engineering of new ecosystem designs that primarily rely on self-organizing systems". While there were some sporadic university courses on ECO in the mid-1970s, it wasn't until a decade later that Mitsch and Jørgensen (1989) published the first significant work outlining the definitions and principles of ECO (Mitsch, 2012) (Figure 2.1).

Barot et al. (2012) suggest that there are numerous indicators pointing towards a growing acceptance and utilization of the concept of ECO, and these trends are expected to continue and strengthen in the coming decades. However, as can be seen in Figures 2.1 and 2.2, the growth of this term is somewhat stagnant, which could be the result of some confusion. On one hand, some scientists believe they are working in the field of ECO but are probably not. Conversely, many others are doing research relevant to ECO but never refer to ECO. To fully realize its potential and establish itself as a fundamental approach for addressing environmental and sustainability challenges, ECO must quickly meet three main key challenges: ethical, intellectual, and relational (Jones, 2011; Barot et al., 2012). The relational challenge is to foster collaboration among scientists from diverse disciplines including ecology, chemistry, engineering, social sciences, and economics, as well as practitioners and policymakers. This collaborative effort is crucial for ECO

to gather substantial support from both the academic and economic spheres, enabling it to reach its ambitions (Barot et al., 2012).

Environmental regulation presents a wide range of challenges and opportunities for businesses, as their performance is closely tied to their compliance with these regulations. Companies that adhere to environmental regulations can stimulate technological advancements; optimize resource utilization; minimize economic losses; enhance their reputation; foster green process innovation and drive innovation overall; attract clients, investors, and potential partners; and enhance existing relationships with governmental bodies or other institutions (Qiu et al., 2017; Qiu et al., 2020; Zhang et al., 2020; Martínez Hernández et al., 2021).

In the last couple decades NBS and GE appear to be attractive, becoming more popular with the highest average number of citations per year (Figure 2.1 and 2.2). “Green” is in some way “smart” and that is interesting as the high-technology company Wilkinson S.L. suggested that “green” can be a profitable endeavor if it is embraced as a core policy and central strategy for firms, commonly referred to as sustainability (Wilkinson, (1997); García-Serna et al., 2007). The issue of climate change mitigation has been politicized in many countries, including the United States, Canada, Australia, and the United Kingdom, where partisanship and ideological divides persist (Hale, 2010; Young and Coutinho, 2013; Carter et al., 2014; Carter and Clements, 2015; McCright et al., 2016; Cheung and Davis, 2017; Mildemberger et al., 2017; Lockwood, 2018; Mayer, 2019; Hess, 2019; Sovacool and Brisbois, 2019; Geddes et al., 2020). In general, coupled human-natural systems are shaped by social processes and decisions, making them fundamentally political and characterized by the need to navigate tradeoffs (Meerow, 2020). Sustainability is an agenda that promotes growth and is driven by market forces, where decision-makers and elites

strategically choose certain policies, such as prioritizing livability, to enhance competitiveness and attract investment (Krueger and Gibbs, 2007; Tubridy, 2020).

2.4.2. Geographical distribution of publications

The results for the geographical distribution of publications indicate that countries in which the highest range of publications is focused are considered world and economic powers (Figure 2.3). Regions and countries such as North America, Europe, China, and Australia have the highest numbers of article publications for all the terms, with most articles originating from the USA and China. Despite the increasing attention given to environmental issues in developing countries (Figure 2.3), they still require access to the latest environmental technologies and management practices from developed countries, which have accumulated valuable experience through their long history of environmental assessment and management (Li and Zhao, 2015).

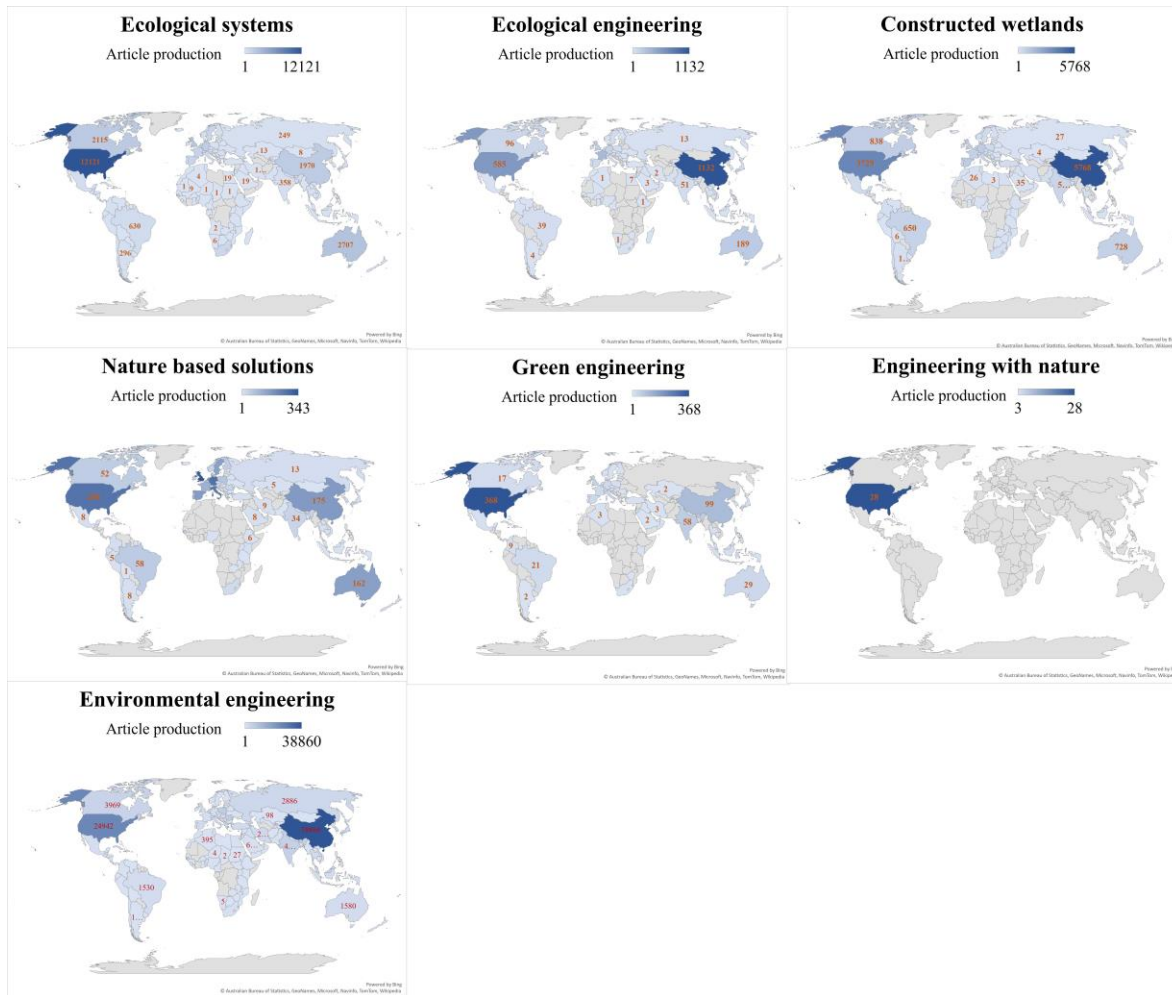


Figure 2.3. Geographical distribution of publications for ES, CWs, ECO, NBS, GE, EWN, and ENV retrieved from Web of Science (Scopus had a similar trend).

A developed and sustainable financial sector is crucial for achieving sustainable economic growth (GDP), as it facilitates efficient allocation of resources and supports GDP growth. However, it is important to consider the potential environmental consequences associated with this development (Hafeez et al., 2019; Usman et al., 2021). The exploration of natural resources, while contributing to economic development, can also lead to increased environmental pollution (Bekun et al., 2019; Usman et al., 2022). It is understandable that the positive role of a developed financial

system in promoting economic growth may also result in increased energy demand and unintended environmental implications (Islam et al., 2013; Usman et al., 2020).

Based on the findings of Dragos and Dragos (2013), governmental support for environmental programs plays a crucial role in promoting academic research output. The study reveals a strong correlation between research output and the level of financial investment (Dragos and Dragos, 2013). Another study conducted by Mozahid et al. (2022) suggests that a 1% increase in GDP per capita leads to a corresponding increase of 0.68% in CO₂ emissions per capita. However, the study also highlights a negative nonlinear relationship, indicating a decoupling of CO₂ emissions by 0.024% as GDP reaches a higher level of 5% in the long run.

Countries with higher total GDP have a higher number of publications using all these terms, which may express a bigger concern about environmental issues in these countries that are considered economic powers (Figure 2.4). The Pearson correlation coefficient of 0.95 shows a significant correlation between these 2 variables (p-value <0.01). According to Coba Salcedo et al. (2018), it can be assumed that the great predisposition of the wealthier countries to mitigate the harmful effects on the environment can be tied to the fact that countries such as United States and China are among the countries that produce the most pollution from their industry and the pollution can be penalized by the local environmental legislation. However, if considering the GDP per capita, there is no correlation with the total number of publications (Table 2.1, supplementary material), since there are countries with lower GDP per capita and high number of publications such as India that has a low GDP and higher number of publications, compared to many other countries, i.e., United Kingdom, Australia, Germany, Spain, South Korea, France, Netherlands, etc.

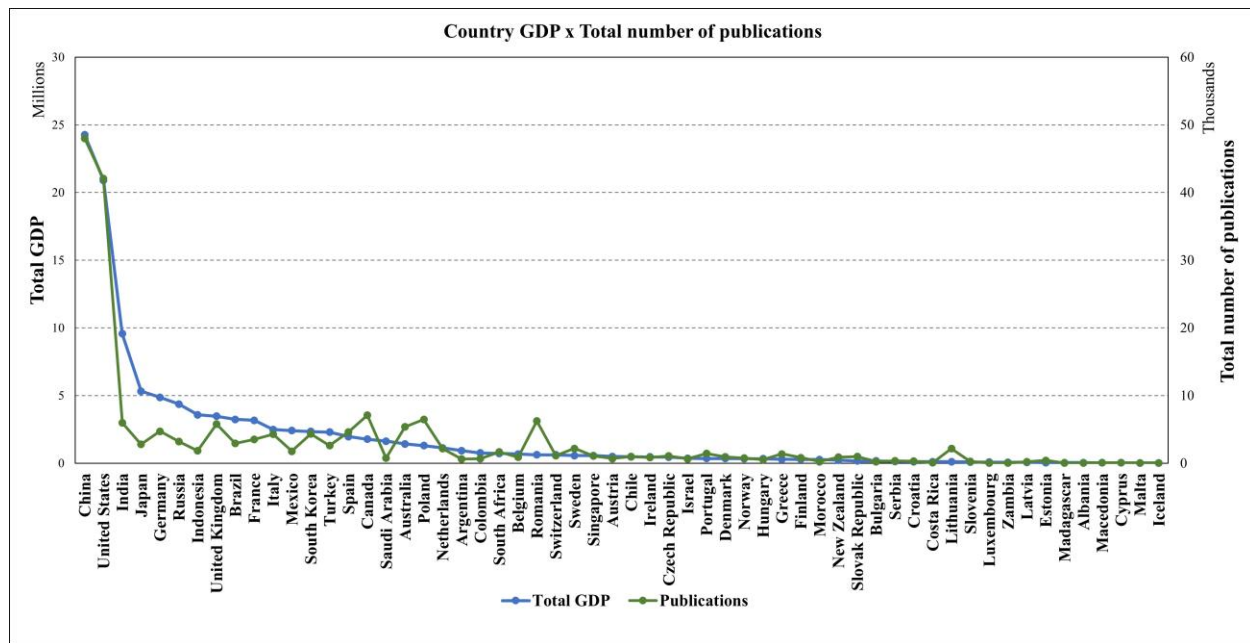


Figure 2.4. Relationship between country total GDP and total number of publications summing the 7 terms. GDP data obtained from OECD, 2022.

Certain bibliometric studies examining multiple countries take into account two aspects of academic output: quantitative and qualitative dimensions (Davaranpanah, 2010; Nejati and Hosseini Jenab, 2010; Dragos and Dragos, 2013). The quantitative dimension, on a country level, is typically assessed based on the total number of published articles (Figure 2.3), while the qualitative dimension is evaluated through indicators such as the total number of citations (Figure 2.5) and the average number of citations per year (Figure 2.6) (Dragos and Dragos, 2013).

ENV and GE have the highest average number of citations per year in the most cited countries such as United Kingdom, Poland, and United States (Figure 2.5), contributing to the high ranges of citations per year that these countries have, even though ECO, CWs, and ES have the highest numbers for article production widely (Figure 2.3), probably for being the first terms to be developed compared to GE (Figure 2.1).

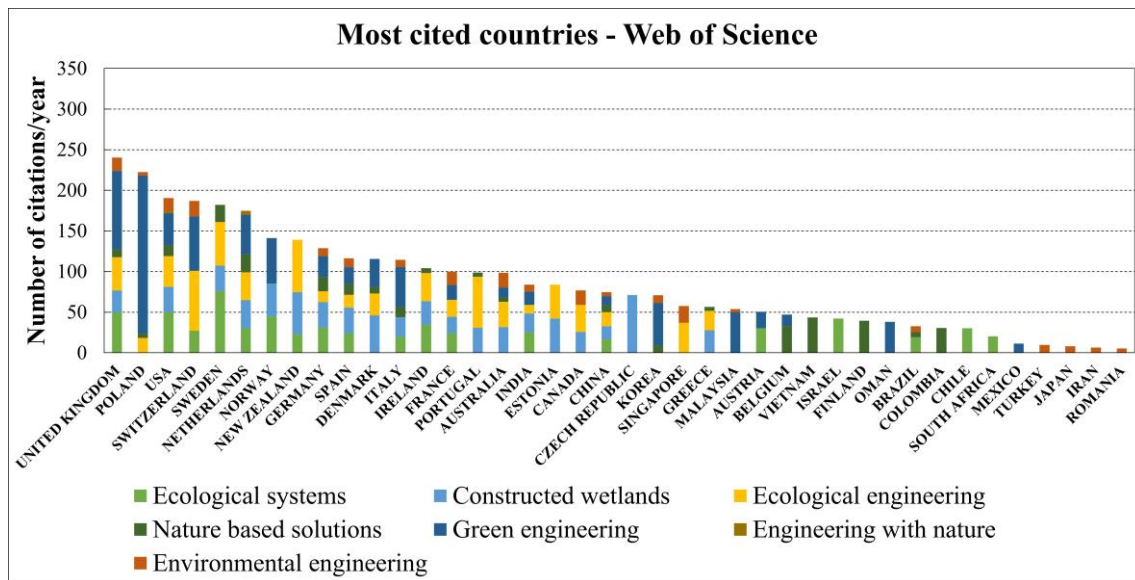


Figure 2.5. Number of citations per year for the most cited countries on Web of Science.

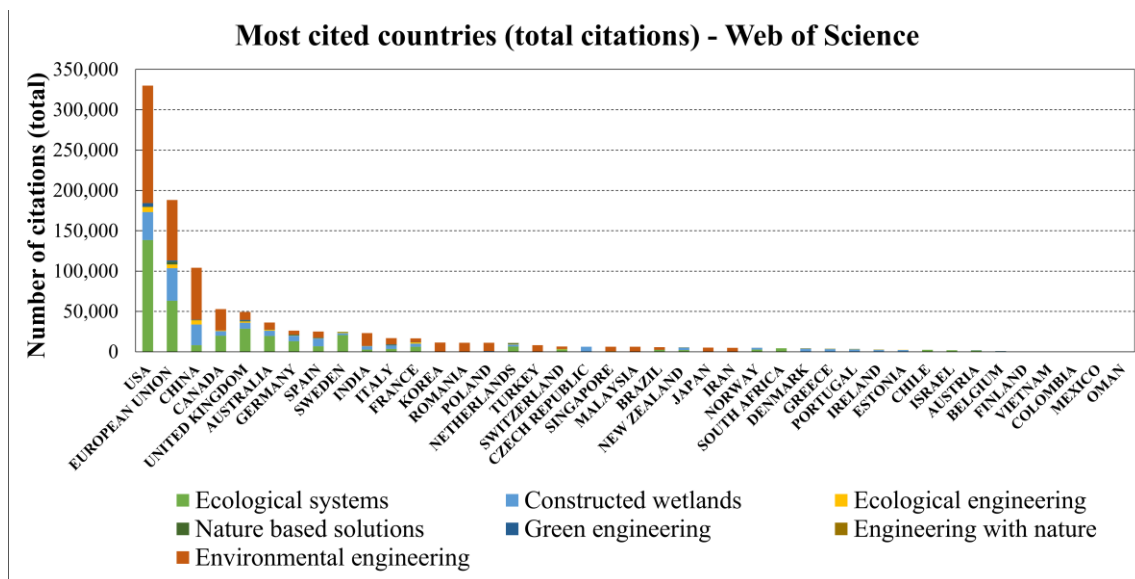


Figure 2.6. Average number of citations per year for the most cited countries on Web of Science.

2.4.3. Distribution of the publications by journals

The 8 most relevant journals in terms of publications are shown in Figure 2.7. The top journal from Web of Science publishing with the term ENV is the Journal of Environmental Science and Health and have published 4,429 articles (Figure 2.7a), whereas the top journal from Scopus publishing with the same term is the Earth and Environmental Science Journal and have published 2,731 articles (Figure 2.7b). The Ecological Engineering journal is ranked the most relevant in article publications for the remaining terms, except for ENV, compared to the other journals. This journal has published 939 articles with the term CWs and 285 articles using the term ECO from Web of Science (Figure 2.7a) and 1035 articles and 578 articles using the terms CWs and ECO, respectively from Scopus (Figure 2.7b). The Sustainability journal has 72 and 84 publications from Web of Science and Scopus, respectively, using the term NBS. Ecology and Society had published over 600 articles with the term ES. The term GE has the highest numbers of publications in the ASEE Annual Conference and Exposition Conference with 32 articles (Figure 2.7b) and in the Environmental Science and Technology with 19 articles (Figure 2.7a). EWN has 2 publications in the journal Integrated Environmental Assessment and Management and is ranked as the top journal for this term.

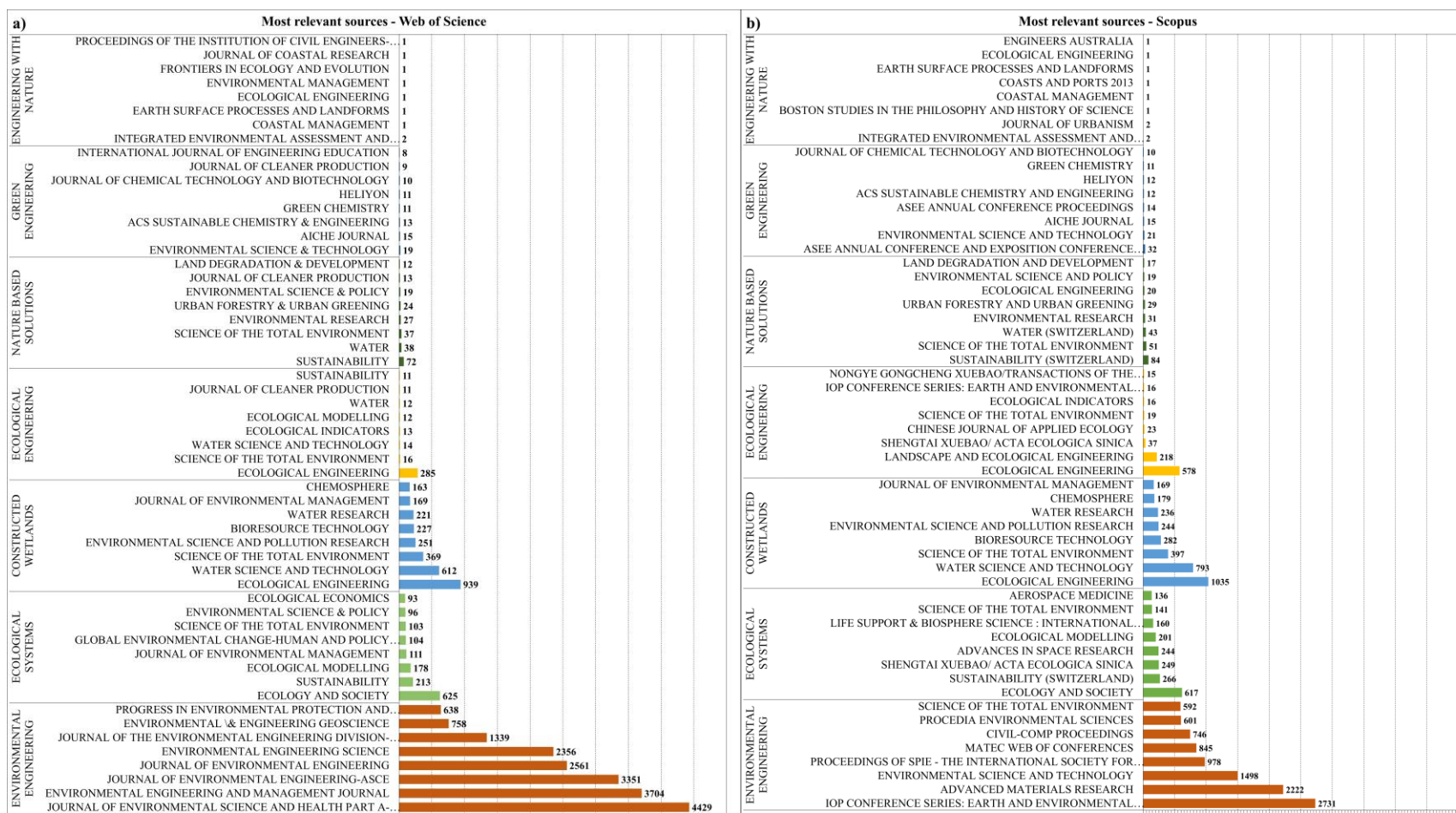


Figure 2.7. Main sources of ENV, ES, CWs, ECO, NBS, GE, and EWN research in the period 1945-2021.

2.4.4. Keyword Trends

The result of running the software Gephi 0.9.2 considering a minimum number of 50 occurrences of a keyword for each term is shown in Figure 2.8. The different colors of the nodes indicate the term to which the keyword is connected with and the order that the terms were entered in the analysis. The distance between two nodes reflects the strength of the relation between them, i.e., shorter distance means stronger relationship. The network connections show the keywords that appear together more frequently in the analyzed articles. Finally, the thickness of the line indicates the frequency. The thicker the line is, the greater the co-occurrence frequency (Niñerola et al., 2019).

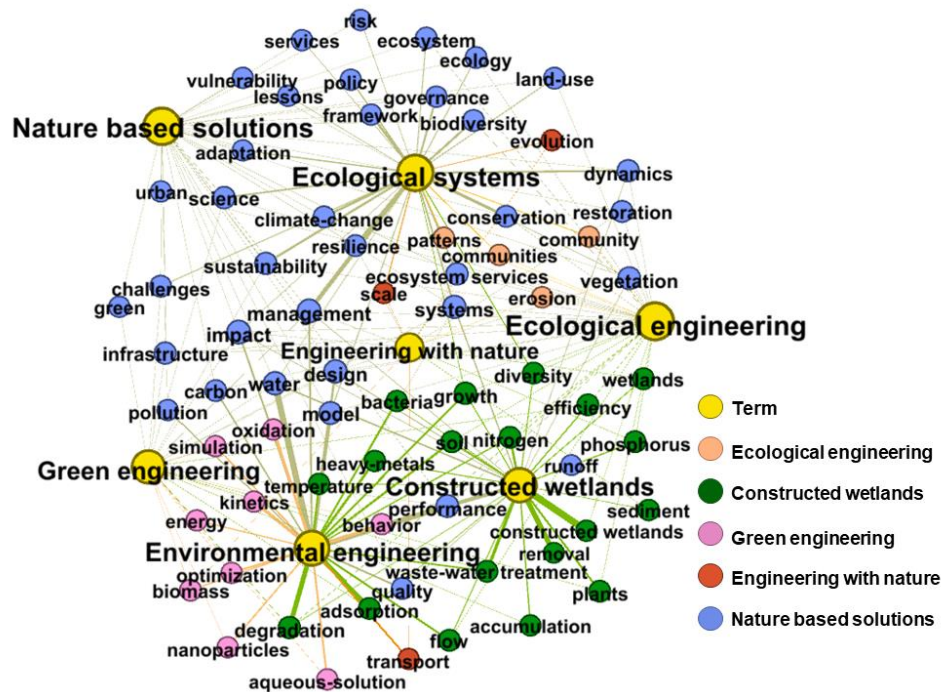


Figure 2.8. Co-occurrence map and link of the most frequent keywords.

Keywords serve as a representation of the primary subjects explored in existing research, outlining the specific areas examined within a given topic. The co-occurrence of keywords allows for the identification and emphasis of the major research areas (Chàfer et al., 2021). As can be

seen in Figure 2.8, ECO, NBS, and ES have some keywords in common such as management, ecosystems services, climate-change, ecosystems, vegetation, and biodiversity. CWs are used mostly for wastewater treatment and removal of contaminants from the environment, which explains the use of keywords such as wastewater, removal, performance, nitrogen, phosphorus, heavy metals, and phytoremediation. Even though the term CWs was chosen in this study as one application of ECO while providing ecosystems services and being a self-organizing ecosystem design, the co-occurrence map shows the strongest link between CWs and ENV.

It is noteworthy the importance that NBS is gaining in the sector from a strategic point of view. Keywords as policy, governance, framework, management, etc., first appear for this term (Figure 2.8). Given its various applications, NBS can be conceptualized as a comprehensive framework encompassing a wide array of ecosystem-based approaches. These approaches collectively tackle critical societal issues such as climate change, food security, water security, disaster risk, human health, and economic and social development. Moreover, these approaches exhibit numerous similarities, including the ecosystem services they target and the types of interventions they employ (Cohen-Shacham et al., 2016). ECO is one of the ecosystem-related approaches that make up the current scope of NBS. The concept of green infrastructure serves as a link between GE and NBS, characterized as a thoughtfully designed and managed network of natural and semi-natural areas, along with other environmental features designed and managed to deliver a wide range of ecosystem services (European Commission, 2013; Cohen-Shacham et al., 2016).

Wang et al. (2014) mentioned in their study that to clear up the hot topics is the key to grasp the development trends of one subject. As a research field evolves, researchers tend to converge on significant research directions or focus on intensive studies at various levels,

reflecting the maturity of the discipline. Therefore, identifying hotspots or the latest advancements in this field helps track trends, preserve existing knowledge within this research tradition, and enhance our understanding of the subject.

In addition to seeing the evolution and connection of these main terms, the identification of the keywords is relevant for researchers to use the correct terms to describe their articles and thus improve their visibility (Niñerola et al., 2019). Figure 2.9 presents the Word Clouds of the top 50 keywords in each related subject presented from (a) Web of Science and (b) Scopus, showing the focus of the research in each field of ECO, ENV, NBS, EWN, CWs, GE, and ES. There is a certain vulnerability of the science to link these terms and their concepts through the keywords since they do not usually appear together in the same publications (Figure 2.9). Generally speaking, the use of the keywords is high correlated to the probability to be cited or searched, as keywords provide insights into the current focal points of each field (Wang et al., 2014).



Figure 2.9. Word Clouds of the top 50 keywords related to each term presented from (a) Web of Science and (b) Scopus.

2.5. Conclusion

To build a strong field of sustainable science many terms were created as an initiative to find the most advantageous term politically, economically, and environmentally. These terms developed over different periods of time with a recent increase in the scientific literature. Scientific production in ENV and ES was dated in the early 1960s, both gaining force in the 1990s and

reaching a peak in 2020 and 2019 with 4779 and 1398 publications, respectively. New engineering approaches started at different times, ECO had its first publications in 1971, reaching a peak in 2018 with 145 publications. NBS had its first publication in 2009, thriving in 2020 with 323 publications, which indicates a shift in how solutions are categorized and implemented. EWN, on the other hand, was dated in 2001, reaching a peak of 5 in 2018. CWs and GE started in 1985 and 1991, reaching a peak in 2020 with 818 and 55 publications, respectively.

Wealthier countries appear to express a great predisposition to mitigate the harmful effects on the environment, considering that there is a strong correlation between total GDP and number of publications using all terms. GE has highest average number of citations per year in the most cited countries such as United Kingdom, Poland, and United States, even though ECO, ENV, CWs, and ES have the highest numbers for article production widely and highest total numbers of citations. Considering the number of publications by journal, the Environmental Science and Health Journal has more publications with 4,429 articles for the term ENV, followed by the Earth and Environmental Science Journal with 2,731 publications for the same term. The Ecological Engineering journal is ranked the most relevant in article publications for the remaining terms compared to the other journals.

As theoretically sound, CWs was chosen to be an example of ECO while providing ecosystems services and being a self-organizing ecosystem design, however, the strongest link appears to be between CWs and ENV. Furthermore, it is noteworthy the importance that NBS is gaining in the sector from a strategic point of view. This term covers a whole range of ecosystem-related approaches and ECO is one of these approaches that appears to make up the current scope of NBS. As a research field develops, the researchers seem to converge in certain directions. ECO is the term that at first appears attractive, marrying engineering and ecological scientific methods

under the banner of increasing respect for nature. However, the growth of this term is somewhat stagnant, which can be tied to the ENV remaining the predominant area over time and to the term NBS gaining popularity in lieu of ECO, considering the latest publications. Thus, there is a certain vulnerability of the science to link these terms and their concepts since they do not usually appear together in the same publications.

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2.7. Supplementary material

Table 2.1 shows the relationship between country GDP (top 20 countries with higher GDP) and the number of publications per country using each term. The number of publications is higher in countries with higher GDP, e. g., United States, China, Germany, Switzerland, Netherlands, and United Kindom, however, there are countries with lower GDP and high number of publications such as India that has a low GDP of 7686 US dollares/capita and high number of publications (Environmental engineering = 4962; Ecological systems = 358; Contructed wetlands = 520; Ecological engineering = 51; Nature based solutions = 34; and Green engineering = 58).

Table 2.1. Relationship between country GDP and number of publications.

Country	GDP	Environmental eng.	Ecological eng.	Ecological systems	Green eng.	Eng. with nature	Nature-based solutions	Constructed wetlands
	US dollares/capita	-----Number of publications-----						
Luxemburg	117721.2	23	6	3	-	-	11	1
Singapore	98480.0	838	37	73	5	-	16	121
Ireland	93450.4	375	22	100	-	-	43	294
Switzerland	71687.3	475	28	496	10	-	27	79
Netherlands	64288.1	582	94	973	10	3	194	295
United States	63285.2	24942	585	12121	368	28	268	3729
Norway	62650.4	256	9	316	3	-	38	146
Denmark	60244.4	349	31	182	5	-	69	315
China	59210.5	38860	1132	1970	99	-	175	5768
Germany	58552.5	1549	125	1908	24	-	272	839
Austria	55686.1	251	24	226	13	-	24	149
Australia	55626.8	1580	189	2707	29	-	162	728
Sweden	55037.7	477	47	1201	3	-	160	293
Iceland	53611.3	16	-	23	-	-	1	3
Belgium	53090.1	394	13	238	10	-	65	177
Finland	50506.4	347	15	268	6	-	51	138
France	46691.1	1085	322	1261	24	-	118	719
Canada	46611.3	3969	96	2115	17	-	52	838
United Kingdom	46575.9	1863	165	2529	42	-	343	856
Saudi Arabia	46342.6	675	3	19	2	-	8	35

(GDP data obtained from OECD, 2022).

Chapter 3 - Removal of antibiotics from swine wastewater using an environmentally friendly biochar: performance and mechanisms

This chapter is a manuscript in preparation to be submitted for publication. The co-authors on this manuscript include Stacy Hutchinson, Prathap Parameswaran, Ganga Hettiarachchi, and Trisha Moore.

3.1. Introduction

Antibiotics are widely used in the swine industry to treat, prevent, and control the diseases caused by bacterial infections and hence improve the growth of pigs (Cheng et al., 2020a). These compounds are often added in the feed and water for animal feeding (Ben et al., 2009). Due to the over-dosage and low assimilation by animals, most antibiotics (70% - 90%) are excreted into the environment through swine waste, threatening the health of humans and other organisms by inducing the prevalence of antibiotics resistant genes in pathogenic bacteria (Ben et al., 2009; Pan et al., 2011; Cheng et al., 2018; Xu et al., 2019). Several antibiotics have been identified in different environmental compartments, such as livestock farms, river water and sediment, soils, and groundwater (Zhang et al., 2015).

The treatment facilities employed in farms are ineffective in removing antibiotics from animal waste (Zhou et al., 2013; Chen et al., 2017). Sulfonamides and tetracyclines are two classes of antibiotics most common in swine wastewater, frequently detected at concentrations of up to 710 and 1000 µg/L, respectively (Zhang et al., 2012; Jiang et al., 2014; Lekagul et al., 2019; Chan et al., 2020; Wan et al., 2021; Udebuani et al., 2022). Li et al. (2018) investigated the concentrations of 10 commonly used veterinary antibiotics in samples of treated slurries and groundwater to understand the effect of swine feedlot as sources on groundwater quality

downstream. They concluded that all types of antibiotics were detected in either discharged wastewater or groundwater samples, however, particularly tetracyclines and sulfonamides were detected in high concentration and frequency in the water samples. Thus, there is a need for cost-effective wastewater treatment techniques to remove antibiotics in animal waste, thereby protecting human health and the environment (Wen et al., 2016; Zhang et al., 2016; Chen et al., 2017).

Biochar is an excellent biomass-derived carbonaceous sorbent for organic contaminants due to its pore structures and good surface characteristics (Peiris et al., 2017; Qin et al., 2019). These carbonaceous materials are produced through pyrolysis of organic materials, such as plant residue, agricultural waste, or wood chips at high temperature (usually ≤ 800 °C) (Wang et al., 2009; Zhang et al., 2020; Biswal and Balasubramanian, 2022). For instance, Zhang et al. (2012) found that biochar derived from corn straw pyrolyzed at 600 °C had the highest adsorption capacity for tetracycline removal when compared to temperatures ranging from 100 to 600 °C. Similarly, Hu et al. (2022) demonstrated effectiveness in removing sulfonamides using an attapulgite-modified rice straw biochar pyrolyzed at 700 °C. However, when high pyrolysis temperatures are used, the use of biochar is not feasible for practical applications due to the high costs associated with their production and surface modification (Jang and Kan, 2019; Biswal and Balasubramanian, 2022).

Pyrolysis is the most-costly stage when producing biochar, accounting for 36% of the total production cost due to the consumption of large amounts of energy (Homagain et al., 2016). The pyrolysis process also generates bio-oil, a liquid product that may be used to generate energy or as feed to generate chemicals (Vuppaladadiyam et al., 2023). Therefore, reducing the energy requirements for biochar production would improve its economic feasibility for large-scale

application (Amoah-Antwi et al., 2020). Another crucial factor in the widespread production and commercialization of biochar is to identify abundant, sustainable, and readily available feedstock options that have significant environmental and economic implications (Liu et al., 2015).

Eastern red cedar is native to the eastern United States and southern Canada but is considered an invasive species in areas of the Great Plains where it is displacing ideal native grass species (Pierce et al., 2010; Vaughn et al., 2021). Unfortunately, eastern red cedar rapid expansion into grassland prairies has led to several environmental problems including greater wildfire risk, reduced water yield, unfavorable wildlife habitat, changes in nutrient cycling and carbon sequestration, and reduced forage (Van Els et al., 2010; Kaur et al., 2020; Jeffries et al., 2023). Biochar produced from hardwood was found to have high porosity and thus may be effective in absorbing large amounts of organic chemicals (Vaughn et al., 2020). However, there is a lack of research regarding the adsorption of antibiotics using biochar derived from eastern red cedar (*Juniperus virginiana* L.). To the best of our knowledge, for the first time the present research investigated the adsorption characteristics and mechanisms for adsorption of tetracyclines and sulfonamides onto eastern red cedar derived biochar.

The objective of this study, therefore, was to investigate the capacity of eastern red cedar biochar pyrolyzed at 450 °C to remove tetracycline and sulfonamide antibiotics. Specifically, the adsorption mechanism of three tetracyclines (tetracycline, oxytetracycline, and chlortetracycline) and two sulfonamides (sulfadiazine and sulfamethazine) at different concentrations were investigated. The conversion of this invasive species into biochar at a temperature of 450 °C offers a potential solution to mitigate its negative environmental impact. Moreover, this process yields a pollutant removal source that could be effectively used for practical purposes.

3.2. Methods

3.2.1. Material

Tetracycline hydrochloride (CAS: 64-75-5, $C_{22}H_{24}N_2O_8 \cdot HCl$), oxytetracycline hydrochloride (CAS: 2058-46-0, $C_{22}H_{24}N_2O_9 \cdot HCl$), chlortetracycline hydrochloride (CAS: 64-72-2, $C_{22}H_{23}ClN_2O_8 \cdot HCl$), sulfadiazine (CAS: 68-35-9, $C_{10}H_{10}N_4O_2S$), and sulfamethazine (CAS: 57-68-1, $C_{12}H_{14}N_4O_2S$) were purchased from Sigma-Aldrich. Eastern red cedar biochar was obtained from Blue Earth LLC, located in Manhattan, Kansas, USA. Biochar was produced by pyrolysis from eastern red cedar at 450 °C. The pyrolyzed biochar was ground and passed through a sieve <595 μm .

3.2.2. Characterization of biochar

Surface morphology and elemental composition of the eastern red cedar biochar were determined using an FEI Nova NanoSEM 450 scanning electron microscopy (SEM) with an Oxford X-Max 20mm² integrated energy dispersive X-ray spectroscopy analysis (EDS) silicon-drift detector located at the Electron Nanoscopy Instrumentation Facility, University of Nebraska, Lincoln, USA with a working voltage of 15 kV. Fourier transform infrared spectroscopy (FTIR) was performed to identify the main chemical groups on biochar using the Thermo iS-50 FTIR spectrometer in the range of 450-4000 cm^{-1} with a diamond attenuated reflectance. The Elemental Analysis was done by using PerkinElmer 2400 Series II CHNS/O Elemental Analyzer. The mineral phases and crystal structure of the biochar was identified by means of EMPYREAN X-ray diffractometer from PANalytical (XRD) at a scanning rate of 10 °/min from 0° to 90° (2-theta). The specific surface area, pore volume, and pore size distribution of the biochar were measured from N₂ adsorption-desorption isotherms at 77 K using a surface area analyzer (ASAP

2460, Micrometrics, USA). The surface area (S_{BET}) was calculated by the Brunnauer-Emmet-Teller (BET) method.

3.2.3. Adsorption experiments

Sorption tests were performed to evaluate the removal of tetracycline, oxytetracycline, chlortetracycline, sulfadiazine, and sulfamethazine from an aqueous solution. 2 mg of biochar was dispersed in a scintillation vial with screw caps containing 20 mL of deionized water with known concentration of each antibiotic (100, 300, 600, and 900 $\mu\text{g L}^{-1}$). Combinations of antibiotics were prepared to evaluate if the biochar would have a preference for a certain antibiotic: Tetracyclines (tetracycline, oxytetracycline, and chlortetracycline) were mixed with the same concentrations (100, 300, 600, or 900 $\mu\text{g L}^{-1}$); Sulfonamides (sulfadiazine and sulfamethazine) were also mixed with the same concentrations (100, 300, 600, or 900 $\mu\text{g L}^{-1}$); and finally, all tetracyclines and sulfonamides were combined at concentrations of 600 and 300 $\mu\text{g L}^{-1}$, respectively. Different concentrations for tetracyclines and sulfonamides ranging from 100-1000 $\mu\text{g L}^{-1}$ can be found in the literature (Xu et al., 2017; Cheng et al., 2020b; Cheng et al., 2021; Harb et al., 2021; Liu et al., 2022).

NaOH and HCl solutions (0.01 M to 1 M) were used to change the pH to 7. For the majority of adsorbents used for adsorption, adsorption affinity is favorable within a limited range of solution pH or the adsorption decreases with the increase in the negative surfaces of the sorbents with increasing pH (Ashiq et al., 2021). Samples were placed in a thermostatic oscillator at 150 rpm for 24 h contact time in room temperature (25 °C) to achieve adsorption equilibrium (Wu et al., 2016). The resultant solid was withdrawn using a 0.22 μm filter and the residual antibiotics were analyzed

by a high-performance liquid chromatography (HPLC) system (Waters Acquity HPLC System with Xevo TQ-S Mass Spectrometer). Sorption tests were performed in 4 replicates.

The amount of antibiotic adsorbed on biochar (Q_e , mg/g) was calculated from the difference in concentration between the initial (C_0 , mg/L) and the equilibrium (C_e , mg/L) solutions (Eq. 1).

$$Q_e = \frac{C_0 - C_e}{m} \times \frac{V}{1000} \quad (\text{Eq. 1})$$

, where V (mL) is the volume of antibiotic solution, m (g) is the weight of biochar used.

3.2.4. Adsorption isotherm models

In order to better understand the adsorption process, the Langmuir and the Freundlich adsorption isotherm models were utilized to fit the experimental data (Rajahmundry et al., 2021). The Langmuir model (Eq. 2) hypothesizes that a monolayer or shorter adsorption process is proportional to the homogeneous energy on the surface sites (Alabbad et al., 2022):

$$q_e = \frac{bq_{max} C_e}{1 + bC_e} \quad (\text{Eq. 2})$$

The Freundlich model (Eq. 3) describes multilayer adsorption on a heterogeneous adsorbent surface (Alabbad et al., 2022):

$$q_e = K_F C_e^{1/n} \quad (\text{Eq. 3})$$

, where q_e (mg g⁻¹) and C_e (mg L⁻¹) are the equilibrium adsorption capacity and concentration, q_{max} (mg g⁻¹) denotes the maximum adsorption capacity, b (L mg⁻¹) refers to the Langmuir model parameters and K_F and n are the Freundlich model parameters.

3.2.5. Statistical analysis

Statistical analyses were performed in R statistical software (R Core Team, 2021). One-way ANOVA and Fisher's LSD test was used to assess statistically significant differences ($p < 0.05$) among the antibiotic concentrations.

3.3. Results and discussion

3.3.1. Characterization of biochar

The surface morphology and chemical composition of the biochar were determined using SEM and EDS. According to SEM images in Figure 3.1a and Figure 3.1b, eastern red cedar biochar had an irregular surface with a wide range of pore openings. The biochar surface was smooth containing rod-like structures and pores (Figure 3.1c and Figure 3.1e). Previous research demonstrated that the microporous structure and high surface area of biochar would provide more adsorption sites for adsorbate (Ahmad et al., 2012; Kong et al., 2017; Shao et al., 2021). The EDS (Figure 3.2a) indicated traces of elements such as magnesium (Mg), potassium (K), and calcium (Ca) on the biochar surface (Figure 3.2b). These minerals were distributed across the surface (Figure 3.2) and the Mg, K, and Ca content was found to be 16.76%, 12.29%, and 70.95%, respectively. Sharma and Ratner (2021) compared the mineral composition of wood biochar from previous studies using surface area analysis and concluded that most studies indicated the presence

of these minerals next to porous regions. The presence of these Mg, K, and Ca can be a result of the pyrolysis process (Sharma and Ratner, 2021).

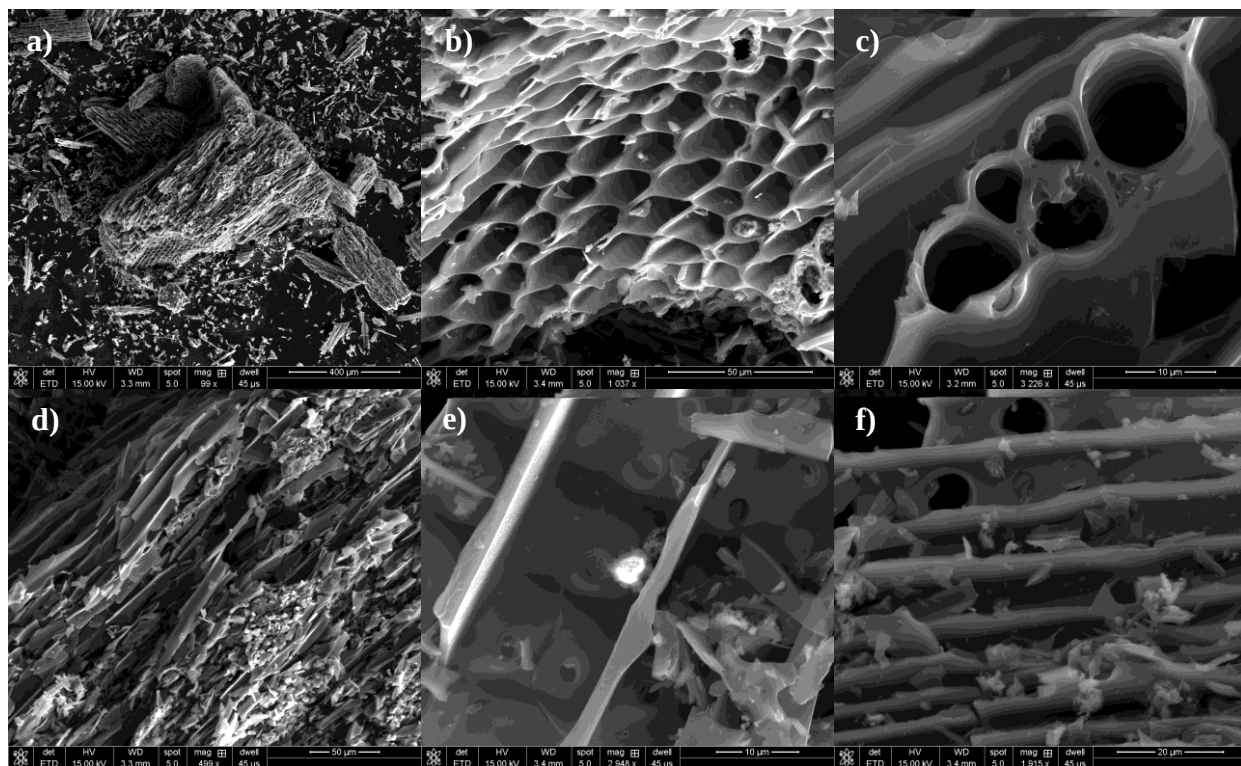


Figure 3.1. SEM images of eastern red cedar biochar.

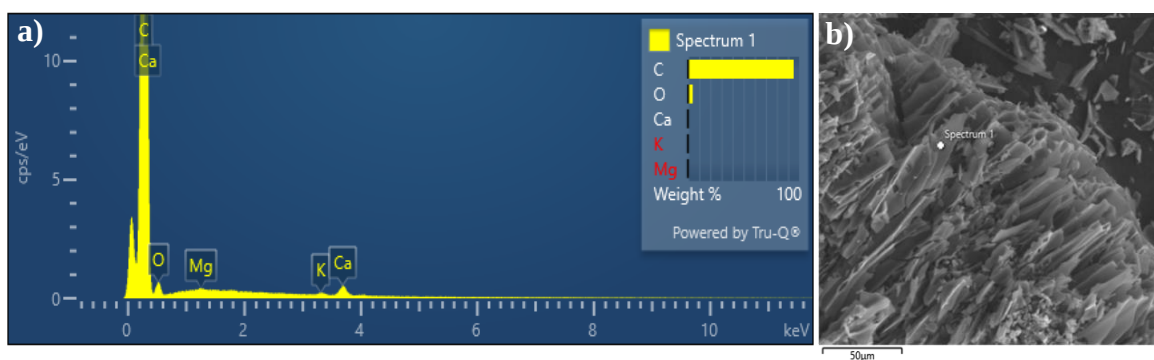


Figure 3.2. Energy dispersive X-ray spectroscopy analysis (EDS) (a) from eastern red cedar biochar surface (b).

The results of the physicochemical characteristics of eastern red cedar biochar showed that the surface of biochar mainly comprised carbon (C), oxygen (O), and Ca (Table 3.1). A high C content was exhibited in the biochar, which can be explained by the biochar preparation

temperature (450 °C). Typically, a high pyrolysis temperature can lead to a greater level of carbonization and the formation of more aromatic structures, which is associated with the dehydration and condensation reactions (Keiluweit et al., 2010; Zhao et al., 2019). As previously indicated by Yargicoglu et al. (2015), biochars with higher ratios of carbon to nitrogen (C:N) and lower ratios of hydrogen to carbon (H:C) are more likely to have experienced significant thermal alterations due to the greater loss of hydrogen and nitrogen relative to carbon, which can be observed in the eastern red cedar biochar. The eastern red cedar biochar had a BET specific surface area of 262.13 m² g⁻¹, a total pore volume of 0.1060 cm³ g⁻¹, and an average pore size of 2.33 nm.

Table 3.1. Physicochemical characteristics of eastern red cedar biochar.

Element analysis (wt%)									
C	O	H	N	Na	Mg	Si	Ca	K	P
70.1	14.5	2.3	0.58	0.2	2.4	0.7	6.1	0.6	1.8
S _{BET} (m ² g ⁻¹)		S _{mic} (m ² g ⁻¹) ^a		V _{TOT} (cm ³ g ⁻¹) ^b		V _{miv} (cm ³ g ⁻¹) ^c		D _{av} (nm) ^d	
262.13		203.92		0.1528		0.1060		2.33	

^aMicropore surface area calculated using the t-plot method.

^bTotal pore volume.

^cMicropore volume calculated with the t-plot method.

^dAverage pore diameter

Figure 3.3 represents the FTIR spectra of eastern red cedar biochar. Most of the FTIR peaks that contribute to the formation of striation features are from organic functional groups commonly present in biochar (Chia et al., 2012). The cracking of aliphatic groups, such as methyl, methylene, and methoxyl, and reformation of other functional groups such as carbonyl and carboxyl occurs with a temperature around 400 °C (Elnour et al., 2019). The aromatic groups in the eastern red cedar biochar sample give rise to C=C stretching at 1605 cm⁻¹ and aromatic C—H deformation modes around 871 cm⁻¹ and 711 cm⁻¹ (Chia et al., 2012; Liu et al., 2015). The 2080 cm⁻¹ peak could be arising from >C=C=O (ketone group). The FTIR spectra shows a strong peak at 1408 cm⁻¹

which corresponded to the —COOH (carboxyl) symmetric stretching vibration and C—C stretching vibrations in the aromatic ring, which can be confirmed by Shao et al. (2021). The peak at 1063 cm^{-1} can be related to stretching from C—O bonds in ethers, esters, and carbonates. The peaks appearing below 1000 cm^{-1} might be related to Si—O , Si—O—Si , and Si—O—Mg stretching vibrations (Cheng et al., 2017; Tang et al., 2021; Premarathna et al., 2019).

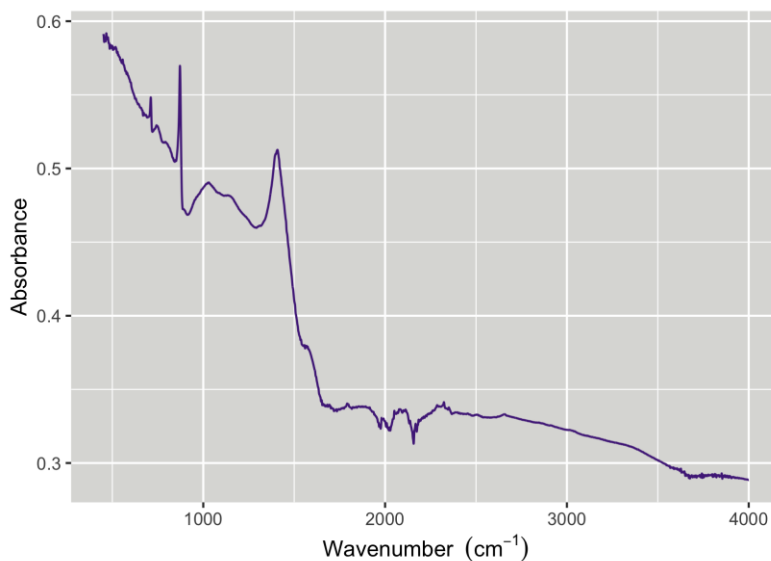


Figure 3.3. FTIR Spectra of eastern red cedar biochar.

XRD patterns indicate the presence of calcite, dolomite, calcium silicate, and bassanite as the primary crystalline phases in eastern red cedar biochar (Figure 3.4). The peaks at 26.7° and 19.5° correspond to silicon and calcium oxides, respectively (Qian et al., 2015). The strong bands at 1408 cm^{-1} and 871 cm^{-1} in the FTIR spectra (Figure 3.3) can be assigned to calcite (Singh et al., 2016), which is consistent with the XRD analysis of the eastern red cedar biochar. The obtained sharp peaks for biochar pyrolyzed at 450°C indicate that the structure of calcite is well-crystallized, which is supported by prior studies (Yuan et al., 2011; Al-Wabel et al., 2013).

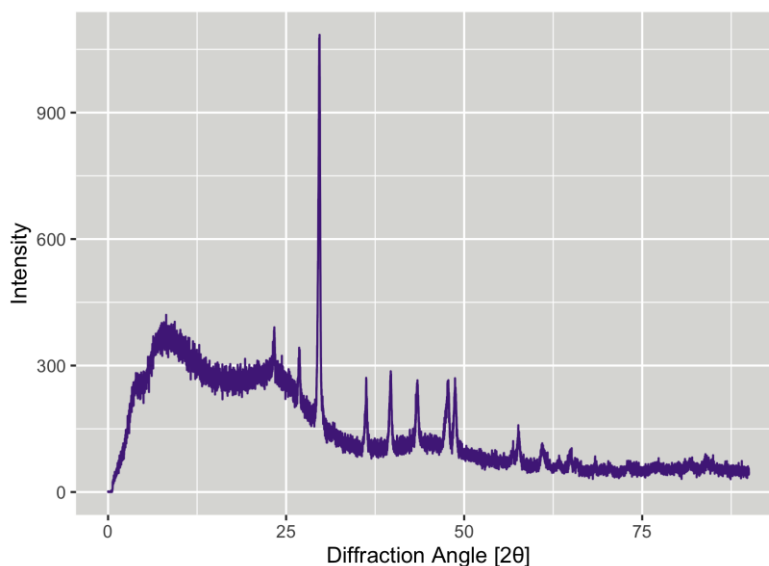


Figure 3.4. X-ray diffraction patterns of the eastern red cedar biochar.

3.3.2. Adsorption capacity

The removal efficiencies of tetracycline (TC), oxytetracycline (OTC), chlortetracycline (CTC), sulfadiazine (SDZ), and sulfamethazine (SMZ) are significantly affected by their initial concentrations ($p < 0.05$) (Figure 3.5). At lowest concentrations, the removal efficiency of TC, OTC, CTC, SDZ, and SMZ are 99.93%, 96.23%, 98.28%, 76.4% and 78.6% respectively, which might be due to the existence of many available binding sites on the surfaces of the eastern red cedar biochar and the formation of a large driving force during mass transfer process (Moussavi and Barikbin, 2010; Hao et al., 2021). When the initial concentration of the antibiotics went up to $900 \mu\text{g L}^{-1}$, the mean removal efficiencies decreased to 83.52%, 47.23%, 64.16%, 69.8%, and 58.4% for TC, OTC, CTC, SDZ, and SMZ, respectively. These unremarkable changes in the amounts of antibiotics adsorbed onto the biochar surface may be attributed to the saturation of the binding sites with higher antibiotic concentrations (Hao et al., 2021). There are other findings in the literature in agreement with our results (Moussavi and Barikbin, 2010; Ersan et al., 2015; Shan

et al., 2016; Hao et al., 2021). The differences in removal efficiency among replicates can be explained due to the heterogeneity of the biochar structure (Figure 3.1). As mentioned by Kong et al. (2021), even if the biochar is from the same source, its significant heterogeneity results in a complex structure and diverse physical properties, thereby affecting the adsorption behavior.

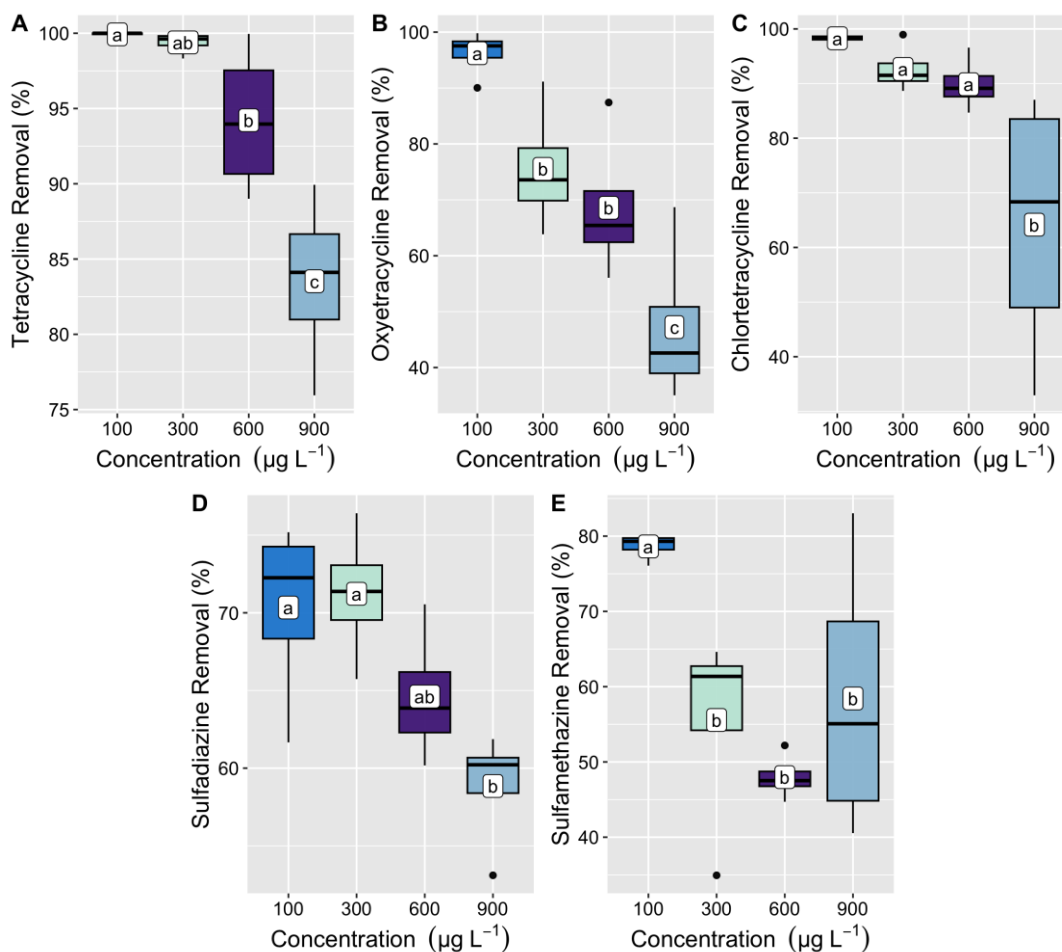


Figure 3.5. Removal efficiency of tetracycline (TC) (A), oxytetracycline (OTC) (B), chlortetracycline (CTC) (C), sulfadiazine (SDZ) (D), and sulfamethazine (SMZ) (E) at different concentrations (single effect). Means followed by the same letter are not statistically different according to Fisher's LSD test at 5% level.

In the mixture, the removal efficiency of CTC and TC at the lowest concentrations is 96.24% and 87.01%, respectively (Figure 3.6). The removal efficiency of OTC with the initial

concentration of $100 \mu\text{g L}^{-1}$ is 84.40%. At the highest concentrations, the removal efficiencies declined up to 72.85% for CTC, 35.19% for OTC, and 7.78% for TC, indicating that CTC has a preference for sites on the biochar surface compared to OTC and TC. The sorption affinity can be written in the following order as $\text{CTC} > \text{OTC} > \text{TC}$. The sorption affinity presumed that when antibiotics are sorbed onto the surface of biochar in competitive mode, they all share the same sorption sites. However, the degree of sorption depends on the physicochemical properties of antibiotics and biochar. As a result, the eastern red cedar biochar is capable of adsorbing a mixture of antibiotics onto its surface, which was consistent with the study of Ahmed et al. (2017) on eucalyptus wood biochar.

The additional chlorine atom in the chemical structure of CTC has the potential effect on electric density of the whole molecules and enhanced polarity of CTC's functional groups, leading to stronger adsorption and increased affinity for the biochar compared to OTC and TC. Moreover, the eastern red cedar biochar contains carboxyl groups (Figure 3.3) that can form hydrogen bond with hydroxyl groups of OTC. Therefore, the adsorption capacity of eastern red cedar biochar to OTC is higher than the adsorption capacity to TC. These findings are consistent with the results obtained by Lu et al. (2021).

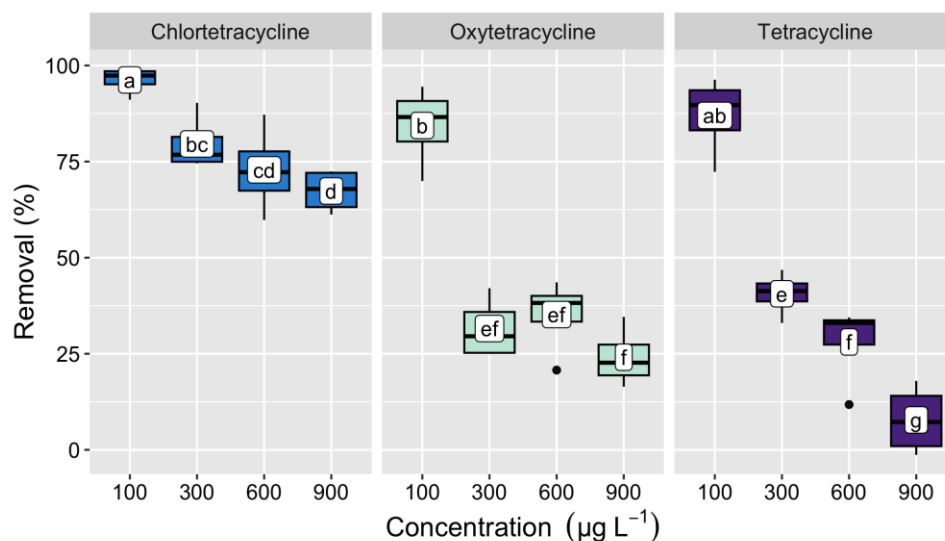


Figure 3.6. Removal efficiency of chlortetracycline (CTC), oxytetracycline (OTC), and tetracycline (TC) at different concentrations in the mix. Means followed by the same letter are not statistically different according to Fisher's LSD test at 5% level.

SDZ removal efficiencies are 70.92%, 50.05%, 33.93%, and 43.25% at the concentrations of 100, 300, 600, and 900 $\mu\text{g L}^{-1}$, respectively when mixed with SMZ (Figure 7). The mean SMZ removal when combined with SDZ is 81.23% at the concentrations of 100 and 900 $\mu\text{g L}^{-1}$ and 71.84% at the concentrations of 300 and 600 $\mu\text{g L}^{-1}$. Overall, SMZ has the highest removal efficiency compared to SDZ. Similarly, Zhao et al. (2016) observed that SMZ exhibited an adsorption affinity on biochar surface that was an order of magnitude higher compared to SDZ. The varying adsorption behavior of these sulfonamides can be attributed to the different substituents connected to the amino groups (-NH-) (Zhao et al., 2016), which lies in the extra dimethyl group that is present in the 4th and 6th carbon of the pyridine ring having much stronger π -electron-conjugating potential (4-amino-N-(4, 6-dimethylpyrimidin-2-yl) benzene-sulphonamide for SMZ and 4-amino-N-(pyrimidin-2-yl) benzene-1-sulphonamide for SDZ, respectively) (Ovung and Bhattacharyya, 2021). The presence of aromatic ring in SMZ may

enhance its affinity for the hydrophobic carbonaceous structure of biochar, leading to higher adsorption capacities compared to SDZ, as previously supported by Serna-Carrizales et al., 2021.

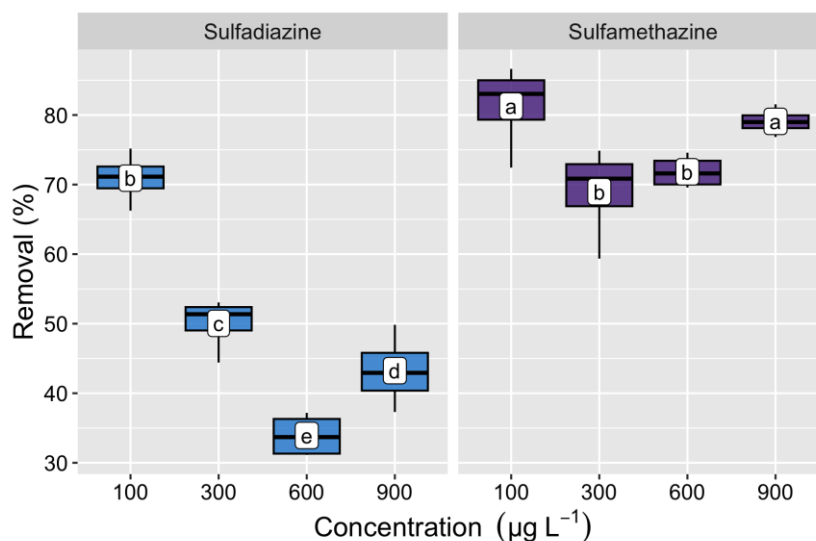


Figure 3.7. Removal efficiency of sulfadiazine (SDZ) and sulfamethazine (SMZ) at different concentrations in the mix. Means followed by the same letter are not statistically different according to Fisher's LSD test at 5% level.

Tetracyclines and sulfonamides were mixed at concentrations of 600 µg L⁻¹ and 300 µg L⁻¹. These concentrations were selected based on the relative proportions of tetracyclines and sulfonamides previously reported in the literature for swine wastewater (Cheng et al., 2020b; Wan et al., 2021). The removal efficiency was significantly affected by antibiotic ($p < 0.05$) (Figure 3.8). The highest removal efficiencies are 77.35% and 50.26% for CTC and SMZ, respectively. As previously stated, the presence of functional groups in the molecular structures of CTC and SMZ can enhance adsorption onto the surface of eastern red cedar biochar, resulting in higher removal efficiencies of CTC and SMZ compared to TC, OTC, and SDZ.

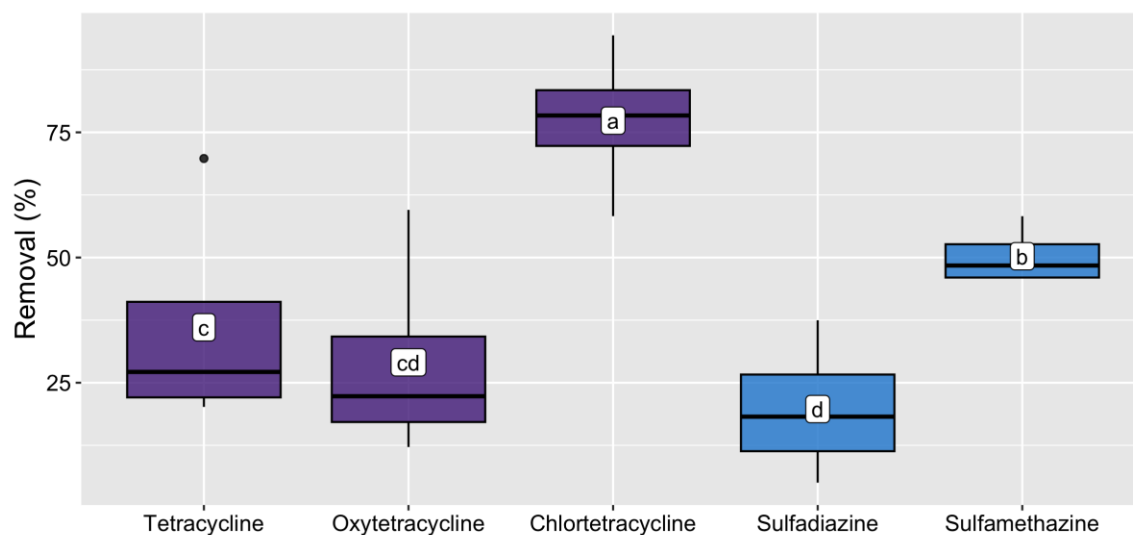


Figure 3.8. Removal efficiency of tetracyclines at $600 \mu\text{g L}^{-1}$ and sulfonamides at $300 \mu\text{g L}^{-1}$. Means followed by the same letter are not statistically different according to Fisher's LSD test at 5% level.

3.3.3. Adsorption isotherms

The Langmuir and Freundlich models are two common isotherm models used to describe the adsorption of antibiotics onto solid surfaces (Erucar and Avci, 2018). The Langmuir isotherm model assumes that the adsorption process is a monolayer process, where each molecule adsorbs onto a specific site on the solid surface. The model also assumes that the adsorption process is spontaneous and reversible and that the adsorption sites have the same energy (Liu et al., 2019). On the other hand, the Freundlich isotherm model assumes that the adsorption process is multilayer and that the adsorption sites have different energies. The value of n (slope) provides information about the adsorption mechanism. A value of n close to 1 indicates a physical adsorption process, while a value of n greater than 1 suggests a chemical adsorption process (Kalam et al., 2021).

The results for the Linear, Langmuir, and Freundlich models for the tetracycline class individually (Figure 9a) and in the mix (Figure 9b) indicate that the Langmuir model has the best fit for the experimental data with a larger correlation coefficient (single effect = $R^2 \geq 0.93$ and mixture effect = $R^2 \geq 0.50$), suggesting that the adsorption of tetracyclines onto eastern red cedar biochar is a reversible monolayer sorption mechanism.

The experimental data for the sulfonamide class individually and in the mix displayed stronger correlation with the Freundlich model (Figure 3.10a and 3.10b), as evidenced by the higher correlation coefficients R^2 (single effect = $R^2 \geq 0.67$ and mixture effect = $R^2 \geq 0.86$) than those in Langmuir model. This correlation indicates that the interactions between sulfonamides molecules and the eastern red cedar biochar are multilayer adsorption taking place on the biochar's heterogeneous surfaces (Figure 3.10b).

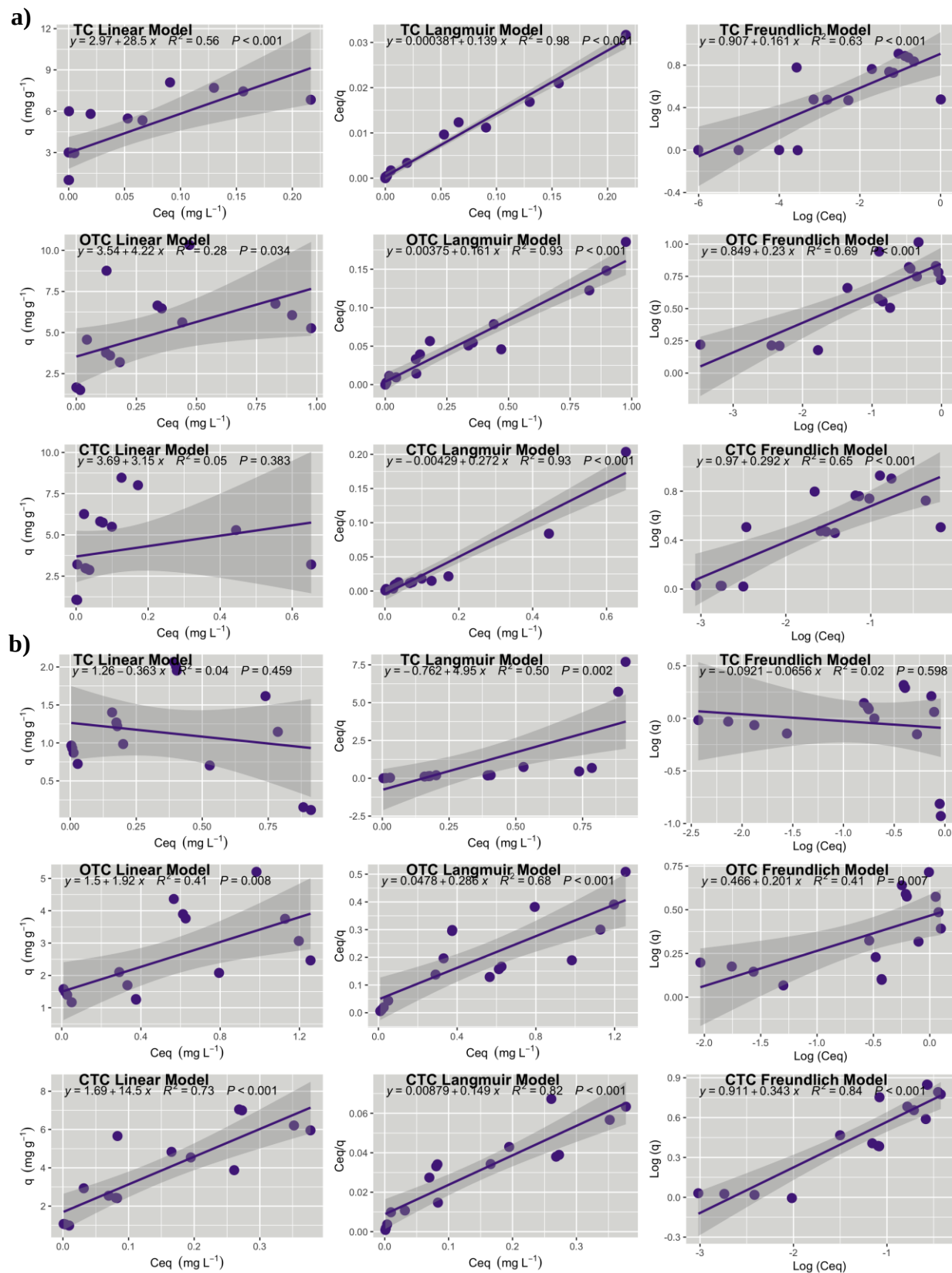


Figure 3.9. Linear, Langmuir, and Freundlich models for tetracycline (TC), oxytetracycline (OTC), and chlortetracycline (CTC) single effect (a) and mix effect (b).

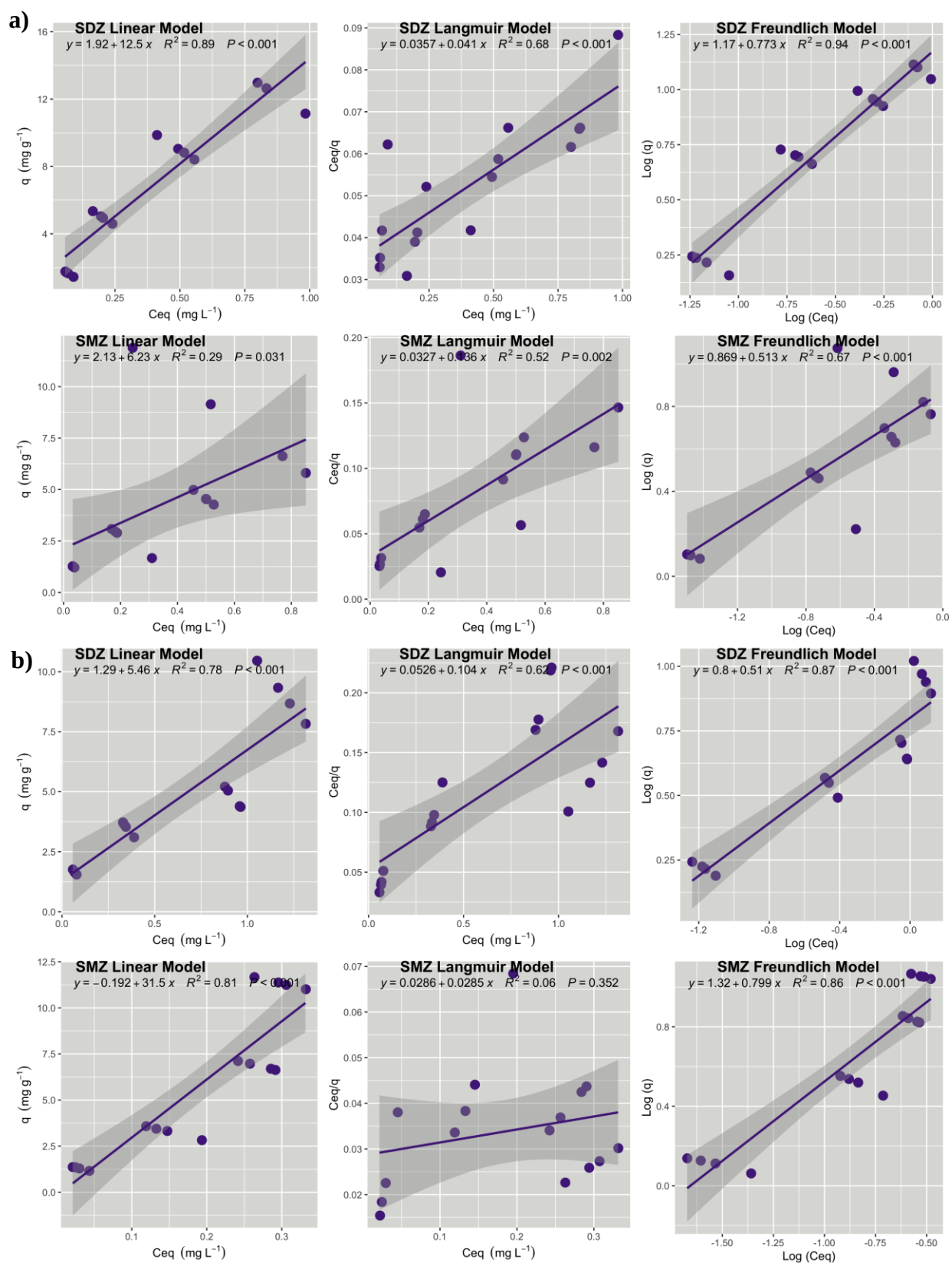


Figure 3.10. Linear, Langmuir, and Freundlich models for sulfadiazine (SDZ) and sulfamethazine (SMZ) single effect (a) and mix effect (b).

3.3.4. Adsorption mechanisms

The functional groups of tetracyclines can undergo numerous electronic coupling interactions including electrostatic interactions, $\pi - \pi$ electron-donor-acceptor, and Lewis acid-base interactions (Peiris et al., 2017). Similarly, the adsorption of sulfonamides was attributed to various mechanisms, such as hydrogen bonds, $\pi - \pi$ electron-donor-acceptor interactions, van der Waals forces, hydrophobicity, and pore-filling (Ahmed et al., 2017; Sun et al., 2018; Li et al., 2019; Zhang et al., 2020). Generally, hydrogen-bonding and $\pi - \pi$ electron-donor-acceptor seem to be the major mechanisms which drive the adsorptive removal of these two classes of antibiotics from aqueous solutions using carbon-based materials (Biswal and Balasubramanian, 2022).

On eastern red cedar biochar, hydrogen bonds played an important role in both tetracyclines and sulfonamides removal due to the carboxyl group confirmed by the FTIR spectra (Figure 3.3), which indicates a possible adsorption mechanism involving hydrogen bonds between the antibiotics and the carboxyl group around 1408 cm^{-1} . Phenol, amine, hydroxyl, and enone moieties of tetracyclines can form hydrogen bonding with carboxyl functional groups on biochar surfaces (Peiris et al., 2017). Likewise, the amino and amine groups from sulfonamides can interact with carboxyl and hydroxyl groups on the surface of eastern red cedar biochar through hydrogen bonding (Zhao et al., 2016).

Conjugated enone structures of tetracyclines can act as π electron-acceptors considering the strong electron-withdrawing ability of the ketone group (Jing et al., 2014). Sulfonamides can be strong π electron-acceptor due to the presence of amino and aromatic groups in the molecular structure. On the other hand, the presence of a significant number of oxygen-containing functional groups on the eastern red cedar biochar surface (Figure 3.3) indicates its potential to act as an

electron-donor (Geng et al., 2021). Thus, the $\pi - \pi$ electron-donor-acceptor interaction is crucial in the adsorption process of tetracyclines and sulfonamides on eastern red cedar biochar.

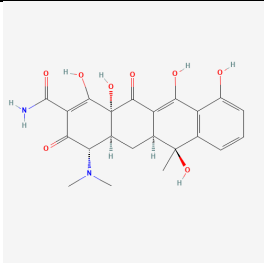
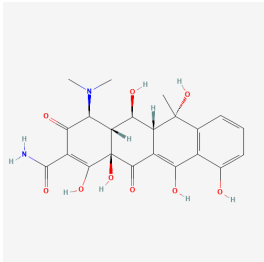
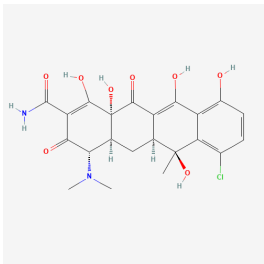
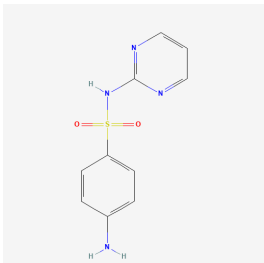
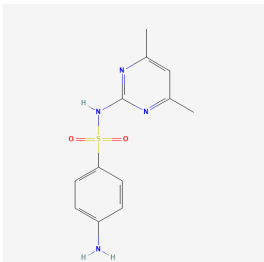
Lewis acid-base interactions can also occur between Lewis acids (-OH and C=O) on the eastern red cedar biochar surface and Lewis base (-NH₂) on tetracyclines and sulfonamides (Peiris et al., 2017; Ma et al., 2022). Furthermore, considering the surface area (S_{BET}) and pore volume (V_{TOT}) (Table 1) of the eastern red cedar biochar providing abundant adsorption sites (Figure 3.1), the favorable adsorption between the antibiotics and the biochar could be due to pore-filling effect (SEM and BET analysis) (Shikuku et al., 2018; Ma et al., 2022).

Nevertheless, the different adsorption efficiencies obtained for tetracyclines and sulfonamides onto biochar can be linked to particular properties of the antibiotics (Table 2). Chemical properties, specifically octanol-water partitioning coefficient (K_{ow}) and acidity constant (pK_{a}) play major roles in assessing the adsorption behavior of different tetracyclines and sulfonamides. The K_{ow} is commonly used as an indicator of the adsorbate's hydrophobicity, thus antibiotics with low log K_{ow} are more hydrophilic (Harrower et al., 2021). The pK_{a} is related to the speciation of the antibiotics. Hence, the capacities of different antibiotics under the same conditions result from a combination of multiple forces (Zhang et al., 2020).

In this study, hydrophobicity can play a more important role in the sorption of SMZ and CTC on eastern red cedar biochar, because these antibiotics had higher log K_{ow} than SDZ, OTC and TC. In addition, based on the pK_{a2} values (Table 2), SDZ molecules ($\text{pK}_{\text{a2}} = 6.5$) were negatively charged at pH of 7, while SMZ molecule ($\text{pK}_{\text{a2}} = 7.65$) existed in more neutral species. Since neutral molecules tend to be more strongly sorbed on biochar than negatively charged molecules (Zhang et al., 2020), SMZ with its more neutral species will likely have a higher affinity for sorption on eastern red cedar biochar compared to SDZ with its negatively charged species at

pH 7. Likewise, TC ($\text{pK}_{\text{a}2} = 7.68$), OTC ($\text{pK}_{\text{a}2} = 7.32$), and CTC ($\text{pK}_{\text{a}2} = 7.55$) existed in both neutral and negatively charged forms at pH 7, but OTC will be more neutral as the $\text{pK}_{\text{a}2}$ is lower, which explains the higher sorption capacity when compared to TC. However, the higher sorption behavior of CTC may be explained by the enhanced polarity of CTC's functional groups due to the additional chlorine atom and thus stronger polar-polar interactions with the eastern red cedar biochar surface, which is coherent with the results found by Chen et al. (2010) on aluminum oxide surfaces.

Table 3.2. Physico-chemical properties of TC, OTC, CTC, SDZ, and SMZ.

Antibiotic	Chemical structure	Chemical formula	pKa	Log Kow
TC		$C_{22}H_{24}N_2O_8$	pKa ₁ = 3.30 pKa ₂ = 7.68 pKa ₃ = 9.69	-1.30
OTC		$C_{22}H_{24}N_2O_9$	pKa ₁ = 3.27 pKa ₂ = 7.32 pKa ₃ = 9.11	-0.90
CTC		$C_{22}H_{23}ClN_2O_8$	pKa ₁ = 3.30 pKa ₂ = 7.55 pKa ₃ = 9.15	-0.62
SDZ		$C_{10}H_{10}N_4O_2S$	pKa ₁ = 2.0 pKa ₂ = 6.5	-0.90
SMZ		$C_{12}H_{14}N_4O_2S$	pKa ₁ = 2.65 pKa ₂ = 7.65	0.89

*Data obtained from PubChem (<https://pubchem.ncbi.nlm.nih.gov/>) U.S. National Library of Medicine.

The molar ratios of O/C, H/C, and (N+O)/C represents the hydrophobicity, aromaticity, and polarity of a biochar (Rajapaksha et al., 2014). Eastern red cedar biochar had relatively low

ratios of O/C (0.20), H/C (0.03) and (N+O)/C (0.22) (Table 1), suggesting its high hydrophobicity, aromaticity, and low polarity (Zhang et al., 2020). Usually, these ratios are low with a high pyrolysis temperature, and thus biochars produced under high temperature are highly carbonized, more hydrophobic, and exhibited a highly aromatic structure (Rajapaksha et al., 2014). However, these features are present in eastern red cedar biochar produced at a pyrolysis temperature of 450 °C (Table 3.1 and Figure 3.3), which contributes to its adsorption efficiency.

3.5. Conclusion

In summary, the adsorptive removal of tetracyclines (TC, OTC, and CTC) and sulfonamides (SDZ and SMZ) antibiotics from swine wastewater on eastern red cedar biochar was investigated at four different concentrations. At lowest concentrations, the removal efficiencies of TC, OTC, CTC, SDZ, and SMZ are 99.93%, 96.23%, 98.28%, 76.4%, and 78.6%, respectively. At highest concentrations, the removal efficiencies decreased to 83.52%, 47.23%, 64.16%, 69.8%, and 58.4% for TC, OTC, CTC, SDZ, and SMZ. When antibiotics are combined, the eastern red cedar biochar exhibited stronger adsorption capacity for CTC and SMZ compared to TC, OTC, and SDZ. The adsorption capacity and mechanism can be significantly influenced by the chemical properties of each antibiotic and the surface properties of the biochar. Eastern red cedar biochar has a wide range of pore openings, a specific surface area of $262.13 \text{ m}^2 \text{ g}^{-1}$ providing adsorption sites for antibiotics. Moreover, FTIR characterization revealed the active sites of biochar for antibiotic adsorption. Sorption of tetracyclines can be described by Langmuir adsorption isotherm model adequately, indicating that it is a monolayer sorption on the biochar surface. On the other hand, sorption data of sulfonamides were better fitted to the Freundlich model, implying that electrostatic interactions existed in the midst of heterogeneous sites on eastern red cedar biochar.

Mostly, the major adsorption mechanisms driving the removal of both sulfonamides and tetracyclines from the aqueous solution are hydrogen-bonding and $\pi - \pi$ electron-donor-acceptor, whereas Lewis base-acid interactions and pore-filling may be auxiliary sorption mechanisms. The results highlighted that eastern red cedar biochar was proved to be a promising adsorbent to be used for practical applications, eliminating antibiotic residues from swine wastewater in a cost-effective and environmentally friendly manner due to its relatively low pyrolysis temperature (450 °C) and use of an invasive species.

3.6. References

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Chapter 4 - Performance simulation of constructed wetlands systems for anaerobic membrane bioreactor effluent polishing

This chapter is a manuscript in preparation to be submitted for publication. The co-authors on this manuscript include Stacy Hutchinson, Pankaj Kumar Gupta, Prathap Parameswaran, Ganga Hettiarachchi, and Trisha Moore.

4.1. Introduction

Increasing weather extremes, including elevated temperatures and changes in precipitation patterns and intensities can be expected as a consequence of the ongoing climate change (Petreje et al., 2023). Additionally, the global demand for food is expected to increase due to population growth and change in consumption habits (Rechmann et al., 2013). Agriculture plays a key role in food security by supplying a significant amount of food to meet the needs of society, although this can increase the risk of soil-water pollution (Woonwong et al., 2020). Agricultural runoff, which contains nutrients, represents one of the largest sources of soil, surface water and groundwater pollution in the world (Nzengung and Gugolz, 2022). Livestock operations such as concentrated animal feeding operations (CAFOs) produce large amounts of manure, and their improper management seriously contributes to nutrient pollution of fresh water sources (Zahoor and Mushtag, 2023). Swine wastewater discharged by intensive pig farms can severely pollute soil-water systems, because it contains high concentrations of organic matter and nutrients (Zeng et al., 2019). Several contaminants contribute to water pollution, including elevated levels of nitrogen and phosphorus, which can lead to eutrophication and the proliferation of harmful algal blooms, resulting in oxygen depletion and fish kills (Zahoor and Mushtag, 2023).

In recent years, many treatment technologies, such as anaerobic digestion (AD) and constructed wetlands (CWs), have been studied individually to treat swine wastewater (Feng et al., 2020; Wang et al., 2022). AD technologies are widely used to treat animal manure due to their efficient biodegradation of pollutants and production of bioenergy in the form of biogas (Zeng et al., 2019; Chen et al., 2023). Through anaerobic biodegradation, organic matter can be biologically converted into methane (CH₄)-rich biogas, bioproducts, and digested effluent containing bioactive nutrients (Dai et al., 2015; Zhang et al., 2020; Liu et al., 2022). Among the available AD processes, the anaerobic membrane bioreactor (AnMBR) stands out as an option for anaerobic treatment, delivering high quality treated permeate and energy-rich biogas through the integration of AD process with the membrane filtration processes (Hu et al., 2018; Kannan and Parameswaran, 2021). However, due to the presence of complex components in swine wastewater and the dynamic flux of contaminants, performance of AD is usually unstable to meet the stringent standards of water quality (Tang et al., 2022; Chen et al., 2023).

Constructed wetlands (CWs) are complex biogeochemical systems that are widely recognized as eco-friendly systems for the treatment of such pollutants due to their easy operation, low cost, and high-performance efficiency (Vyzamal, 2002; Nyquist and Greger, 2009, Rai et al., 2013; Dar et al., 2021; Dar et al., 2023). CWs are engineered systems designed for appropriate processes which can improve the efficacy of treatment systems for wastewater. Thus, generally these systems combine plants, filter media, and associated microorganisms to remove target contaminants through a combination of physical, chemical, and biological processes (Almeida et al., 2017; Bôto et al., 2023). Li et al. (2020) studied the application of CW systems for nutrient removal from swine wastewater and concluded that the nitrogen and phosphorus removal efficiencies were higher than 90%. Likewise, Mustapha et al. (2018) evaluated the performance of

duplex CWs to treat wastewater containing complex organic contaminants. As a crucial consideration for the successful function of CWs, the size of these systems must be appropriately designed to accommodate the target treatment needs (Nan et al., 2023). In this context, it is noteworthy to emphasize the importance of integrating AnMBR with CWs to reduce the size requirements of CWs. This integration enhances the overall performance of the system by combining the advantages of AnMBR, such as efficient organic matter degradation and biogas production, with the pollutant removal capabilities of the CWs.

CWs plants play an important role in pollutant removal. However, extreme conditions such as dynamic flux of contaminants, which exceed the tolerance of plants will inhibit their survival and reduce treatment performance (Feng et al., 2021). The presence of toxic substances in wastewater can result in serious acute and chronic health concerns in CWs plants (Li et al., 2023). Exposure of macrophytes to excess of pollutants may result in reduced growth, inhibited photosynthesis, oxidative stress, changes in nutrient uptake, long-term damage to physiological functions, or even plant death (Hu et al., 2018a). Thus, the CW filter media plays a fundamental role in the growth and development of plants and microorganisms and pollutant removal through sorption. Biochar is a carbon-rich material, increasingly recognized as a multifunctional media with the ability to remediate organic and inorganic contaminants through sorption processes (Gupta et al., 2016). Gupta et al. (2016) evaluated the efficiency of CWs systems with biochar for the removal of organic matter, nitrogen, and phosphorus and concluded that highest removal rates were achieved in wetlands containing biochar as filter media. Contaminant removal relied on several factors such as adsorption, precipitation, filtration, sedimentation, microbial degradation, and plant uptake (Gupta et al., 2016).

Numerical approaches are available to model and evaluate CW contaminant removal under varying environmental conditions (Mustapha et al., 2018). The constructed wetland 2D module (CW2D) developed by Langergraber and Šimůnek (2006) is incorporated in the HYDRUS 2D model and is used to simulate multi-reactive transport of pollutants along with varying water flow through the CWs systems (Mustapha et al., 2018). CW2D is able to describe the biochemical elimination and transformation processes for dissolved forms of organic matter, nitrogen and phosphorus (Langergraber, 2007). CW models are suitable for describing the CW system (e.g., water flow, adsorption, O₂ transfer), evaluating the systems behavior under different conditions (e.g., effect of loading characteristics and season), predicting the performance of a given system (e.g., developing design recommendations), and answering “what if?” questions (e.g., over or under loads) (Meyer et al., 2015).

HYDRUS CW2D has simulated different types of CWs successfully, presenting a good accuracy between the simulated and the measured effluent concentrations and increasing the acceptance of CW models in general (Langergraber, 2008; Kumar and Zhao, 2011; Langergraber and Šimůnek, 2012; Meyer et al., 2015; Pálffy et al., 2016; Mustapha et al., 2018; Adhikary et al., 2021). For instance, Raude et al. (2018) compared model-predicted values with laboratory measurement and the correlation values ranging between 0.825 and 0.956 indicated that the model could be used to make accurate predictions. Their results further provided evidence that CW2D can be an effective tool for evaluating the performance of CWs. CW2D is a very complex model, designed to simulate the main biochemical processes that occur in wastewater application to CWs and can serve as a basis for large-scale decision-making processes (Wunsch et al., 2009).

The integration of AnMBR with CWs represents a promising convergence of advanced technology with a nature-based approach. This synergistic relationship takes advantage of the

strengths of each system, providing a holistic solution that combines the precision and efficiency of the AnMBR with the adaptability and resilience of the CW systems. The AnMBR is characterized by its controlled anaerobic conditions and membrane filtration and demonstrates exceptional performance in the removal of organic matter (Pu et al., 2022). On the other hand, CWs utilize the capabilities of plants, filter media, and microorganisms to naturally purify water, adapting to seasonal variations and fluctuations in flow rates (Valipour and Ahn, 2016; Wu et al., 2023). This integration not only addresses the limitations of each system separated but also creates a synergy that optimizes performance across various operating conditions. The integration of AnMBR and CWs represents an innovative approach, demonstrating how the marriage of advanced technology and natural adaptability can yield a robust and sustainable solution for wastewater treatment.

In this paper, CW systems were designed as a polishing step for AnMBR effluent with varying NH_4^+ , P, and chemical oxygen demand (COD). The goal of this study was to evaluate the performance of vertical flow CW systems in removing nutrients from swine wastewater after AnMBR treatment under varying loading rates and temperatures conditions (10, 20, 30, and 40 °C) through simulations conducted with the HYDRUS software using the CW2D module. The numerical simulation of the CWs systems will lay a foundation on the design criteria for its large-scale application.

4.2. Methods

4.2.1. Experimental set-up

A 2D study domain representing a vertical flow CW, hereafter VFCW, was created to model treatment system processes and improve field design (Figure 4.1). The model was designed

based on a bench-scale CW system and parameterized using preliminary data from the bench-scale system augmented with additional information from the literature. The bench-scale system consisted of an influent tank located next to the VFCW, one pump used to pump the influent into the VFCW, and an effluent tank used to collect the treated water. The size of the VFCW was 0.44 m L x 0.225 m W x 0.74 m D, with a surface area of 0.099 m² (L x W), an effective volume of 0.0594 m³ and a hydraulic loading rate (HLR) of 0.125 m d⁻¹. The system was designed to operate with a 10 cm drainage layer (gravel size 19 – 25 mm), a 20 cm main gravel layer (12 – 19 mm), a 3 cm separation layer (gravel 6 – 9 mm), a 20 cm of soil (silt loam:sand, 2:1 ratio) mixed with eastern redcedar biochar (70% soil and 30% biochar), and 7 cm top layer (gravel size 12 – 19 mm). Two observation nodes situated at the top and outlet of the VFCW were considered to represent the sampling ports of the experimental setup (Mustapha et al., 2018). The VFCW were planted with cattails (*Typha spp.*).

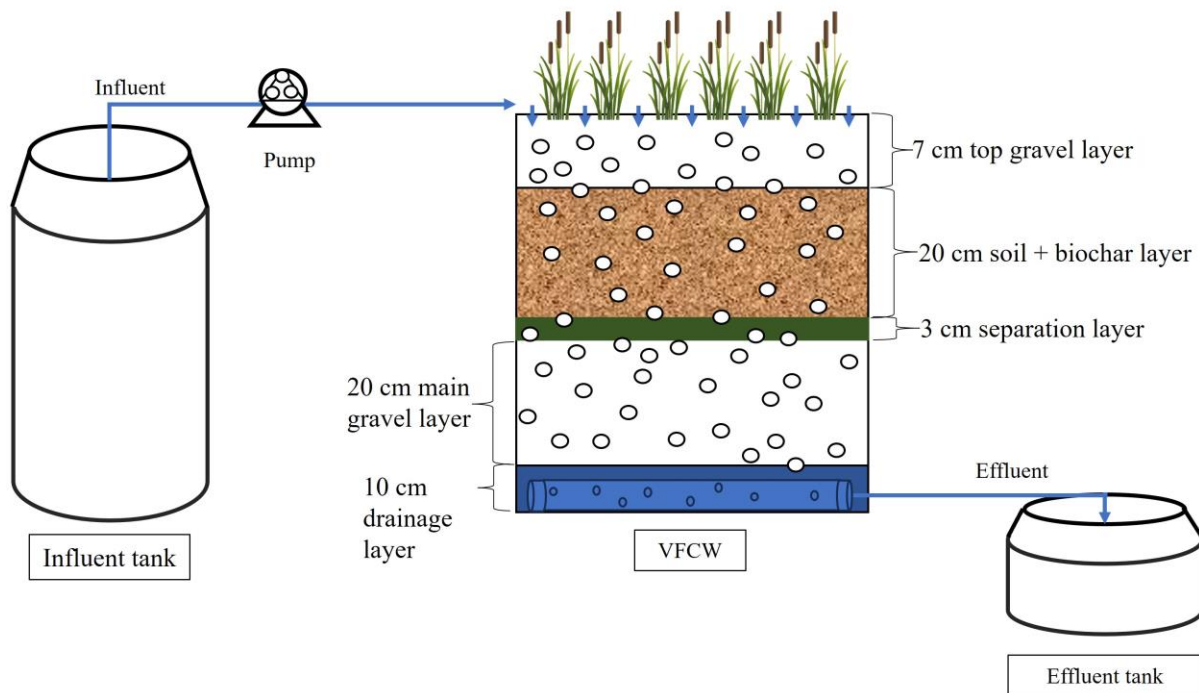


Figure 4.1. Schematic representation of the VFCW configuration.

The hydraulic properties of the filter media were characterized using the van Genuchten-Mualen approach (van Genutchen, 1980). The properties of the porous media were estimated in primary studies (Table 4.1) (Mallants et al., 2003; Arias and Ergas, 2023). Saturated water content (θ_s) was estimated experimentally and matches the values obtained from the literature.

Table 4.1. van Genuchten parameters for soil layers.

Soil layer	θ_r	θ_s	α (1 cm^{-1})	n (-)	K_s (cm h^{-1})	I (-)
Main gravel	0.005	0.42	0.493	2.19	12600	0.5
Soil + biochar	0.0665	0.51	0.012	1.48	4.97	0.5
Separation layer	0.03	0.33	0.007	2.96	1188	0.5
Main gravel	0.005	0.42	0.493	2.19	12600	0.5
Drainage layer	0.045	0.15	0.145	2.68	60000	0.5

θ_r = residual water content;

θ_s = saturated water content;

α (1 cm^{-1}) = describes how the soil water content changes with changes in soil water potential;

n = porosity exponent;

K_s (cm h^{-1}) = saturated hydraulic conductivity;

I = vertical van Genuchten parameter.

The parameters for the soil + biochar layer presented in Table 4.1 were obtained through inverse simulation in HYDRUS by indicating the results measured for soil texture and bulk density. The bulk density of the soil and biochar mix is 0.99 g cm^{-3} and was calculated after determining the volume and weight of soil and biochar mix. Table 4.2 shows the characterization of the soil and Table 4.3 presents the characterization of the biochar from eastern red cedar selected for utilization in the VFCW. The concentrations of Zn, Fe, Cu, and Mn in the soil (Table 4.2) were determined using the DTPA (Diethylene Triamine Pentaacetic Acid) extraction method (Whitney, 1998). Details on the procedure for table 4.3 can be found in Chapter 3.

Table 4.2. Characteristics of the soil selected for utilization in the VFCW.

Sand	Silt	Clay	pH	Zn	Fe	Cu	Mn	Total N	TOC	CEC
-----%	-----%	-----%		-----	mg kg ⁻¹	-----	-----	-----%	-----	cmol+ kg ⁻¹
52	30	18	7.8	0.2	10	0.7	9	0.07	0.75	10.3

Table 4.3. Characterization of eastern red cedar biochar.

Element analysis (wt%)										
C	O	H	N	Na	Mg	Si	Ca	K	P	
70.1	14.5	2.3	0.58	0.2	2.4	0.7	6.1	0.6	1.8	

Biochar acts as a powerful amendment with the potential to enhance pollutant removal, nutrient retention, and overall ecosystem functioning in CWs. The presence of biochar in CWs can improve water retention capacity, helping to maintain stable hydrological conditions (Li et al., 2019). Additionally, its porous structure facilitates the colonization of beneficial microorganisms, promoting biodegradation of contaminants and supporting nutrient cycling in the CWs (Hu et al., 2023). Therefore, biochar is added to the soil layer to increase nutrient retention, contributing to an enhanced water polishing treatment of AnMBR permeate. The adsorption coefficient (K_d) was determined in the soil + biochar layer for NH_4^+ and P. A solution containing a known concentration of NH_4^+ and P was mixed with a soil + biochar sample for 24 hours until reached equilibrium. The solution was filtered, and the equilibrium concentration (C_e) was measured. The K_d was calculated using the Eq. 4.1:

$$K_d = \frac{(C_o - C_e) \times V}{C_e \times m}, \quad (4.1)$$

where, C_o is the initial concentration of NH_4^+ and P (mg L^{-1}), C_e is the equilibrium concentration of NH_4^+ and P (mg L^{-1}), V is the volume of solution (L), and m is the mass of soil and biochar (g). The results obtained for NH_4^+ and P are 2.43 L g^{-1} and 2.19 L g^{-1} , respectively.

4.2.2 Numerical simulations

Numerical simulations were conducted to assess the capacity of VFCW in removing NH_4^+ and P from AnMBR permeate. Specifically, this study seeks to establish how CWs can function as a robust buffer mechanism for the AnMBR technology, particularly under conditions relevant to practical and operational challenges in wastewater treatment. These simulations aimed to evaluate concentrations of nutrients previously measured under several conditions, including the unpredictability of AnMBR system failures, operational instabilities, and challenges associated with treating very high nutrient concentrations. All simulations were differentiated by their nutrient levels, corresponding to concentrations of 50, 175, and 325 mg L^{-1} of NH_4^+ -N and 10, 40, and 100 mg L^{-1} of PO_4^{3-} -P (Table 4.4). The variation in NH_4^+ , P, and COD concentrations is substantial due to changes in pig weight during production cycles (Vanotti et al., 2018). NH_4^+ -N and PO_4^{3-} -P concentrations in the AnMBR permeate usually are in the range from 200 to 400 mg L^{-1} and 15 to 85 mg L^{-1} , respectively (Kannan et al., 2022; Chen et al., 2023). COD levels in swine lagoon effluent typically range from 1,000 to 25,000 mg L^{-1} (Aggarangsi and Teerasountornkul, 2011; Vanotti et al., 2018), with AnMBR treatment capable of effectively removing up to 90% of this COD (Pu et al., 2022). Thus, the simulations were performed to evaluate the impact of COD concentrations of 100, 500, 1,500, and 2,500 mg L^{-1} on nutrient removal (Table 4.4).

Table 4.4. Initial concentrations of COD, $\text{NH}_4^+\text{-N}$, and $\text{PO}_4^{3-}\text{-P}$ used to simulate VFCW performance on AnMBR effluent polishing for each temperature condition.

COD	$\text{NH}_4^+\text{-N}$	$\text{PO}_4^{3-}\text{-P}$
-----mg L⁻¹-----		
100	50	10
500	50	10
1,500	50	10
2,500	50	10
100	175	40
500	175	40
1,500	175	40
2,500	175	40
100	325	100
500	325	100
1,500	325	100
2,500	325	100

For this simulation study, the HYDRUS CW2D biokinetic model was used (Langergraber and Šimůnek, 2012). HYDRUS was selected because it is a comprehensive tool for modeling water and solute flow in soil (Šimůnek et al., 2007; Šimůnek et al., 2008; El-Nesr et al., 2014; Brunetii et al., 2019; Dong et al., 2019; Zhou et al., 2021). HYDRUS numerically solves the Richards equation and the advection-dispersion equation to determine water flow and solute transport (Šimůnek et al., 2011). The Richards equation identifies saturated or unsaturated conditions based on pressure head values. For example, it assumes saturated conditions for positive pressure head values and unsaturated conditions for negative pressure head values (Khan et al., 2022). Because nitrogen is affected by soil water content, the aerobic and anaerobic conditions within the VFCW influence nitrification and denitrification. Therefore, the correct water flow modeling is crucial to understand the nitrogen transformation processes (Dong et al., 2019). No flux boundary was selected for the side faces of the domain because there is no water inflow and outflow in this

region. Additionally, a constant head was selected for the drainage layer of the lower portion of the VFCW with a pressure head of 5.5 cm.

The CW2D biokinetic model is based on the International Water Association Activated Sludge Models (ASM) (Henze et al., 2000), which considers processes affecting organic matter, N, and P. It is assumed that all components except bacteria are soluble (including the particulate COD fraction) and that bacteria are immobile (Langergraber and Šimůnek, 2012). CW2D incorporates aerobic and anoxic transformation and degradation processes, such as hydrolysis, growth of heterotrophic bacteria (XH) describing mineralization of organic matter as well as denitrification on nitrate and lysis for XH, nitrification as a two-step process describing the growth and lysis of autotrophic bacteria, specifically ammonium oxidation by *Nitrosomonas spp.* (XANs) and nitrite oxidation by *Nitrobacter spp.* (XANb) (Pucher and Langergraber, 2019).

The biogeochemical transformation and degradation processes are modelled using the Monod rate equations as defined in ASM (Henze et al., 2000; Langergraber and Šimůnek, 2012). The growth and decay rate parameters as well as the diffusion coefficients are temperature dependent and are estimated from the literature (Table 4.5). Kinetic parameters for 10 °C and 20 °C are used from Henze et al. (2006) and for 30 °C are used from Jayswal and Rodríguez (2021). Those parameters for 40 °C are estimated as per Tchobanoglous et al. (2003). The saturation/inhibition coefficients are considered constant for all temperatures (Jayswal and Rodríguez, 2021) (Table 4.5).

Table 4.5. Kinetic parameters in CW2D (Langergraber and Šimůnek, 2005^a; Jayswal and Rodriguez, 2021^b).

Kinetic parameter	Description	10 °C ^a	20 °C ^a	30 °C ^b	40 °C Estimated
K_h [1/h]	hydrolysis rate constant	0.083	0.125	0.1825	0.2662
K_X [mg _{COD,CS} /mg _{COD,BM}]	saturation/inhibition coefficient for hydrolysis	0.22	0.10	0.05	0.02
μ_H [1/h]	maximum aerobic growth rate on CR	0.125	0.25	0.4775	0.9674
b_H [1/h]	rate constant for lysis	0.0083	0.017	0.032	0.061
K_{het,O_2} [mg _{O2} /l]	saturation/inhibition coefficient for O ₂	0.20	0.20	0.20	0.20
$K_{het,CR}$ [mg _{COD,CR} /l]	saturation/inhibition coefficient for substrate	4.00	4.00	4.00	4.00
K_{het,NH_4N} [mg _{NH4N} /l]	saturation/inhibition coefficient for NH ₄ (nutrient)	0.05	0.05	0.05	0.05
$K_{het,IP}$ [mg _{IP} /l]	saturation/inhibition coefficient for P	0.01	0.01	0.01	0.01
μ_{DN} [1/h]	maximum denitrification rate	0.1	0.2	0.382	0.732
K_{DN,O_2} [mg _{O2} /l]	saturation/inhibition coefficient for O ₂	0.20	0.20	0.20	0.20
K_{DN,NO_3N} [mg _{NO3N} /l]	saturation/inhibition coefficient for NO ₃	0.50	0.50	0.50	0.50
K_{DN,NO_2N} [mg _{NO2N} /l]	saturation/inhibition coefficient for NO ₂	0.50	0.50	0.50	0.50
$K_{DN,CR}$ [mg _{COD,CR} /l]	saturation/inhibition coefficient for substrate	4.00	4.00	4.00	4.00
K_{DN,NH_4N} [mg _{NH4N} /l]	saturation/inhibition coefficient for NH ₄ (nutrient)	0.05	0.05	0.05	0.05
$K_{DN,IP}$ [mg _{IP} /l]	saturation/inhibition coefficient for P	0.01	0.01	0.01	0.01
μ_{ANs} [1/h]	maximum aerobic growth rate on NH ₄	0.0125	0.0375	0.1046	0.1506
b_{ANs} [1/h]	rate constant for lysis	0.0021	0.0063	0.0175	0.0490
K_{ANs,O_2} [mg _{O2} /l]	saturation/inhibition coefficient for O ₂	1.00	1.00	1.00	1.00
K_{ANs,NH_4N} [mg _{NH4N} /l]	saturation/inhibition coefficient for NH ₄	0.50	0.50	0.50	0.50
$K_{ANs,IP}$ [mg _{IP} /l]	saturation/inhibition coefficient for P	0.01	0.01	0.01	0.01

μ_{ANb} [1/h]	maximum aerobic growth rate on NO ₂	0.0146	0.0417	0.1113	0.1414
b_{ANb} [1/h]	rate constant for lysis	0.0021	0.0063	0.0175	0.0490
K_{ANb,O_2} [mg _{O2} /l]	saturation/inhibition coefficient for O ₂	0.10	0.10	0.10	0.10
K_{ANb,NO_2N} [mg _{NO2N} /l]	saturation/inhibition coefficient for NO ₂	0.10	0.10	0.10	0.10
K_{ANb,NH_4N} [mg _{NH4N} /l]	saturation/inhibition coefficient for NH ₄ (nutrient)	0.05	0.05	0.05	0.05
$K_{ANb,IP}$ [mg _{IP} /l]	saturation/inhibition coefficient for P	0.01	0.01	0.01	0.01

4.2.3 Plant uptake simulation

For evaluating the influence of wetland plants on the removal of contaminants in CWs systems, the spatial distribution of root water uptake in the vertical domain was assumed to be in the upper half of the VF bed (Headley et al., 2005). The same assumption that the roots are dense in the upper 30 cm and then decrease rapidly with depth was made here. According to Pedescoll et al. (2013), the transpiration rate of cattails (*Typha spp.*) is assumed to be 22.78 mm d⁻¹ in summer (average obtained with maximum temperatures between 20 and 30 °C) and 6.50 mm d⁻¹ in winter (average obtained with maximum temperature of 10 °C).

4.3. Results and discussion

Our results suggest that VFCW consistently increased the overall NH₄⁺-N and PO₄³⁻-P removal from AnMBR effluent. This VFCW design demonstrated a notable capacity to efficiently reduce nutrient concentrations across various influent conditions and temperature variations, highlighting the efficacy of VFCW as a complementary component to AnMBR technology. In addition, the results emphasize the need for considering factors such as seasonal variability and

loading rates when designing CWs for an integrated wastewater treatment system, ensuring optimal performance under varying conditions.

4.3.1 VFCW performance on NH_4^+ -N removal

NH_4^+ -N removal from AnMBR effluent depends on the NH_4^+ -N initial concentration and temperature rather than being affected by the COD concentration (Figure 4.2). At the NH_4^+ -N initial concentration of 50 mg L^{-1} , VFCW can remove up to 91.7% of NH_4^+ -N at 20°C (Table 4.6). As the NH_4^+ -N initial concentration increases to 175 mg L^{-1} and 325 mg L^{-1} , the removal efficiencies decrease to 87.2% and 81.7%, respectively, for the same temperature. However, at 10°C , there is a reduction in removal efficiencies up to 75.7% with the initial concentration of 175 mg L^{-1} and up to 61.2% with the initial concentration of 325 mg L^{-1} . At 30°C , the removal efficiencies remain relatively stable across different initial concentrations with a slight decrease observed at 40°C (Table 4.6). This indicates a temperature-dependent influence on the VFCW ability to remove NH_4^+ -N. According to Kadlec and Reddy (2001), nitrification is more sensitive to colder temperatures ($<15^\circ\text{C}$) due to reduced microbial activity. Likewise, higher removal rates are usually obtained in the temperature range between 15 and 31°C (Jing and Lin, 2004). According to Liu et al. (2016), temperature and soil water content are the predominant factors affecting nitrification. In addition to temperature, soil moisture can decrease the abundance of nitrifiers due to decreased diffusion of O_2 into the soil (Liu et al., 2016).

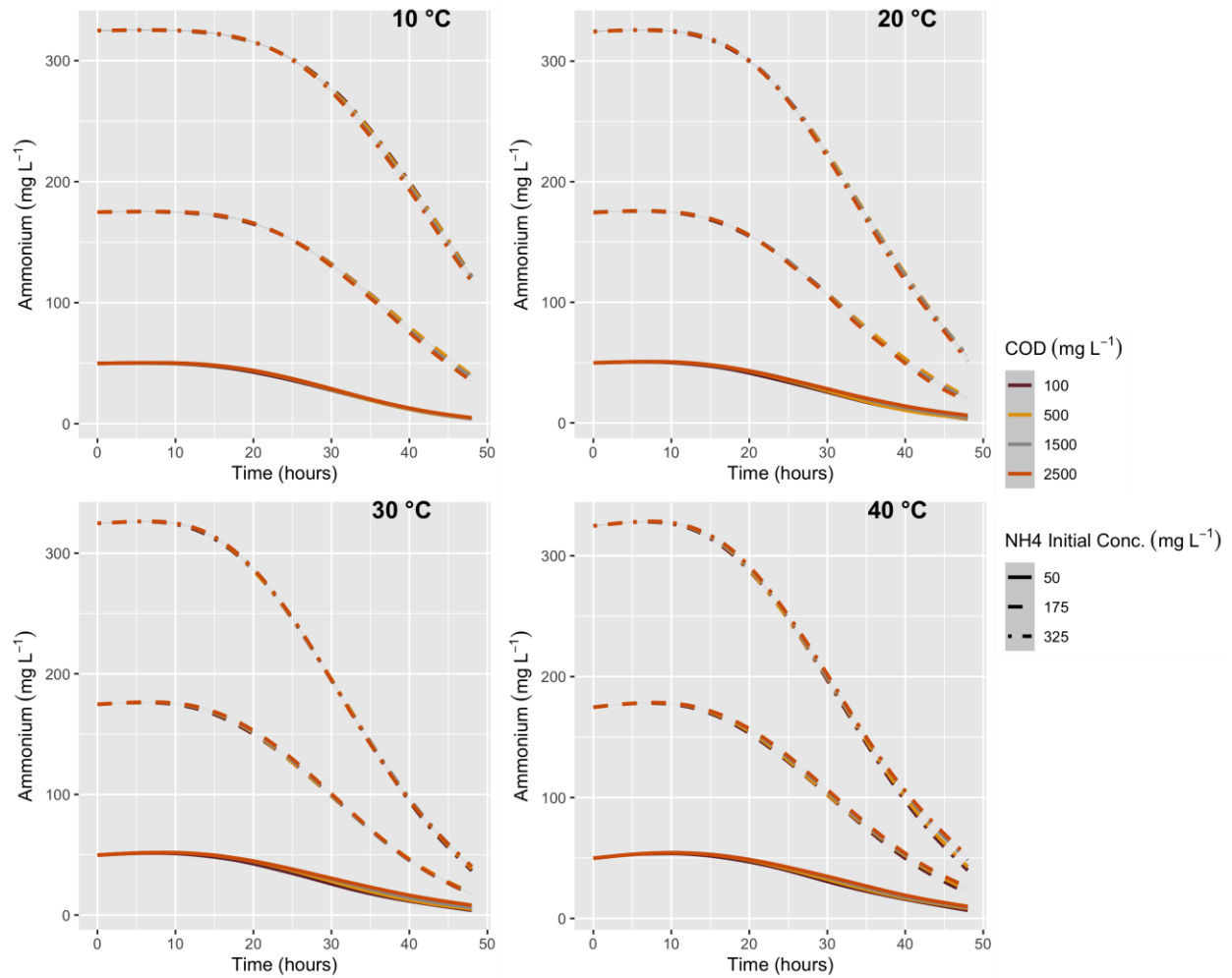


Figure 4.2. Influence of COD concentrations, $\text{NH}_4^+\text{-N}$ initial concentrations, and temperature on $\text{NH}_4^+\text{-N}$ removal in VFCWs simulated with HYDRUS CW2D. Distinct colors represent varying COD concentrations, while different line types are indicative of $\text{NH}_4^+\text{-N}$ initial concentrations.

Table 4.6. NH_4^+ -N removal efficiency at different temperatures.

COD initial (mg L⁻¹)	NH_4^+-N initial (mg L⁻¹)	Removal (%)			
		10 °C	20 °C	30 °C	40 °C
100	50	90.8	91.7	90.1	83.4
500	50	91.0	91.6	89.0	81.9
1,500	50	90.7	89.5	86.5	80.5
2,500	50	89.2	86.7	82.6	78.8
100	175	76.1	87.2	89.2	87.7
500	175	75.7	87.2	88.6	85.7
1,500	175	77.0	87.7	88.8	84.2
2,500	175	78.6	88.9	89.0	84.3
100	325	61.2	82.1	87.6	86.7
500	325	61.2	81.7	87.1	85.8
1,500	325	61.7	81.7	86.6	84.1
2,500	325	62.7	82.5	86.6	83.1

Higher rates of nitrification are associated with lower NH_4^+ -N loading rates (Wang et al., 2016). Autotrophic nitrification consists of two successive aerobic reactions, the conversion of NH_4^+ -N to NO_2^- -N by ammonium oxidizing bacteria (AOB) and the conversion of NO_2^- -N to NO_3^- -N by nitrite oxidizing bacteria (NOB) (Hooper et al., 1997, Faulwetter et al., 2009). The growth rate of AOB is directly linked to the availability of NH_4^+ -N and the kinetics of its oxidation since NH_4^+ -N is the sole energy source for AOB (Martens-Habbena et al., 2009; Dong et al., 2012). When the NH_4^+ -N loading rate is reduced, it creates conditions that favor the growth and activity of these nitrifying bacteria. At higher NH_4^+ -N initial concentrations, the potential decrease in the effectiveness of mechanisms for NH_4^+ -N removal could be a response to oxygen competition of these aerobic removal processes (Wießner et al., 2005). Therefore, optimizing and managing NH_4^+ -N loading rates in the AnMBR system to achieve higher nitrification levels in the VFCW can enhance the overall efficiency of NH_4^+ -N removal.

4.3.2. Influence of COD, $\text{NH}_4^+\text{-N}$, and temperature on effluent $\text{NO}_3^-\text{-N}$ concentration

The concentration of $\text{NO}_3^-\text{-N}$ in VFCW effluent is influenced by COD and $\text{NH}_4^+\text{-N}$ initial concentrations and temperature (Figure 4.3). At 10 °C, as the COD concentration increases from 100 to 2,500 mg L^{-1} , with a constant $\text{NH}_4^+\text{-N}$ concentration of 50 mg L^{-1} , the $\text{NO}_3^-\text{-N}$ concentration decreases from 39.9 mg L^{-1} to 0.06 mg L^{-1} . A similar trend is observed at temperatures of 20 °C, 30 °C, and 40 °C where $\text{NO}_3^-\text{-N}$ concentrations decrease from 33.9, 14.5, and 12.5 mg L^{-1} , respectively, to 0 mg L^{-1} . Microbial activities such as denitrification have the optimum performance temperature ranges reported between 35 and 45 °C (Kadlec and Reddy, 2001). Conversely, increasing the influent $\text{NH}_4^+\text{-N}$ concentration to 175 mg L^{-1} and 325 mg L^{-1} , with a constant COD concentration of 100 mg L^{-1} results in effluent $\text{NO}_3^-\text{-N}$ concentration increases to 139 and 256.9 mg L^{-1} , respectively. Nevertheless, COD inputs of 2,500 mg L^{-1} , with $\text{NH}_4^+\text{-N}$ concentrations of 175 mg L^{-1} and 325 mg L^{-1} , yield $\text{NO}_3^-\text{-N}$ concentrations of 0.03 mg L^{-1} and 85.5 mg L^{-1} , respectively. Therefore, higher COD concentrations in the influent are inversely correlated with $\text{NO}_3^-\text{-N}$ levels in the effluent for all temperatures and $\text{NH}_4^+\text{-N}$ concentrations (Figure 4.3).

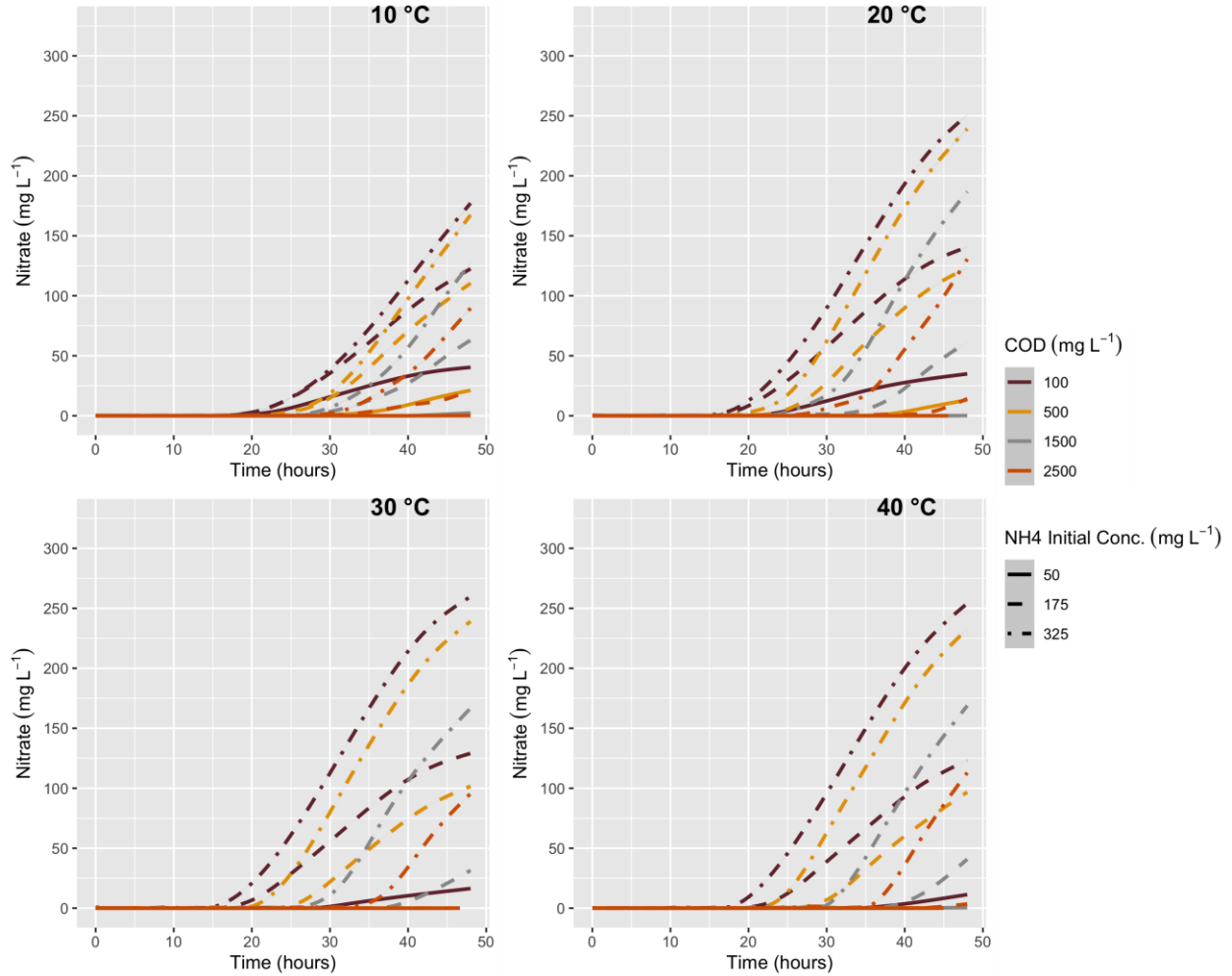


Figure 4.3. Influence of COD, NH₄⁺-N, and temperature on effluent NO₃⁻-N concentration in VFCWs simulated with HYDRUS CW2D. Distinct colors represent varying COD concentrations, while different line types are indicative of NH₄⁺-N initial concentrations.

Modelled results from HYDRUS CW2D confirm that the nitrification-denitrification process is the primary nitrogen pathway in the VFCW (Figures 4.2 and 4.3). As can be seen in Figure 4.3, effluent NO₃⁻-N concentrations were generally higher than the influent NO₃⁻-N concentrations. Thus, the NH₄⁺-N transfer to NO₃⁻-N can be pronounced in the VFCW and effluent NO₃⁻-N concentrations are likely due to nitrification. Denitrification is the biochemical process by which denitrifying bacteria reduce the nitrogen in NO₃⁻-N to N₂ through a sequence of

intermediates (NO_2^- , NO , N_2O) (Ma et al., 2020). Denitrification was found to be limited by the COD concentration, especially by the readily biodegradable fraction of this component in CWs (Kozub and Liehr, 1999; Sirivedhin and Gray, 2006; Truu et al., 2009). In denitrification process, nitrite-based growth of heterotrophs can be modeled based on readily biodegradable COD. This process consumes NO_2^- -N, organic matter, NH_4^+ -N, and inorganic phosphorus, and produces N_2 (Gupta et al., 2022).

NO_3^- -N accumulation seemed to be occurring under higher temperatures and low COD concentrations (Figure 4.3), especially with higher concentrations of NH_4^+ -N being removed at these conditions (Figure 4.2). In theory, 2.86 g COD/g N is needed for the traditional nitrogen removal via nitrate reduction without assimilation. However, considering COD consumption by aerobic heterotrophic bacteria, the COD/N ratio required for denitrification in practice is normally much higher than that in theory (Hou et al., 2018). For example, Fan et al. (2013) found that a COD/N ratio over 10 g COD/g N was needed for classical nitrification-denitrification process to decrease the substantial NO_3^- -N accumulation in CWs. Oxidized nitrogen compounds (NO_3^- -N and NO_2^- -N) as electron accepters could not be removed effectively unless there is adequate availability of organic matter as electron donor. Our findings align with the results reported by Ding et al. (2012). Ensuring sufficient carbon loadings in the AnMBR permeate proves to be a key factor in promoting denitrification, leading to a significant decrease in NO_3^- -N in the VFCW effluent.

4.3.3. Influence of COD, PO_4^{3-} -P, and temperature on PO_4^{3-} -P removal

The removal of PO_4^{3-} -P from AnMBR effluent in VFCW appears to be linked to the initial concentration of PO_4^{3-} -P and temperature, while presenting relative indifference to COD

concentrations (Figure 4.4). At 10 °C, the higher removal rate of 96.5% was achieved for higher $\text{PO}_4^{3-}\text{-P}$ initial concentration of 100 mg L^{-1} , while the lower removal rate of 90.2% was obtained for 10 mg L^{-1} (Table 4.7). A similar trend can be observed for the temperature of 20 °C, where the higher removal efficiency of 92.6% and the lower removal efficiency of 88.5% were found for the concentrations of 100 mg L^{-1} and 10 mg L^{-1} , respectively.

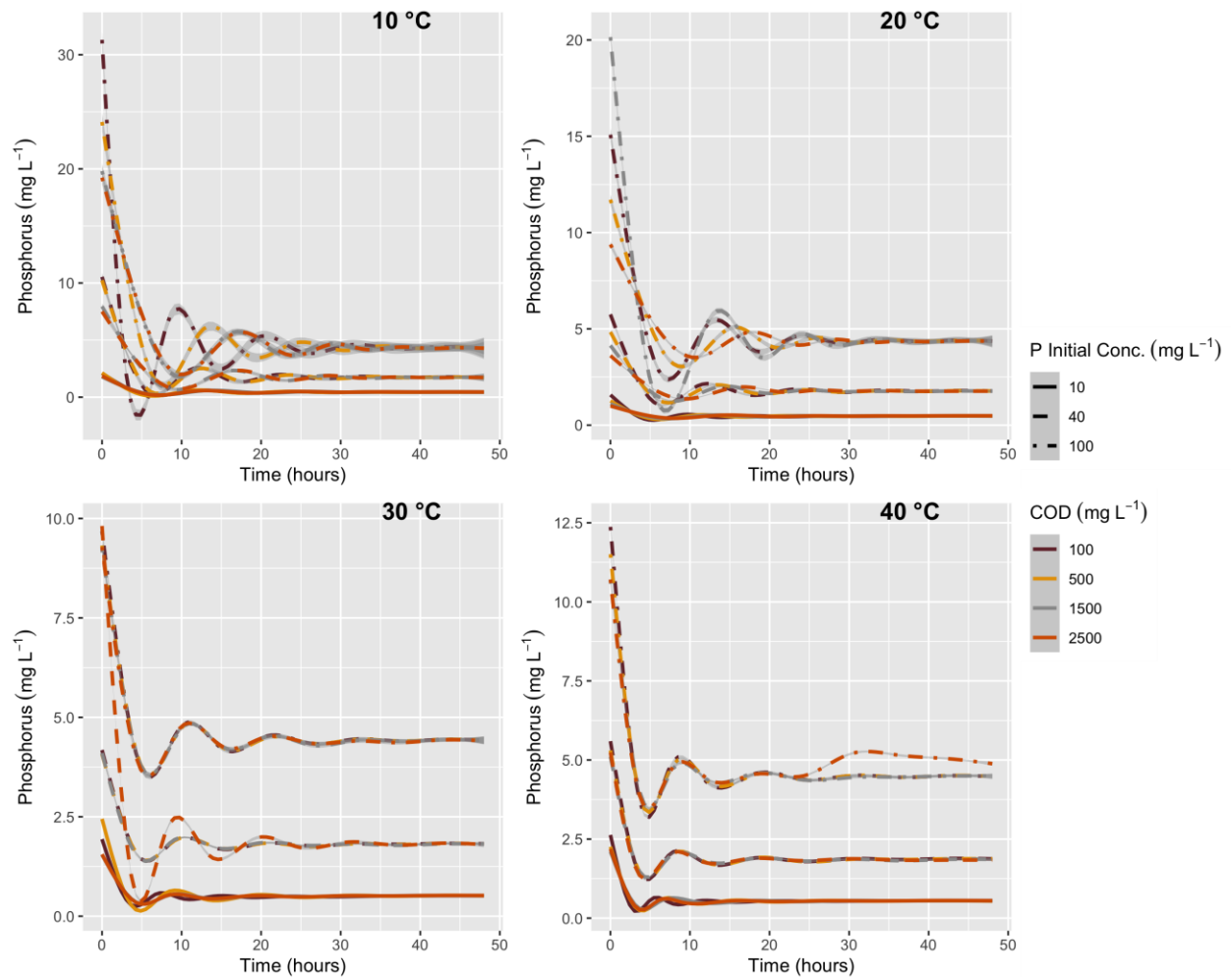


Figure 4.4. Influence of COD, $\text{PO}_4^{3-}\text{-P}$, and temperature on effluent $\text{PO}_4^{3-}\text{-P}$ concentration in VFCWs simulated with HYDRUS CW2D. Distinct colors represent varying COD concentrations, while different line types are indicative of $\text{PO}_4^{3-}\text{-P}$ initial concentrations.

Table 4.7. $\text{PO}_4^{3-}\text{-P}$ removal efficiency at different temperatures.

COD initial (mg L⁻¹)	$\text{PO}_4^{3-}\text{-P}$ initial (mg L⁻¹)	Removal (%)			
		10 °C	20 °C	30 °C	40 °C
100	10	90.2	88.5	89.5	93.3
500	10	90.2	88.7	90.5	93.9
1,500	10	90.4	90.8	92.3	94.4
2,500	10	91.5	92.5	94.0	94.8
100	40	95.8	92.0	90.3	91.6
500	40	95.9	92.0	90.8	92.5
1,500	40	95.7	91.7	90.7	93.2
2,500	40	95.4	90.9	90.5	93.3
100	100	96.5	92.5	89.0	89.6
500	100	96.5	92.6	89.4	90.3
1,500	100	96.5	92.6	89.8	91.3
2,500	100	96.4	92.3	89.8	91.0

On the other hand, at temperatures of 30 °C and 40 °C, the higher removal efficiencies were achieved for the lower $\text{PO}_4^{3-}\text{-P}$ concentrations, which could be linked to microbial activity associated with the optimal nitrification-denitrification performance that can be seen after 20 hours (Figures 4.2 and 4.3). Afterwards, $\text{PO}_4^{3-}\text{-P}$ concentrations showed steady-state conditions until the end of the simulations (Figure 4.4). Akrotos and Tsihrintzis (2007) concluded that the temperature-dependent variations in $\text{PO}_4^{3-}\text{-P}$ levels in CWs are primarily associated with the process of plant decomposition and, hence, return of phosphorus in the system. In addition, temperature also influences phosphorus release from precipitates since variations in temperature may affect the solubility of $\text{PO}_4^{3-}\text{-P}$ (Akrotos and Tsihrintzis, 2007).

Denitrifying microorganisms are able to accumulate phosphate under aerobic conditions (Jørgensen and Pauli, 1995). This indicates that $\text{PO}_4^{3-}\text{-P}$ uptake by microbes increases with an increase in $\text{NO}_3^-\text{-N}$ concentrations, which can be further confirmed with the findings presented by Merzouki et al. (1999). Biological phosphorus removal is based on the ability of some microorganisms to accumulate excess orthophosphate in the form of polyphosphate. Under anaerobic conditions, phosphate-accumulating bacteria take up short-chain fatty acids and convert

them into poly- β -hydroxybutyrate (PHB), which they store as an endogenous source of carbon. The energy required for this conversion is derived from the hydrolysis of polyphosphate into phosphate, subsequently released into the extracellular medium (Merzouki et al., 1999).

In addition to biological transformations, PO_4^{3-} -P removal in CWs is controlled by physical (sedimentation) and chemical (sorption) processes (Yalcuk and Ugurlu, 2009). However, the overall PO_4^{3-} -P removal capacity of a CW system is strongly dependent on the sorption characteristics of the substrate (Ballantine et al., 2010). The presence of iron (10 mg kg^{-1}) in the soil (Table 4.2) could enhance PO_4^{3-} -P removal. Iron is an active element involved in geochemical cycle of phosphorus, and it could react with PO_4^{3-} -P to form insoluble precipitate, removing P from wastewater (Lu et al., 2023). In addition, the presence of calcium (6.1%) in the biochar composition (Table 4.3) can increase PO_4^{3-} -P removal. According to Nassef (2012), calcium ions will react with phosphate to precipitate hydroxylapatite $[\text{Ca}_9(\text{OH})(\text{PO}_4)^3]$. It has been reported that an increase in calcium concentrations increases the percentage removal of PO_4^{3-} -P (Nassef, 2012). An additional comparative simulation using HYDRUS CW2D was performed to assess the impact of sorption on the removal of PO_4^{3-} -P in the VFCW. The simulation was conducted with and without $K_d = 2.19 \text{ L g}^{-1}$ (Figure 4.5). The results indicate that the mechanism driving PO_4^{3-} -P removal in the VFCW involves sorption within the combined soil and biochar layer.

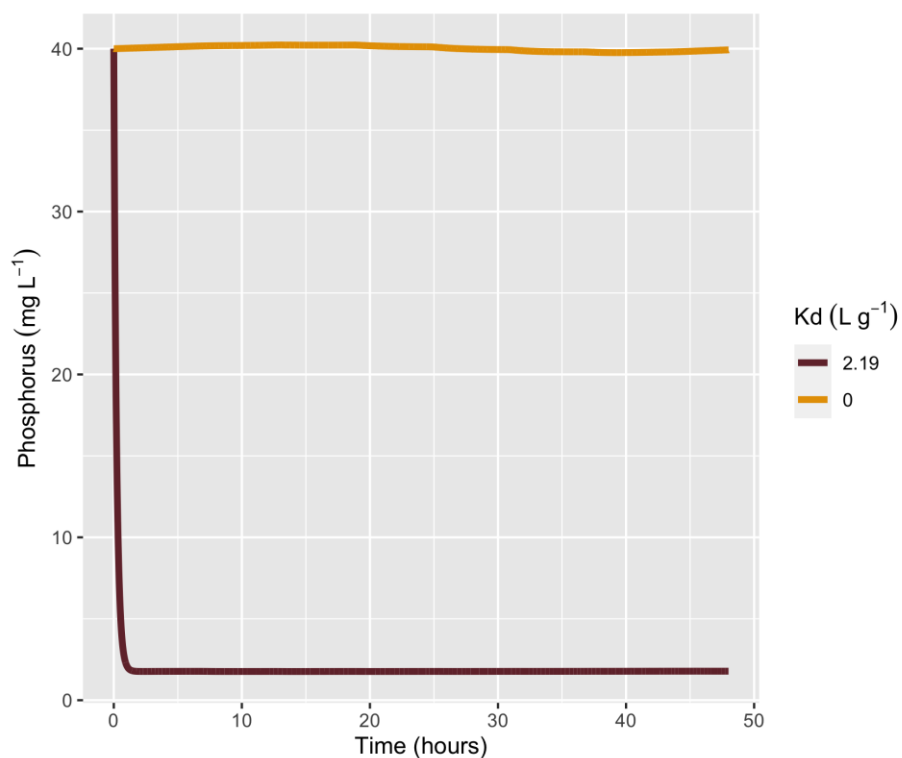


Figure 4.5. Simulations of $\text{PO}_4^{3-}\text{-P}$ performance with and without adsorption coefficient (K_d) in VFCWs.

As can be seen in Figure 4.5, the removal of $\text{PO}_4^{3-}\text{-P}$ with the K_d was very effective and substantial. Adsorption and precipitation onto the substrate are the primary mechanisms involved in $\text{PO}_4^{3-}\text{-P}$ removal in CWs (Vohla et al., 2011), and, therefore, the choice of substrate incorporated material is essential for the removal of $\text{PO}_4^{3-}\text{-P}$ (Gotore et al., 2022). Thus, the soil and biochar mix layer exhibited to have the capability to be incorporated into the VFCW for an increased $\text{PO}_4^{3-}\text{-P}$ removal performance.

4.3.4 VFCW system as a polishing step to treat AnMBR permeate

According to the simulations, the addition of eastern red cedar biochar and soil in the VFCW design increased the overall performance of the systems. There are studies showing that the microporous structure of biochar and its surface properties can enhance nutrient adsorption in soil and provide good habitats for microbes, which is advantageous for the enrichment of functional microorganisms (Yue et al., 2017; Kizito et al., 2017; Meng et al., 2019). Besides, biochar contains C, H, O, N, and the mineral elements of Ca, Na, Mg, and K which may improve microbial abundance and activity (Yuan et al., 2016; Meng et al., 2019). Biochar adsorption and biochar promoting effect on microorganisms are reported to be the key to improve the efficiency of CWs in wastewater treatment (Jiang et al., 2021; Wang et al., 2022a). Therefore, adding eastern red cedar biochar as a filter media component adds significant value to the VFCW performance.

Temperature also plays a vital role in the efficient functioning of plants and microorganisms in CW systems and, hence, seasonal variation becomes a primary aspect that significantly affects the nutrient removal performance of CWs (Vyzamal et al., 1998; Varma et al., 2021). There is a direct relationship between temperature and microbial activity and the consequent impact on contaminant removal efficiency (Varma et al., 2021). However, the simulations showed that it is possible to have NH_4^+ -N removal performance higher than 90% in low temperatures (10 °C) by controlling NH_4^+ -N influent concentrations.

Therefore, the simulation results provide support to assume that the given VFCW design can be a robust and efficient polishing step for AnMBR permeate. Our research has demonstrated the capacity of VFCW to remove more than 90% of NH_4^+ -N and PO_4^{3-} -P at the temperatures of 10, 20, and 30 °C, confirming its potential as a sustainable solution for effluent high-quality reuse.

The effectiveness of this design relies on the natural processes for nutrient removal that can be optimized by altering nutrient and COD loading rates from the AnMBR system.

Through this research, CWs have emerged as a highly effective and versatile solution for AnMBR permeate treatment. Their capacity to adapt to diverse conditions makes them exceptionally appropriate to handle effluent under a spectrum of circumstances, including the unpredictability of AnMBR system failures, operational instabilities, and the challenges associated with treating very high nutrient concentrations. Our results provide insights for optimal performance of the integrated systems. Particularly, when the AnMBR was highly effective in removing COD, VFCW exhibited high NO_3^- -N levels in the effluent at low influent COD and high influent NH_4^+ -N concentrations. To enhance overall effluent quality, supplying a carbon source from the swine wastewater to the VFCW emerges as an option, increasing the COD influent concentration. Additionally, optimizing NH_4^+ -N capture through ion-exchange from the membrane permeate offers the potential to increase overall VFCW performance while obtaining a high value commodity product (Kannan and Parameswaran, 2021). Likewise, NH_4^+ -N capture can reduce the nitrogen effluent concentrations when CWs need to deal with low temperatures, providing a high-quality effluent under seasonal variations. This strategic approach addresses the challenges associated with varying influent conditions and seasonal fluctuations, ensuring high-quality effluent even during adverse scenarios.

In the face of a potential AnMBR system failure, VFCW demonstrates its capability to handle the effluent with high nutrient concentrations. The anticipated high COD concentrations during such failures provide the carbon source needed for effective denitrification. Thus, CWs not only demonstrate resilience in the face of system fluctuations but also provide a sustainable and ecological approach to mitigating the complexities associated with AnMBR treatment. VFCW

serves as a valuable backup treatment option in scenarios where unpredictability, operational instabilities, and challenges arise in the AnMBR system. In situations where AnMBR systems may face unexpected failures or technical issues, the integration of CWs provides a reliable contingency plan, ensuring a practical and resilient wastewater treatment process.

4.4. Conclusion

The simulations using HYDRUS CW2D provide a mechanistic insight into the possible effects of seasonal variations and NH_4^+ -N, P, and COD concentrations on the performance of VFCW in terms of nutrient removal. These insights can be used to formulate the operational strategies for AnMBR treatment to improve the overall performance and capacity of generating high quality effluent.

The results suggest that NH_4^+ -N removal from AnMBR effluent is intrinsically related to the NH_4^+ -N initial concentration and temperature. At an NH_4^+ -N initial concentration of 50 mg L^{-1} and temperature of 20°C , the VFCW exhibits exceptional performance, achieving more than 91% of NH_4^+ -N removal efficiency. At similar conditions and higher COD concentrations, NO_3^- -N concentrations in the effluent were reported as 0 mg L^{-1} showing a great nitrification-denitrification performance of the system. At higher NH_4^+ -N initial concentrations, there is a gradual decline in removal efficiencies and increase in NO_3^- -N concentrations in the effluent. Likewise, the VFCW were effective in removing more than 90% of PO_4^{3-} -P for different influent concentrations. Sorption was found to be the main mechanism driving PO_4^{3-} -P removal in the VFCW system and is happening within the soil + biochar layer.

Thus, this study confirms that VFCW can effectively treat AnMBR permeate from swine wastewater. The VFCW offers the advantage of achieving the highest performance levels for the AnMBR technology by providing high-quality effluent. The simulated performance indicates that these systems could reliably produce high-quality effluent throughout the entire year when accounting for seasonal variations. VFCW is a cost-effective and environmentally friendly solution for the treatment and reuse of swine wastewater, contributing to the broader goals of sustainable water management and agricultural practices.

4.5 References

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Chapter 5 - Performance of constructed wetlands systems treating AnMBR effluent under different influent COD concentrations

Three greenhouse scale constructed wetland (CWs) systems were designed and built with the goal of evaluating the removal of nitrogen (N) and phosphorus (P) from swine wastewater post Anaerobic Membrane Bioreactor (AnMBR) treatment under different influent chemical oxygen demand (COD) concentrations. This study aimed to complement the results obtained from the simulations using HYDRUS CW2D module [Chapter 4], using real AnMBR permeate. This experimental setup allows for the following observations: 1) evaluate overall system performance for NH_4^+ -N and PO_4^{3-} -P removal; and 2) assess NO_3^- -N concentration that persisted in the effluent. These observations are essential for understanding the complete nitrogen transformation process within the CWs, providing insights into the system's effectiveness under different conditions.

5.1. Methods

5.1.1. Experimental set-up

The CWs systems were set up in the greenhouse located in the Department of Agronomy at Kansas State University, Manhattan, Kansas, USA, with an average daily temperature of 26 °C. The experimental set up consisted of three evenly spaced laboratory scale vertical flow constructed wetlands (VFCWs), one influent tank having a capacity of 87 L made of high-density polyethylene plastic containers located next to the VFCWs, one pump used to pump the influent into the VFCW, and three effluent tanks with a capacity of 30 L used to collect the treated water (Figure 5.1).



Figure 5.1. VFCWs systems set-up.

The size of the VFCW was 0.44 m L x 0.225 m W x 0.74 m D, with a surface area of 0.099 m² (L x W), an effective volume of 0.0594 m³ and a hydraulic loading rate (HLR) of 0.125 m d⁻¹. The system was designed to operate with a 10 cm drainage layer (gravel size 19 – 25 mm), a 20 cm main gravel layer (12 – 19 mm), a 3 cm separation layer (gravel 6 – 9 mm), a 20 cm of soil (silt loam:sand, 2:1 ratio) mixed with eastern redcedar biochar, and 7 cm top layer (gravel size 12 – 19 mm). The soil and biochar were manually mixed in a container, ensuring a defined volume ratio (70% soil and 30% biochar). All the gravel layers were washed with tap water to remove any debris. The VFCW were planted with cattails (*Typha spp.*). *Typha spp.* is a species of aquatic plants that have a wide distribution throughout the world and have a high performance in pollutant treatment (Nguyen and Nguyen, 2023). More details on the characteristics of the filter media can be found in Chapter 4.

5.1.2. Wastewater sampling and analysis

Before starting the data collection, the VFCWs were allowed to acclimatize for approximately 6 weeks (40 days). Real AnMBR effluent from swine wastewater treatment was used to evaluate the performance of the VFCWs on removing $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$, however, during this period the AnMBR system experienced a discontinuity in the treatment due to technical issues. Thus, the data collection was conducted in October, November, and March. Influent and effluent concentrations were determined for electrical conductivity (EC), pH, total N, total P, $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, and $\text{PO}_4^{3-}\text{-P}$. Influent concentrations were also determined for chemical oxygen demand (COD).

5.1.3. Statistical analysis

Statistical analyses were performed in R statistical software (R Core Team, 2021). One-way analysis of variance (ANOVA) was applied to evaluate significant differences in the VFCWs effluent parameters among several influent COD conditions. The values were considered statistically significant when $p < 0.05$.

5.2. Results and discussion

5.2.1. VFCWs performance based on influent COD concentration

The VFCWs presented an optimal performance in treating swine wastewater post AnMBR treatment throughout the experimental period (Figure 5.2). In this study, higher COD concentrations exhibited higher $\text{NH}_4^+\text{-N}$ removal and lower $\text{NO}_3^-\text{-N}$ concentrations in the effluent. COD concentrations of 720 and 1500 mg L^{-1} showed 99.98% of $\text{NH}_4^+\text{-N}$ removal considering influent $\text{NH}_4^+\text{-N}$ concentrations up to 181.79 mg L^{-1} (Table 5.1). For the same amount of COD,

the NO_3^- -N concentrations in the effluent were lower than 4.59 mg L^{-1} . On the other hand, NH_4^+ -N removal was 63.90% and effluent NO_3^- -N concentration was 48.64 mg L^{-1} for 115 mg L^{-1} of COD.

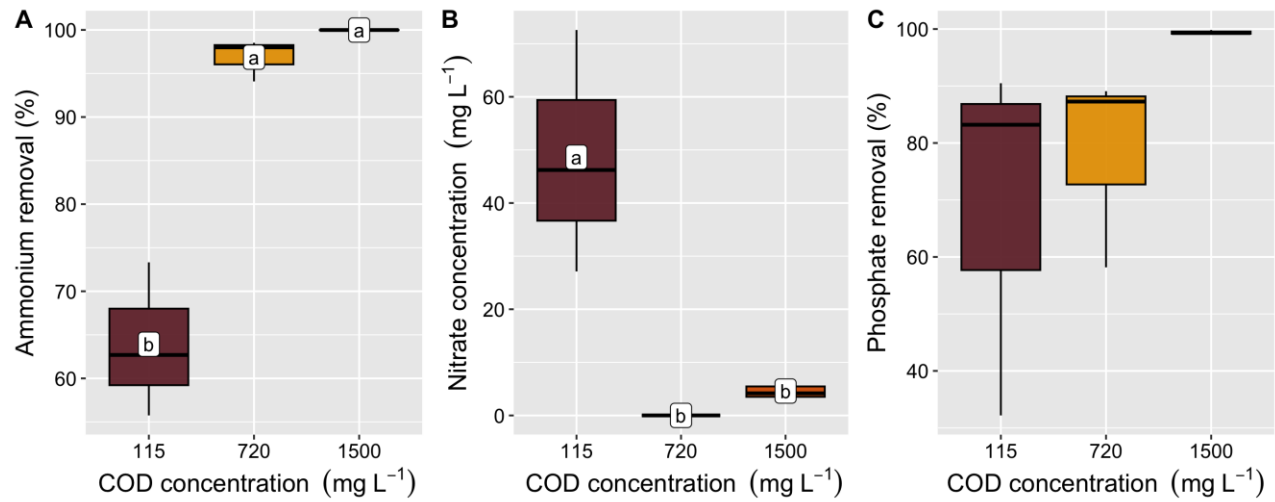


Figure 5.2. VFCWs performance for NH_4^+ -N removal (A), effluent NO_3^- -N concentrations (B), and PO_4^{3-} -P removal (C) based on influent COD concentrations.

Table 5.1. Influent and effluent concentrations in the VFCWs.

	ID	COD	NH ₄ ⁺ -N		NO ₃ ⁻ -N	Total N		Total P		PO ₄ ³⁻ -P		pH	EC
		mg L ⁻¹	mg L ⁻¹	%	mg L ⁻¹	mg L ⁻¹	%	mg L ⁻¹	%	mg L ⁻¹	%		
Oct 2022	Influent	1500	181.79	-	0.57	193.75	-	15.60	-	15.72	-	7.96	2.64
	CW 1	-	0.05	99.97	2.85	7.56	96.10	0.13	99.17	0.15	99.05	7.88	1.41
	CW 2	-	0.01	99.99	6.76	11.96	93.83	0.06	99.62	0.03	99.83	7.93	1.33
	CW 3	-	0.01	99.99	4.17	9.25	95.23	0.11	99.29	0.11	99.30	7.82	1.40
	Mean	-	0.02	99.98	4.59	9.59	95.10	0.10	99.36	0.59	99.40	7.88	1.38
Nov 2022	Influent	720	69.41	-	<0.01	89.57	-	6.68	-	0.55	-	7.68	1.92
	CW 1	-	1.03	98.52	<0.01	21.12	76.42	0.23	96.56	0.07	87.27	7.11	1.98
	CW 2	-	4.10	94.09	<0.01	44.86	49.92	0.34	94.91	0.23	58.18	7.10	1.92
	CW 3	-	1.39	98.00	<0.01	19.55	78.17	0.14	97.90	0.06	89.09	7.02	1.94
	Mean	-	2.17	96.90	<0.01	28.51	68.20	0.24	96.50	0.59	78.20	7.08	1.95
Mar 2023	Influent	115	133.82	-	0.02	132.37	-	6.93	-	4.94	-	8.39	2.03
	CW 1	-	35.70	73.32	72.58	104.87	20.78	1.64	76.33	0.47	90.49	8.30	1.95
	CW 2	-	59.22	55.75	46.22	120.98	8.60	3.45	50.22	3.35	32.19	8.29	1.98
	CW 3	-	49.93	62.69	27.12	76.78	42.00	0.74	89.32	0.83	83.20	8.08	2.17
	Mean	-	48.28	63.90	48.64	100.88	23.80	1.94	72.00	0.59	68.60	8.22	2.03

% = removal efficiency.

The nitrification process is generally catalyzed by autotrophs under aerobic conditions (Faulwetter et al., 2009). However, considering that autotrophic nitrification is directly linked to the availability of NH₄⁺-N and the kinetics of its oxidation (Martens-Habbena et al., 2009; Dong et al., 2012), the effect of COD concentrations suggests the occurrence of heterotrophic nitrification in the VFCWs, especially at very low permeate COD values (as shown in Table 5.1 for the March 2023 data) Heterotrophic nitrification can be implemented by bacteria oxidizing NH₄⁺-N to NO₂⁻-N, which are highly different from *Nitrosomonas* or *Nitrosococcus*. *Arthrobacter* sp., *Alcaligenes* sp., and *Pseudomonas* sp., for example, have been documented to exhibit heterotrophic nitrification capability (Verstraete and Alexander, 1972; Castignetti and Hollocher, 1984; Hu et al., 2023) and their performance is extremely affected by the carbon source and C/N

ratio, with higher carbon concentrations leading to enhanced performance (Hu et al., 2023). Because many of the heterotrophic nitrifiers are also denitrifiers, it is easy to underestimate the significance of this process in the nature (Vyzamal, 2007). The observed differences between the effect of COD in the experimental measurements and the simulated results can be attributed to the fact that HYDRUS CW2D only considers autotrophic nitrification (Langergraber and Šimůnek, 2006).

Conversely, the COD concentrations were not significant for $\text{PO}_4^{3-}\text{-P}$ removal ($p>0.05$). $\text{PO}_4^{3-}\text{-P}$ concentrations in the effluent were below 0.6 mg L^{-1} (Table 5.1). Therefore, considering $\text{NO}_3^{-}\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ concentrations in the effluent, the experimental measurements for the influence of COD closely correspond with the simulated trends. It confirms that denitrification is limited by COD concentrations, while $\text{PO}_4^{3-}\text{-P}$ exhibits relative indifference to the amount of COD in the influent.

The average removal efficiency of total N was 95.10%, 68.20%, and 23.80% for the influent COD concentrations of 1500, 720, and 115 mg L^{-1} , respectively (Figure 5.3). The data showed that total N removal was highly affected by the influent COD concentration. Nitrification and denitrification are considered to be the main dominant nitrogen removal mechanisms in CWs (Vyzamal and Kropfelova, 2009; Ayaz et al., 2012, Zhu et al., 2014). Since the lack of carbon source restrains these mechanisms (Figure 5.2), it significantly impacts total N removal (Figure 5.3). These findings are consistent with the results reported by Zhu et al. (2014). In addition, Xu et al. (2021) concluded that sufficient COD had a greater impact on improving total N removal compared to dissolved oxygen conditions. Similarly, the average total P removal efficiency was 99.40%, 96.50%, and 72.00% for the influent COD concentrations of 1500, 720, and 115 mg L^{-1} , respectively (Figure 5.3). Although COD concentrations were not significant on $\text{PO}_4^{3-}\text{-P}$ removal

and $\text{PO}_4^{3-}\text{-P}$ removal was mainly attributed to the adsorption and/or precipitation by filter media or in the CW (Figures 4.5 and 5.2), higher COD concentrations exhibited efficient total P removal performance (99.40%) (Figure 5.3). As can be seen in Figure 5.3, total N and total P were removed almost simultaneously. *Pseudomonas sp.*, identified as a potential bacterium for heterotrophic nitrification, is reported to enable simultaneous removal of nitrogen and phosphorus (Tan et al., 2021). These heterotrophic nitrifying bacteria mineralize organic P by the production of phosphatases that hydrolyze organic forms of phosphate compounds, thereby releasing inorganic forms that will be immobilized by plants or removed by sorption (Samal et al., 2020). These microorganisms are more metabolically versatile, producing and storing polyhydroxybutyrate (PHB) using either dissolved oxygen or $\text{NO}_3^- \text{-N}$ as an electron acceptor to achieve total P removal (Tan et al., 2021).

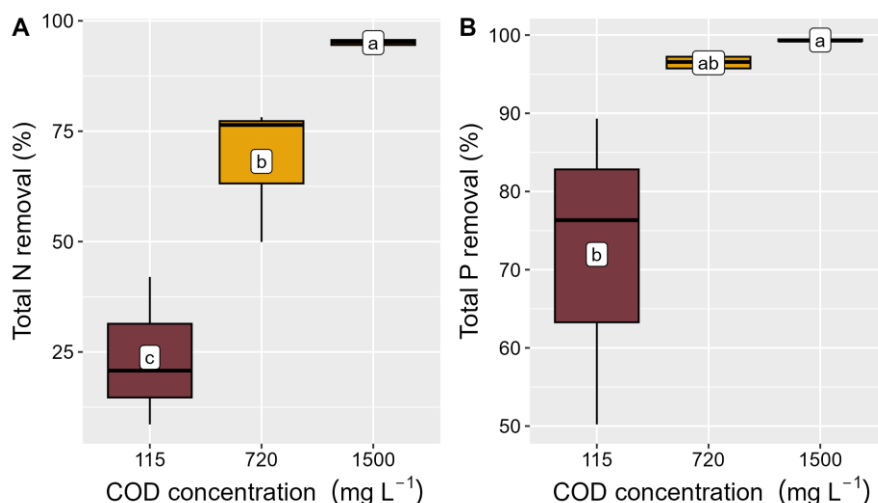


Figure 5.3. VFCWs performance for total N (A) and total P (B) removal based on influent COD concentrations.

A relatively high pH was observed for influent COD of 115 mg L⁻¹ and 1500 mg L⁻¹, and a pH closer to neutral was observed for influent COD of 720 mg L⁻¹. The pH ranges were 8.22,

7.88, and 7.08, respectively. The reduction of pH at higher COD levels might be an indicator of nitrification and oxidation of organic matter (La Mora-Orozco et al., 2018). Alkalinity is consumed during nitrification and generated during denitrification in CWs (Lyu et al., 2018), which explains the pH values observed for the COD concentrations of 720 and 1500 mg L⁻¹ (Figure 5.4). Additionally, a lower EC value of 1.38 mS cm⁻¹ was obtained for the influent COD of 1500 mg L⁻¹ compared to the EC value of 2.03 mS cm⁻¹ obtained for the COD concentrations of 115 and 720 mg L⁻¹. The lower EC value may be due to the lower concentrations of nutrients, hence decreasing the dissolved ions content (Mashauri et al., 1999). EC shows a close correlation with the dissolved salt content found in the water (Ohoro et al., 2022).

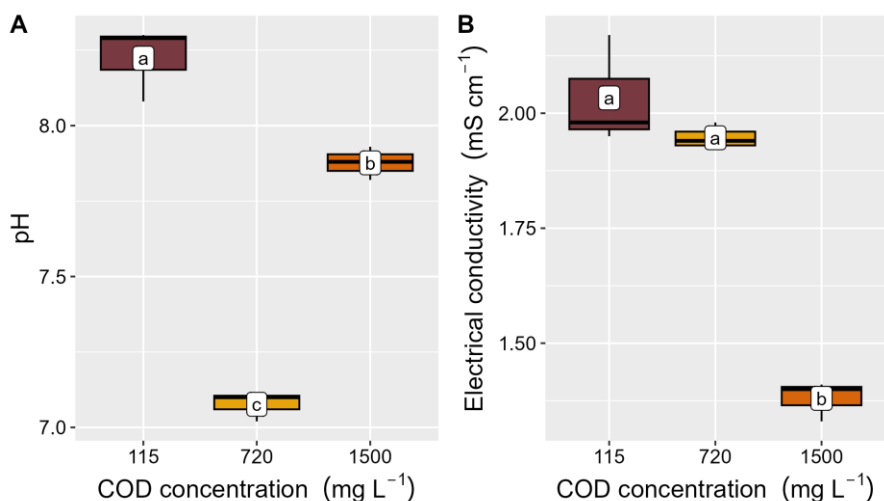


Figure 5.4. Effect of influent COD on pH and electrical conductivity (EC).

5.2.2. VFCWs as a polishing step to AnMBR effluent

VFCWs may serve as an efficient polishing step for AnMBR effluent. Two distinct phases of the treatment processes are visually represented in Figure 5.5. The observed change in water quality from Figure 5.5 (A) to Figure 5.5 (B) highlights the effectiveness of VFCWs in further polishing the AnMBR effluent. The darker coloration in Figure 5.5 (A) is suggestive of dissolved

and particulate substances. The transition to a clearer water in Figure 5.5 (B) indicates the successful removal or transformation of these substances in the CWs systems that may have persisted after AnMBR treatment. Moreover, the visual improvement aligns with established literature on the efficacy of CWs in enhancing water quality (Perez et al., 2023).

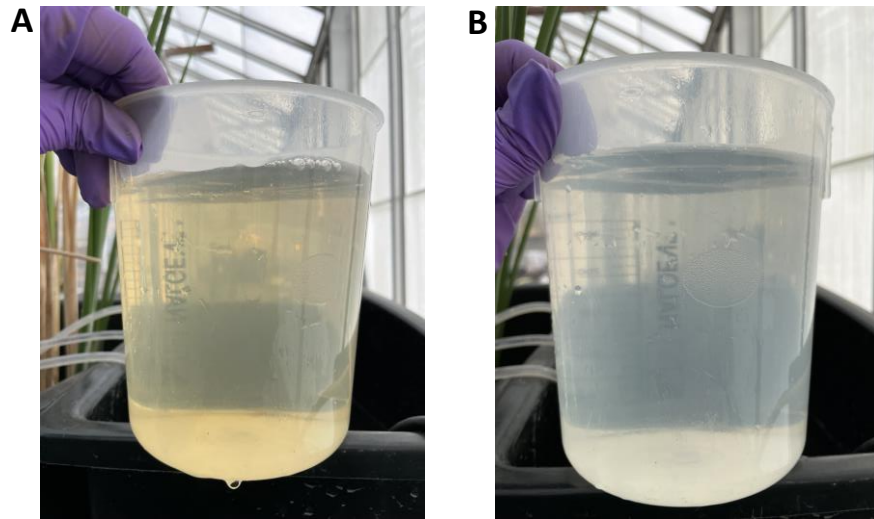


Figure 5.5. Visual representation of VFCWs performance as a polishing step to AnMBR effluent before (A) and after (B) VFCWs treatment.

5.3. Conclusion

This study investigated the treatment performance of VFCWs in treating real AnMBR permeate with different COD concentrations. The systems demonstrated a remarkable performance as a polishing step for AnMBR effluent with removal efficiencies up to 99.98% of $\text{NH}_4^+\text{-N}$, 95.10% of total N, 99.36% of total P, and 99.40% of $\text{PO}_4^{3-}\text{-P}$. Higher COD concentrations, particularly 720 and 1500 mg L^{-1} , demonstrated the highest $\text{NH}_4^+\text{-N}$ removal with correspondingly lower $\text{NO}_3^-\text{-N}$ concentrations in the effluent.

The influence of COD on nitrification processes suggests the occurrence of heterotrophic nitrification in the VFCWs. In contrast, COD concentrations were not significant for PO_4^{3-} -P removal. The experimental results closely align with the results from the simulations using HYDRUS CW2D, confirming that denitrification is limited by COD concentrations, while PO_4^{3-} -P removal exhibits relative indifference to COD variations in the influent.

Total N and total P removal efficiencies were significantly influenced by the influent COD concentration. Furthermore, the simultaneous removal of total N and total P supports the potential dominance of heterotrophic nitrification and denitrification mechanisms in the VFCWs. The observed pH trends also suggest nitrification and denitrification processes due to alkalinity dynamics. Additionally, the lower EC value for higher COD concentrations reflects the decreased dissolved ions content, possibly due to lower nutrient concentrations.

Therefore, VFCWs emerge as highly effective polishing systems for AnMBR effluent, confirming their potential to enhance water quality by effectively removing nutrients from swine wastewater. These findings provide valuable contributions to the field of wastewater treatment, offering a sustainable and ecologically friendly approach to further refine effluent quality.

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Chapter 6 - Conclusion

CWs systems stand as a compelling and sustainable solution for water purification, while addressing pollution concerns through natural processes and contributing to the conservation of ecosystems. Integrating CWs as a final polishing step, particularly in conjunction with advanced systems such as the AnMBR, holds significant promise for treating swine wastewater and agricultural runoff. This combined ecological and environmental engineering approach provides the ability to explore the removal of pollutants, while aligning human activities with the environment through innovative and nature-based solutions.

To enhance the effectiveness of these solutions in wastewater management practices, it is crucial to increase understanding and communicate advancements in the environmental and ecological fields. Many terms were created as an initiative to find the most advantageous term politically, economically, and environmentally, such as ecological engineering, environmental engineering, nature-based solutions, engineering with nature, constructed wetlands, green engineering, and ecological systems. Through a bibliometric analysis, it has been demonstrated that there is a certain vulnerability of the science to link these terms and their concepts since they do not usually appear together in the same publications.

Furthermore, to achieve a holistic treatment of swine wastewater, the capacity of eastern red cedar biochar to remove target compounds was investigated. Eastern red cedar biochar proved to be a promising adsorbent to be used for practical applications, such as filter media in CWs configuration, effectively eliminating antibiotic residues from swine wastewater in a cost-effective and environmentally friendly manner due to its relatively low pyrolysis temperature (450 °C) and use of an invasive species. The adsorption capacity and mechanism can be significantly influenced by the chemical properties of each antibiotic and the surface properties of the biochar.

CWs demonstrated to be effective in polishing swine wastewater from AnMBR effluent. The proposed CWs design allows the removal of nutrients and provides resilience to handle flowrate variabilities, reducing the impacts caused by the presence of wastewater contaminants. The simulations using HYDRUS CW2D provided insights on the performance of CWs in terms of nutrient removal and the possible effects of seasonal variation. These insights can be used to formulate the operational strategies for AnMBR treatment to improve the overall performance and capacity of generating high quality effluent. The greenhouse scale CWs demonstrated a remarkable performance in treating real AnMBR permeate with high COD concentrations. Therefore, CWs emerge as highly effective polishing systems for AnMBR effluent, confirming their potential to enhance water quality by effectively removing nutrients from swine wastewater. These findings provide valuable contributions to the field of wastewater treatment, offering a sustainable and ecologically friendly approach to further refine effluent quality.

6.1. Future prospects

While this research made several contributions towards the combination of ecological and environmental engineering approaches, the study raises several potential avenues of research to pursue in future work. First, there is a substantial need to integrate these approaches to foster a more cohesive understanding and application of environmentally friendly solutions in wastewater treatment. Closing this conceptual gap is essential for establishing a unified and comprehensive framework, optimizing the potential of ecological and environmental engineering practices in wastewater treatment.

Additionally, the findings from this study contribute to the growing body of knowledge on biochar application for antibiotic removal from swine wastewater. Further research could explore

the adsorption performance of eastern red cedar biochar using real swine wastewater containing other compounds, such as nitrogen and phosphorus, and investigate the regeneration and reusability of the biochar through desorption tests. Overall, eastern red cedar biochar shows promise as a sustainable and environmentally friendly solution to mitigate antibiotic contamination in water sources.

The insights obtained from simulations using HYDRUS CW2D offer a foundation for refining operational strategies in AnMBR treatment performance, indicating a path towards optimizing overall system performance and generating high-quality effluent consistently. In the context of sustainable wastewater treatment, the future prospects suggest a continued exploration of the fundamental mechanisms behind the nutrient removal. A key aspect of future research involves a detailed characterization of microbial communities within the CWs system. This investigation aims to confirm the specific role of heterotrophic nitrification on nutrient removal processes. Understanding the microbial dynamics and their contributions to nitrogen transformations is essential for elucidating the biological processes at play. Moreover, the assessment of COD levels in the VFCW effluent has emerged as a critical factor to obtain a comprehensive understanding of the organic pollutant load, thus facilitating the optimization of the treatment process. Additionally, the role of biochar in P removal should be further investigated to understand its specific contributions compared to the soil layer.

The envisioned future work extends to the practical application of these insights at a pilot scale. Implementing pilot scale research allows for a more realistic evaluation of the CWs for AnMBR effluent treatment under seasonal variations. This phase of research involves not only validating the findings from simulations at different temperatures, but also addressing the complexities that arise in real-world scenarios, such as varying influent compositions and

fluctuating environmental conditions. The pilot-scale CWs will provide a platform for assessing robustness and long-term stability of the CWs systems. This comprehensive evaluation is critical for transitioning from theoretical insights to practical understanding of system dynamics, which can only improve the CWs performance and effectiveness.