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Chapter 6

The Applications and Performances of Biochar in Constructed Wetlands for Sustainable Wastewater Treatment

Obey GOTORE

1. Introduction

In many developing countries, both point and non-point sources of pollution are increasingly significant concerns. These sources include industrial activities, wastewater treatment plants, and urban agricultural practices, all contributing to environmental degradation. The consequences of this pollution are evident in the eutrophication of surface water resources. Despite efforts to mitigate these issues, implementing measures to improve the trophic status of surface waters remains challenging. Various technologies have been explored for this purpose, yet their application faces hurdles, particularly in developing countries, due to high energy requirements and monitoring costs. However, constructed wetlands (CWs) offer a promising solution for wastewater treatment in such contexts. Their natural and passive treatment approach makes them relatively easy to implement compared to other technologies, providing an effective means of addressing water pollution.

In this study, I initially explored locally available materials in developing countries, focusing on corncob waste from agricultural activities. My emphasis was on developing materials that provide optimal conditions for removing pollutants from wastewater, particularly for application in constructed wetlands. In the first phase of my research, I investigated the impact of various pyrolysis conditions on the production of adsorbents or biochar for removing Ciprofloxacin (CFX), Delafloxacin (DLX), and Ofloxacin (OFX). Initially, I determined the surface area of the biochar post-production and measured its adsorption capacity through isotherms for removing CFX, DLX, and OFX from wastewater. Subsequently, I characterized the physiochemical properties of this corncob under different pyrolysis conditions through proximate analysis, Field emission scanning electron microscopy- energy dispersive X-ray (FESEM-EDX) analysis, Fourier-transform infrared spectroscopy (FTIR) spectroscopy, and determination of effective pore volume. Following these analyses and obtaining results, I further explored the application of this biochar in CWs, both as part of the substrate and as a habitat for microorganisms.

2. Investigating the Effect of Different Pyrolysis Conditions on the Adsorbent and Exploring the Adsorption Properties of Fluoroquinolones

Antibiotic residues are recognized as emerging pollutants in the environment due to their widespread use, release into ecosystems, and biological activities (Ohoro et al. 2019). Unlike many other organic pollutants, antibiotic residues in aquatic environments pose a significant concern due to their complex nature and their ability to hinder the degradation of other organic matter. Moreover, the continuous discharge of antibiotic compounds can contribute to the development of drug resistance among native bacterial populations (Gotore et al. 2022.; Liu et al. 2021; Manaia et al. 2016). Among the antibiotics commonly employed in medical treatment, CFX, DFX, and OFX belong to the fluoroquinolone (FQs) group, ranking fourth in terms of human usage. To mitigate health risks and protect ecosystems, antibiotic removal is crucial. Traditional wastewater treatment processes struggle to effectively remove antibiotics, highlighting the need for alternative treatment approaches.

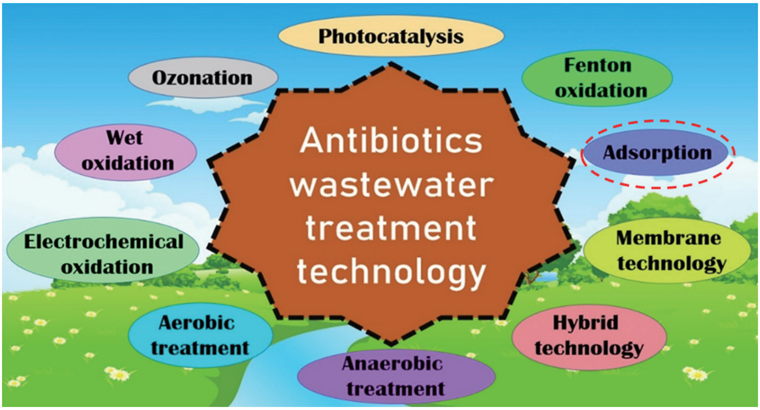

Figure 1: Antibiotic wastewater treatment technology.
Source: Phoon et al. 2020

Various methods are available for addressing antibiotic removal (as illustrated in Figure 1), but I specifically focused on adsorption. My objective was to pinpoint a cost-effective approach applicable in CWs. We sought to integrate this adsorption process into a substrate using biochar and evaluate its effectiveness. Moreover, we emphasized the use of locally sourced materials to ensure affordability and suitability for remote areas in both developing and developed countries, while also prioritizing environmental friendliness.

Several biochar materials or resources are available, such as coconut or wood, corn cobs, tree barks, peanut shells, and rice husks, with numerous studies conducted on their potential. However, their utilization in CWs for antibiotic removal has been limited, which prompted our research focus.

In this research, we utilized corncobs. The laboratory experiment was conducted in Nagasaki, Japan. The corncobs were sourced from a local farmer in Nagasaki and were subsequently packed into small ceramic cups. These cups were then placed inside a microwave oven and subjected to pyrolysis under three different temperature conditions: 900°C, 700°C, and 600°C for durations of one and two hours. After pyrolysis, the corncobs were ground into small granules ranging from 0.25 to 1.00 mm. However, these granules were only utilized for the adsorption experiment and were not used in the constructed wetland. The pyrolysis process is illustrated in Figure 2.

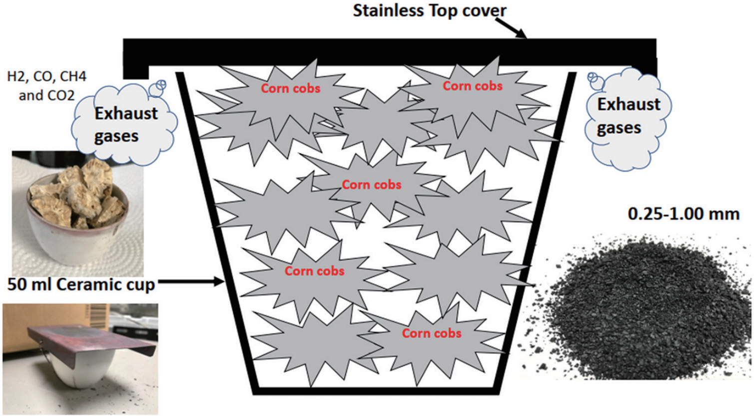

Figure 2: Pyrolysis process. Source: Author

After producing materials under three different temperature and duration combinations—600°C for one hour, 600°C for two hours, 900°C for one hour, and 900°C for two hours—we conducted proximate analysis. The target parameter was fixed carbon content, aiming to ascertain the yield from pyrolysis. Table 1 shows the properties of corn cob biochar were derived from proximate analysis under different pyrolysis conditions.

Table 1: Properties of corn cob biochar under different pyrolysis conditions.

	Pyrolysis temperatures (°C) /time (h)					
	600°C /1 h	600°C /2 h	700°C/1 h	700°C/2 h	900°C/1 h	900°C/2 h
Vpore (%)	80.0 ± 0.589	79.9 ± 0.588	80.0 ± 0.590	79.3 ± 0.589	80.7 ± 0.587	84.0 ± 0.589
Biochar recovery (%)	36.7 ± 0.052	32.2 ± 0.062	30.6 ± 0.041	26.9 ± 0.023	27.7 ± 0.044	26.0 ± 0.013

It was observed that approximately 25% of the material remained as fixed carbon, indicating that about 75% comprised volatile components, water, and other substances decomposable at higher temperatures. Subsequently, pore volume was measured, revealing approximately 80% for the 600°C condition. As pyrolysis conditions intensified, both porosity and pore volume increased to 83%, suggesting a higher pore density within the biochar. Lastly, biochar recovery was assessed, showing a decrease as pyrolysis temperature increased.

The next experiment aimed to evaluate kinetic adsorption, focusing on achieving a material balance between the adsorbate and the adsorbent utilized in this kinetic study. Our objective was to determine whether a 1st order or 2nd order, among other nonlinear equations, best described the rate of removal of various adsorbates. For instance, iodine was employed to assess the surface area. Initially, methylene blue was also considered for surface area measurement; however, it was ultimately disregarded due to its tendency to overestimate the surface area. Consequently, only iodine was utilized to accurately determine the surface area of the produced biochar, as iodine provides a more precise estimation compared to methylene blue. The iodine estimation is closely aligned with BET analysis, which might be prohibitively expensive for implementation in developing countries. Hence, nonlinear regression equations were employed for this analysis, utilizing nonlinear least squares. Alongside the kinetic experiments, we also conducted isothermal experiments. For the isotherm analysis, we considered both Langmuir and Freundlich models to determine the Q_{max}, which represents the maximum absorption capacity of this biochar. The kinetic adsorption and isothermal experiments were conducted and calculated according to Dang et al. (2022). Figure 3 shows the iodine on biochar and the maximum adsorption capacity of CFX, OFX, and DLX

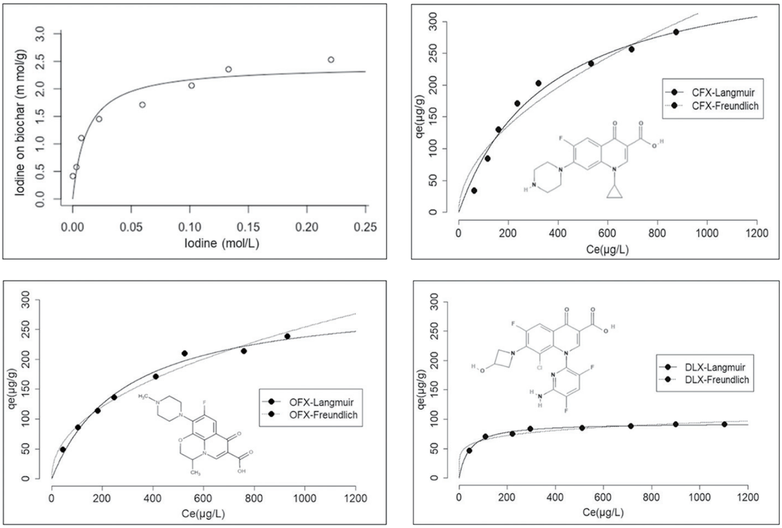

Figure 3: Iodine on biochar and the maximum adsorption capacity of CFX, OFX, and DLX. Source: Dang et al. 2022

After undergoing pyrolysis, higher levels of carbonization resulted in the formation of more pores and voids, particularly evident at 900°C where the abundance of pores surpassed other conditions. Variances in honeycomb structures were observed across different pyrolysis conditions. Typically, surface voids ranging from 12–30 µm were observable, alongside numerous pores measuring 1 to 2 µm on the walls of these voids, facilitating percolation diffusion. The formation of large porous structures was attributed to the rapid volatilization occurring at temperatures exceeding 500°C. As evidenced in Figure 4, images of biochar under various pyrolysis conditions illustrate the development of pores post-pyrolysis. This observation suggests a potential habitat for microorganisms or bacteria within CWs, which could concurrently facilitate the removal or biodegradation of nutrients present in wastewater during CW treatment.

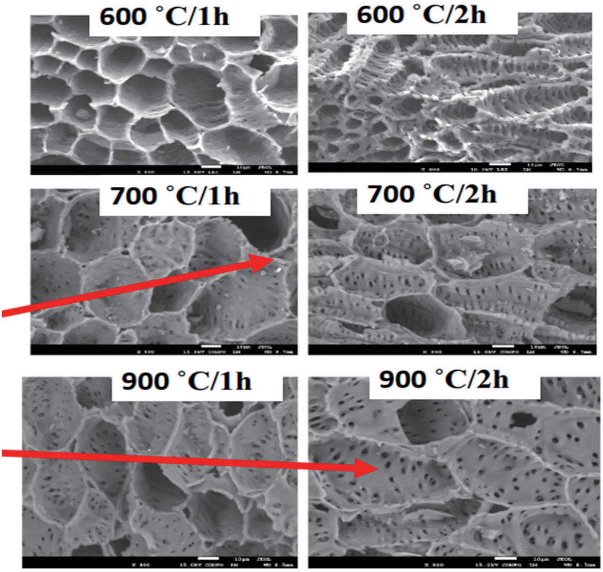

Figure 4: FESEM images showing the surface morphology of corn cob biochar under various pyrolysis conditions. Source: Gotore et al. 2022

Another characterization technique employed was FTIR, as illustrated in Figure 5A. We identified distinct functional groups on the surface of the biochar, notably the CFX antibiotic (Figure 5B). Due to the presence of fluorine, these functional groups could be easily removed owing to the higher electronegativity of fluorine towards the biochar.

Furthermore, DLX was analyzed (Figure 5C), revealing the presence of three fluorine charges. Consequently, we observed an increase in electronegativity, facilitating the easy removal of these functional groups.

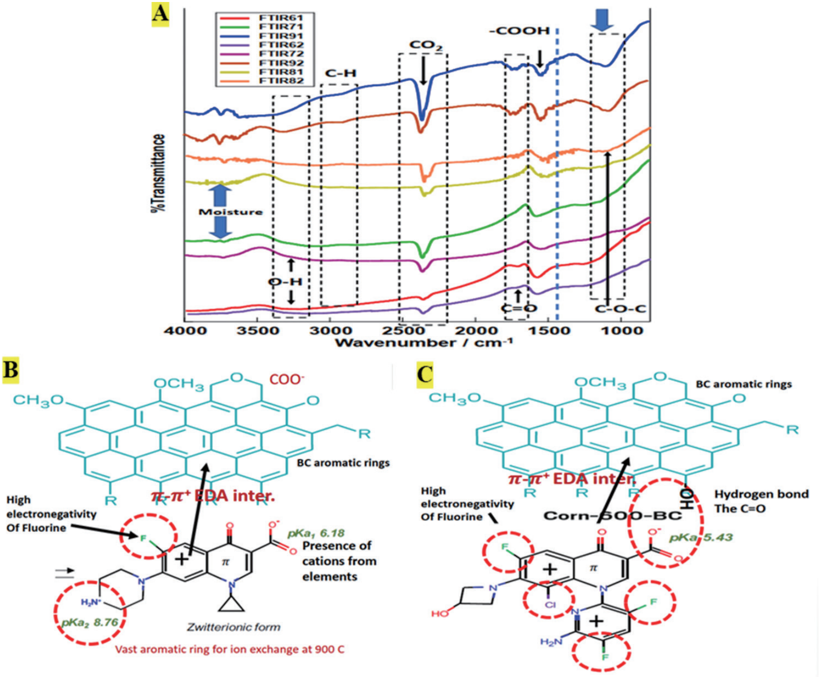

Figure 5: FTIR spectra of corncob biochar under various pyrolysis conditions (A), and the detection of CFX (B) and DLX (C) on the surface of the biochar.

Source: Gotore et al. 2022; Candel and Peñuelas 2017

Figure 6 illustrates the CFX and DLX adsorption isotherms. Regarding CFX removal, it was apparent that higher pyrolysis temperatures facilitate ciprofloxacin removal, while it proved challenging under lower pyrolysis conditions. Increased pyrolysis led to the formation of numerous functional groups capable of removing such contaminants, particularly antibiotics. Similarly, with DLX removal, a comparable trend was observed wherein higher pyrolysis temperatures were more effective in removing delafloxacin from wastewater. Consequently, biochar produced at 900°C demonstrate efficacy in antibiotic removal, even at lower temperatures.

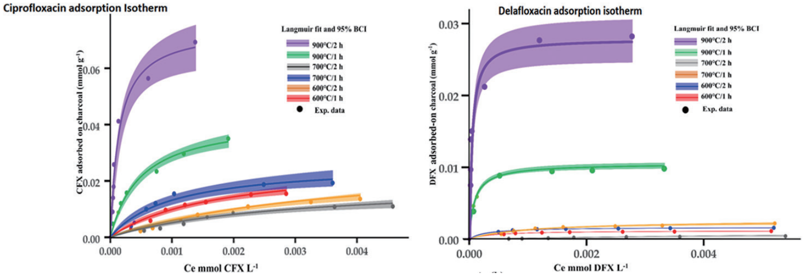

Figure 6: CFC and DFX adsorption isotherms.
Source: Gotore et al. 2022

Figure 7 presents KL, representing the energy present on the surface of the biochar, similar to binding energy. This energy influenced the adsorption and attraction of contaminants in wastewater. The impacts of iodine, CFX, and DLX were compared. In the case of iodine, higher pyrolysis conditions did not lead to its removal from the surface, with higher energy observed under smaller or lower pyrolysis conditions. Conversely, for antibiotics, the opposite trend was observed due to the higher electronegativity of these contaminants. These findings align with those reported by Dang et al. (2022).

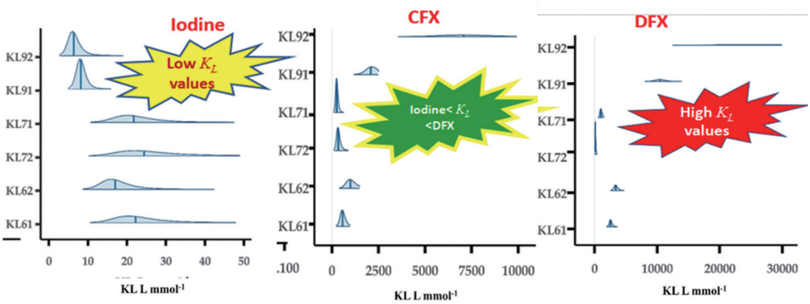

Figure 7: KL distribution parameters of iodine, CFX, and DLX.
Source: Gotore et al. 2022

3. Application of Corncob Biochar as A Substrate in CWs

Once we had obtained data on adsorption, we proceeded with the application of corncob biochar as a substrate in CWs for treating wastewater. This experiment was conducted in Chiang Mai City, northern Thailand. The corncobs were obtained from a local farmer and pyrolyzed at 600°C. We opted for this lowest effective temperature to save energy and reduce the cost of the constructed wetland. After pyrolysis, the biochar was produced over two hours, then washed and dried to prepare it for wetland application. The size of the biochar particles after pyrolysis ranged from approximately 1.5 millimeters to around 3 millimeters in diameter, which was considered relatively large. The fieldwork biochar pyrolysis process is shown in Figure 8.

Figure 8: Preparation of biochar for constructed wetland applications. Source: Author

The CW setup for treating pig manure or swine wastewater was implemented. This experiment was conducted at Maejo University, Chiang Mai, Thailand. The diagram of the experimental setup and operational parameters is presented in Figure 9. In this study, we utilized gravel and biochar as substrates in CWs, which were planted with common reed (*Phragmites australis*).

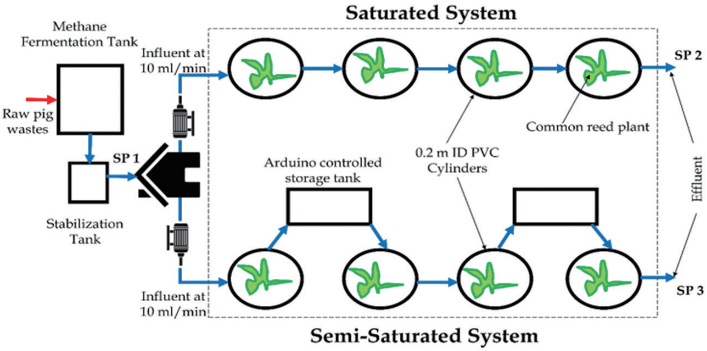

Figure 9: Schematic layout of the integrated constructed wetland system. Source: Gotore et al. 2022

After setting up the experiment, we managed to automatically control the CW, dividing it into two sections: saturated and semi-saturated wetlands. Within the CW, we measured a flow rate of approximately 14.4 liters per day from the pig manure waste. The cylinder volume in the area was calculated to be around 0.03 square meters per column, totaling approximately 0.12 square meters per system. The HRT was approximately 3.5 days for each system (Gotore et al. 2022).

As discussed in the previous chapters, plants play a crucial role in wastewater decontamination through processes such as transpiration and respiration. They contribute to aeration within the root system, facilitating the exchange of carbon dioxide and oxygen during their growth. As plants mature, they supply oxygen to microorganisms residing within the biochar, fostering a favorable environment for microbial activity. This ongoing interaction with microorganisms enables them to biodegrade nutrients present in wastewater, effectively decomposing and removing pollutants. The reeds served as a key component of the treatment process in the CWs. Additionally, leveraging its high porosity and large surface area, corncob biochar can provide a habitat for microorganisms and aid in adsorbing pollutants.

After four months of operation, we found that organic matter and nutrients were effectively removed by CWs, meeting the effluent quality standards for discharge into surface waters. The effluent ammonia and nitrate levels were below approximately 10 mg/L and 2 mg/L, respectively. Both effluent phosphorus and nitrite levels were maintained around 1 mg/L.

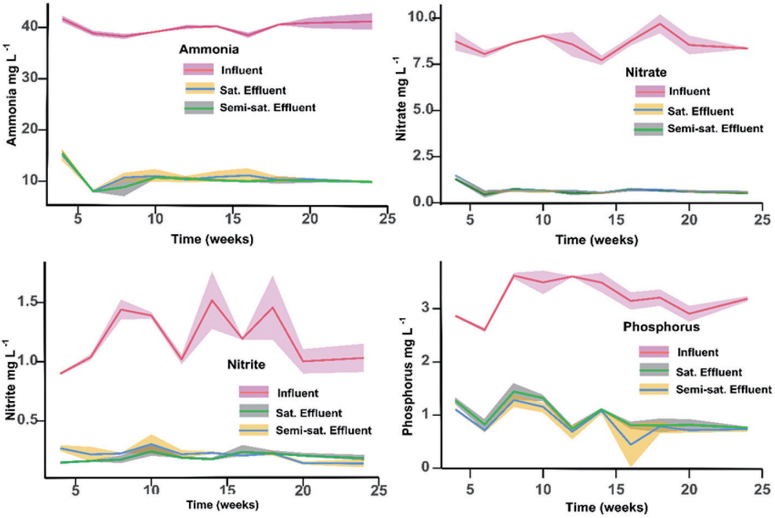

Figure 10: Inlet and outlet concentrations of ammonia, nitrate, nitrite, and phosphorus. Source: Gotore et al. 2022

The COD was also effectively removed in both saturated and semi-saturated CWs, achieving an average removal rate of approximately 70%. Figure 11 shows the concentration of COD in raw wastewater and after treatment with CWs, as well as the COD removal efficiency over time.

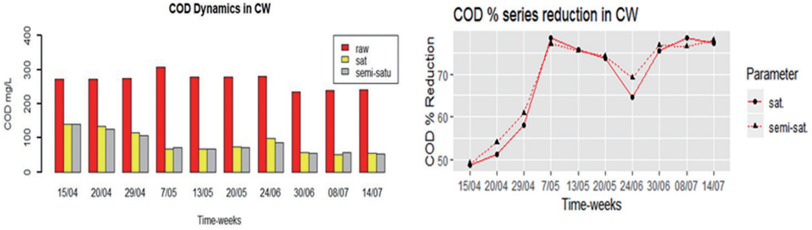

Figure 11: The concentrations of COD in influent and effluent samples, as well as the COD removal efficiency. Source: Gotore et al. 2022

4. Conclusion

In general, corncob biochar demonstrated favorable adsorptive properties and potential suitability as a substrate in CWs. The semi-saturated CWs utilizing corncob biochar and common reeds exhibited higher removal efficiency. With all locally available materials used in the study, the implementation of this approach for wastewater reclamation could prove cost-effective, offering a practical solution to ongoing challenges in rural areas of developing countries. Moreover, we aim to employ this passive technology for treating mine wastewater, particularly targeting the removal of manganese, zinc, and iron from mine drainage systems. Japan has approximately 100 mines still requiring heavy metal processing, and given its mountainous terrain, establishing large artificial wetlands proves challenging, especially in mountainous mining areas. Consequently, we are actively exploring the potential of bioremediation and the application of small-scale CWs for treating metal contamination in these mines' wastewater.

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6. Dr. Obey GOTORE

Chapter 6. The Applications and Performances of Biochar in Constructed Wetlands for Sustainable Wastewater Treatment

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