

UNIVERSIDADE FEDERAL DE VIÇOSA

**Engineered swine manure biochars for nutrient recovery and controlled release
in agriculture**

Larissa Almeida Nascimento
Doctor Scientiae

**VIÇOSA - MINAS GERAIS
2026**

LARISSA ALMEIDA NASCIMENTO

**Engineered swine manure biochars for nutrient recovery and controlled release
in agriculture**

Thesis submitted to the Agricultural Engineering Graduate Program of the Universidade Federal de Viçosa in partial fulfillment of the requirements for the degree of *Doctor Scientiae*.

Adviser: Andre Pereira Rosa

Co-advisers: Fernando F. da Cunha
Rita de C. S. de Sousa

**Ficha catalográfica elaborada pela Biblioteca Central da Universidade
Federal de Viçosa - Campus Viçosa**

T

N244e
2026 Nascimento, Larissa Almeida, 1994-
Engineered swine manure biochars for nutrient recovery
and controlled release in agriculture / Larissa Almeida
Nascimento. – Viçosa, MG, 2026.
1 tese eletrônica (93 f.): il. (algumas color.).

Texto em inglês.

Inclui apêndice.

Orientador: André Pereira Rosa.

Tese (doutorado) - Universidade Federal de Viçosa,
Departamento de Engenharia Agrícola, 2026.

Inclui bibliografia.

DOI: <https://doi.org/10.47328/ufvbbt.2026.618>

Modo de acesso: World Wide Web.

1. Suínos - Criação - Eliminação de resíduos. 2. Carvão.
I. Rosa, André Pereira, 1983-. II. Universidade Federal de
Viçosa. Departamento de Engenharia Agrícola. Programa de
Pós-Graduação em Engenharia Agrícola. III. Título.

CDD 22. ed. 628.7466

LARISSA ALMEIDA NASCIMENTO

**Engineered swine manure biochars for nutrient recovery and controlled release
in agriculture**

Thesis submitted to the Agricultural
Engineering Graduate Program of the
Universidade Federal de Viçosa in partial
fulfillment of the requirements for the degree of
Doctor Scientiae.

APPROVED: July 27, 2026.

Assent:

Larissa Almeida Nascimento
Author

Andre Pereira Rosa
Adviser

Essa tese foi assinada digitalmente pela autora em 09/10/2026 às 08:35:22 e pelo orientador em 09/10/2026 às 08:42:50. As assinaturas têm validade legal, conforme o disposto na Medida Provisória 2.200-2/2001 e na Resolução nº 37/2012 do CONARQ. Para conferir a autenticidade, acesse <https://siadoc.ufv.br/validar-documento>. No campo 'Código de registro', informe o código **VJKK.WOTP.6ETL** e clique no botão 'Validar documento'.

ACKNOWLEDGMENTS

First, I am grateful to God for the strength granted to me throughout this period. Faith and spirituality were fundamental to overcoming the challenges of this stage.

To my advisor, Professor André Rosa, thank you for your dedication, understanding, and the knowledge you shared. Your guidance was essential for my professional and academic growth. To my co-advisors, Professors Rita de Cássia Superbi de Sousa and Fernando França da Cunha, for their contributions and availability, which were essential for the development of this work.

To my family, I am grateful for the encouragement and for being my foundation of strength and love. To my parents, Isabel and Luiz Ricardo, for your unconditional support during this stage, always being there when I needed it most. To my brother and sister-in-law, Pedro and Naiara, thank you for the essential support and shelter during this period, and to my nieces, Alice and Bárbara, for bringing joy and love into my life.

To Tiago, my love, for the companionship, encouragement, and for sharing life with me.

To my friends Elisa (in memoriam) and Laís, I am grateful for your companionship and care since my undergraduate studies. Especially to Laís, who has been a source of comfort, support, and family throughout all the time we have shared in academia and in life.

To Augusto, undergraduate research student, thank you for your commitment. Your dedication was extremely important for this work.

To my colleagues from the Environmental Quality Laboratory (LQA) at UFV, thank you for the companionship and support throughout the development of this work. Special thanks to Moisés, Mariele, Yara, and Rayra for the academic contributions and inspiration.

To the Laboratory of Nanomaterials and Environmental Chemistry (LaNaQuA) at UFV, especially Professor Renata Pereira Lopes Moreira, thank you for the technical support and welcoming environment throughout the experiment.

To the Federal University of Viçosa and the Graduate Program in Agricultural Engineering, for the opportunity to carry out this work, as well as to all professors and technical staff who, in some way, contributed to my education and academic development.

Finally, I would like to thank everyone who contributed, directly or

indirectly, to this work or to my academic journey.

This work has been sponsored by the following Brazilian research agencies: Coordination for the Improvement of Higher Education Personnel (CAPES; Financing code 001), Minas Gerais State Foundation for Research Aid (FAPEMIG) and National Council of Scientific and Technological Development (CNPq).

We cannot solve our problems with the same thinking we used when we created
them.

Albert Einstein.

ABSTRACT

NASCIMENTO, Larissa Almeida, D.Sc., Universidade Federal de Viçosa, July, 2026. **Engineered swine manure biochars for nutrient recovery and controlled release in agriculture.** Adviser: Andre Pereira Rosa. Co-advisers: Fernando Franca da Cunha and Rita de Cassia Superbi de Sousa.

Swine production generates large volumes of waste rich in contaminants that, if improperly managed, can cause serious environmental impacts, including nutrient leaching and the dissemination of pharmaceutical compounds. In this context, biochars produced from animal manure have emerged as promising adsorbent materials capable of recovering nutrients and removing antibiotics, such as enrofloxacin (ENR), from wastewater. Furthermore, the application of nutrient-enriched biochar to soil enables the recovery of nutrients for crops fertilization such as forages, aligning with the circular economy. Therefore, this thesis investigated the use of swine manure-derived biochar for nutrient recovery and antibiotic immobilization, followed by its application as a fertilizer for *Brachiaria* cultivation. Initially, the biochar production conditions, including the activating agent, activating agent ratio, and pyrolysis temperature, were selected based on their performance for nitrogen and phosphorus removal. In addition, nutrient adsorption capacity and adsorption kinetics were investigated. Biochar activated with MgCl at a 3:1 ratio and pyrolyzed at 800 °C exhibited the highest nutrient adsorption. Adsorption kinetics followed the Elovich model for phosphate and the pseudo-second-order model for ammonium. Adsorption followed the Langmuir isotherm for phosphate ($q = 67,56 \text{ mg g}^{-1}$) and the Freundlich isotherm for ammonium ($q = 17,48 \text{ mg g}^{-1}$). In the second stage, the recovery of nutrients and immobilization of enrofloxacin (ENR) by the selected biochar were evaluated. Multicomponent adsorption experiments achieved 100% phosphate removal and 93% ammonium removal, which were attributed to struvite precipitation. In contrast, ENR adsorption was limited due to competition for metal-rich adsorption sites and the antibiotic speciation under alkaline conditions. Desorption assays revealed high nutrient release (150% for phosphorus and 40% for nitrogen) while maintaining reduced ENR leaching (<7%). Finally, the nutrient-enriched biochar was evaluated as a fertilizer for hybrid *Brachiaria* cv. Sabiá. Although biochar resulted in lower initial shoot biomass production, root biomass and total biomass were comparable to those obtained with conventional mineral fertilizer. Furthermore, soil chemical analysis showed that biochar application increased soil organic matter while maintaining high levels of available phosphorus. Foliar analysis demonstrated greater phosphorus

availability to plants and reduced the bioavailability and uptake of potentially toxic elements, such as copper. Overall, the results demonstrate that magnesium-modified swine manure biochar is a multifunctional material capable of promoting nutrient recovery, mitigating emerging contaminants, and supporting sustainable agricultural production. This integrated strategy contributes to reducing environmental impacts, improving nutrient use efficiency, and advancing circular economy practices in swine production systems.

Keywords: biochar; nutrient recovery; enrofloxacin; slow-release fertilizer; circular economy

RESUMO

NASCIMENTO, Larissa Almeida, D.Sc., Universidade Federal de Viçosa, julho de 2026. **Biocarvão de esterco suíno modificado para recuperação e liberação controlada de nutrientes na agricultura.** Orientador: Andre Pereira Rosa. Coorientadores: Fernando Franca da Cunha e Rita de Cassia Superbi de Sousa.

A suinocultura gera grandes volumes de dejetos ricos em contaminantes, que se manejados inadequadamente, podem causar sérios impactos ambientais, incluindo a lixiviação de nutrientes e a disseminação de fármacos no ambiente. Nesse contexto, o uso de biocarvões produzidos a partir de esterco animal apresentam-se como adsorventes capazes de remover nutrientes e antibióticos (como a enrofloxacina) de efluentes. Além disso, a utilização do biocarvão enriquecido no solo permite a recuperação desses nutrientes na fertilização de culturas como as forrageiras, alinhando-se à economia circular. Assim, esta tese investigou o uso de biocarvões derivado de esterco suíno (ES) na recuperação de nutrientes e imobilização de antibiótico para sua aplicação como fertilizante no cultivo de *Brachiaria*. Inicialmente, selecionou-se o biocarvão em termos de agentes ativantes, proporção do ativante e temperatura de pirólise na remoção de nitrogênio e fósforo. Além disso, foram investigados a capacidade de adsorção, cinética de adsorção de nutrientes. A ativação com $MgCl_2$ na proporção de 3:1 produzido a 800 °C favoreceu a adsorção de nutrientes. O ensaio de cinética indicou que a adsorção seguiu o modelo de Elovich para o fosfato e de pseudo-segunda ordem para o amônio. A adsorção seguiu a isoterma de Langmuir para o fosfato ($q = 67,56 \text{ mg g}^{-1}$) e a de Freundlich para o amônio ($q = 17,48 \text{ mg g}^{-1}$). Na segunda etapa, avaliou-se a recuperação de nutrientes e imobilização da enrofloxacina (ENR) pelo biocarvão selecionado. Os ensaios multicomponentes revelaram uma remoção de 100% de fosfato e 93% de amônio, atribuído à precipitação de estruvita. Por outro lado, a retenção da ENR foi limitada devido à disputa por sítios ativos ricos em metais e à especiação do composto em condições alcalinas. Os testes de dessorção apontaram uma elevada liberação de macronutrientes (150% de P e 40% de N) e uma lixiviação reduzida de ENR (<7%). Na etapa final, o biocarvão enriquecido com nutrientes foi avaliado como fertilizante em cultivo de *Brachiaria* híbrida cv. Sabiá. Embora o biocarvão tenha proporcionado menor produção inicial de biomassa da parte aérea, a biomassa radicular e a biomassa total foram equivalentes às obtidas com o fertilizante mineral. Além disso, a análise química do solo mostrou que a aplicação dos biocarvão aumentou o teor de matéria orgânica e manteve o fósforo disponível. A análise química foliar demonstrou que esses

materiais aumentaram a disponibilidade de fósforo para as plantas, enquanto restringiram a biodisponibilidade e a absorção de elementos potencialmente tóxicos, como o cobre. De forma integrada, os resultados demonstram que o biocarvão de esterco suíno modificado com magnésio promove a recuperação de nutrientes, a mitigação de contaminantes e um bom desempenho agrícola. Essa estratégia contribui para reduzir impactos ambientais, aumentar a eficiência do uso de nutrientes e fortalecer práticas de economia circular na cadeia produtiva da suinocultura.

Palavras-chave: biocarvão; recuperação de nutrientes; enrofloxacina; fertilizante de liberação lenta; economia circular

TABLES OF CONTENTS

1. GENERAL INTRODUCTION	13
1.1 References.....	16
2. RESEARCH HYPOTHESES	19
3. OBJECTIVES	19
3.1. General objective	19
3.2. Specific objectives.....	19
4. THESIS STRUCTURE	20
5. CHAPTER 1 - BIOCHAR FROM SWINE MANURE: AN ALTERNATIVE FOR NUTRIENT RECOVERY AND SLOW-RELEASE FERTILIZATION	21
5.1. Introduction	21
5.2. Materials and methods.....	23
5.2.1. Biochar production	23
5.2.3.2. Adsorption isotherms.....	26
5.2.4. Volatilization.....	27
5.2.5. Desorption Test.....	27
5.2.6. Statistical analysis	28
5.2.7. Analytical methods	28
5.3. Results and discussion.....	29
5.3.2. Adsorption kinetics.....	37
5.3.3. Adsorption isotherm	39
5.3.4. Volatilization.....	41
5.3.5. Desorption	42
5.4. Conclusions	43
5.5. References.....	44
6. CHAPTER 2 - SWINE MANURE-BIOCHAR: POTENTIAL AS A SLOW- RELEASE BIOFERTILIZER AND ANTIBIOTIC REMOVAL	48

6.1. Introduction	48
6.2. Material and methods	50
6.2.1. Preparation of biochar	50
6.2.2. Batch adsorption/desorption tests	51
6.2.3. Adsorption capacity of swine manure biochars produced under different conditions 51	
6.2.4. Single-analyte adsorption of nutrients and ENR	51
6.2.5. Desorption assays	52
6.2.6. Competitive (multicomponent) adsorption tests	52
6.2.7. Mass balance and agronomic potential estimation	52
6.2.8. Analytical methods	53
6.3. Results and discussion	54
6.3.1. Preparation of biochar	54
6.3.2. Influence of production conditions on biochar adsorption capacity.....	55
6.3.2. Biochar characterization	56
6.3.3. Adsorption tests	58
6.3.3. Competitive adsorption in multicomponent systems	59
6.3.4. Use of swine manure in the treatment of swine wastewater.....	61
6.4. Conclusions	62
6.5. References.....	63
7. CHAPTER 3: AGRONOMIC PERFORMANCE OF SWINE MANURE BIOCHAR AS A SLOW-RELEASE FERTILIZER FOR HYBRID BRACHIARIA	66
7.1. Introduction	67
7.2. Materials and methods.....	68
7.2.1. Biochar production and characterization.....	68
7.2.2. Biofertilizer experimental design	69
7.2.3. Morphogenetic measurements	70
7.2.4. Biomass evaluation.....	71

7.2.5. Water consumption and water productivity	71
7.2.6. Soil chemical assessment	72
7.2.7. Plant chemical analysis.....	72
7.2.8. Meteorological conditions	72
7.2.9. Statistical Analysis.....	73
7.3. Results and discussion	73
7.3.1. Biochar characterization	73
7.3.2. Morphogenetic Characteristics	75
7.3.3. Biomass production	77
7.3.4. Water Consumption and Productivity Performance	80
7.3.5. Soil chemical properties	81
7.3.6. Leaf nutrient content.....	84
7.4. Conclusions	86
7.5. References.....	86
8. GENERAL CONCLUSIONS AND FUTURE PERSPECTIVES	90
APPENDIX A.....	92

1. GENERAL INTRODUCTION

Global population is projected to reach approximately 10.3 billion by the mid-2080s, representing an increase of about 26% compared with 2024 estimates (ONU, 2024). This growth is expected to intensify food demand and place additional pressure on natural resources, thereby reinforcing the need for more sustainable agricultural systems (FAO, 2017). In this context, fertilizers play a crucial role in ensuring agricultural productivity; however, their manufacture relies on energy and raw materials derived from fossil sources. For example, ammonia synthesis through the Haber–Bosch process consumes more than 1% of the global energy supply and accounts for approximately 1.2% of anthropogenic CO₂ emissions (Spiller et al., 2022). Likewise, phosphate rock, the primary raw material used for phosphate fertilizer production, is a finite, non-renewable resource whose reserves are being progressively depleted due to the intensive use of phosphorus fertilizers in agriculture (Walsh et al., 2023).

Pork is the most consumed type of meat worldwide (USDA, 2024) and Brazil is the fourth largest producer, with approximately 5.6 million tonnes produced in 2025 (Embrapa, 2026). Consequently, pig farming generates large volumes of waste, ranging from 1.31 to 3.6 kg animal⁻¹ day⁻¹ (Aarnink & Ogink, 2007; Oliveira, 1993). Swine waste (SW) is characterized by high pollutant loads, typically containing 1000–30,000 mg L⁻¹ of COD, 400–2000 mg L⁻¹ of ammonium nitrogen (NH₄⁺-N), 600–2400 mg L⁻¹ of total nitrogen (TN), 50–300 mg L⁻¹ of total phosphorus (TP) (Zhou et al., 2024). The high concentrations of nutrients and organic matter make swine waste an attractive alternative source of nutrients for agricultural production, and its land application has therefore become a common management practice (Kunz et al., 2022).

Despite its agronomic value, the direct application of SW to agricultural land may result in nitrogen volatilization, nutrient leaching, and eutrophication of water bodies and microbiological contamination (Rathnayake et al., 2023). In addition, veterinary antibiotics are extensively used in intensive pig production for disease treatment, prevention and growth promotion. However, these compounds are only partially absorbed in the gastrointestinal tract, approximately 50–80% are excreted as parent compounds or metabolites (Sarmah et al., 2006). Once released into the environment, these compounds may impair microalgae growth, bioaccumulate in aquatic ecosystems and promote the dissemination of antibiotic resistance genes (ARGs), posing potential risks to both environmental and public health (Cheng et al., 2018).

To address these environmental challenges, wastewater treatment strategies have increasingly shifted from pollutant removal toward resource recovery, emphasizing both energy production and nutrient valorization. Anaerobic digestion (AD) is widely applied in swine waste treatment, enabling energy recovery through biogas production. However, the resulting effluent still remains rich in COD, N, and P, requiring further treatment to maximize nutrient recovery and minimize environmental disposal (Zhou et al., 2024). Additionally, AD shows limited efficiency in antibiotic removal, with a reduction rate of approximately 55% and concentrations ranging between 550 and 1,050 $\mu\text{g L}^{-1}$ (Wang et al., 2019). These limitations highlight the need for complementary technologies capable of simultaneously recovering nutrients and removing emerging contaminants.

Among the available alternatives, biochar has emerged as a promising adsorbent due to its ability to immobilize a wide range of inorganic and organic pollutants (He et al., 2022). The adsorption performance of biochar is strongly influenced by its physicochemical properties, which depend on the feedstock characteristics and production conditions, including pyrolysis temperature, heating rate, residence time, and reactor configuration (Qambrani et al., 2017). Furthermore, physical and chemical activation strategies are widely employed to enhance pore development, surface area, and the abundance of functional groups, thereby improving adsorption capacity (Sajjadi et al., 2019). However, the combined effects of carbonization temperature and different chemical activators on the adsorption and desorption capacity for both nutrients and enrofloxacin remains poorly understood, limiting the development of safe biochar-based fertilizers.

In addition, nutrient-enriched biochar has attracted increasing interest as a slow-release fertilizer, creating opportunities to integrate wastewater treatment with nutrient recycling within a circular economy framework (Nardis et al., 2021; Shakoor et al., 2021). This aspect is particularly relevant in Brazil, where livestock production relies heavily on pasture-based systems. Indeed, the Brazilian cattle herd was estimated at 197 million head in 2023. However, a large proportion of Brazilian pastures (50 - 70%) show some degree of degradation, often associated with low soil fertility and inadequate nutrient management (Bolfe et al., 2024). In this context, *Brachiaria* species are widely used in tropical pasture systems because they produce palatable and nutritious biomass, tolerance to adverse soil conditions (Mutimura; Ghimire, 2021). However, the agronomic efficiency of biochars is still limited information, particularly forage grasses such as *Brachiaria* spp.

To address these knowledge gaps, this thesis was structured into three complementary studies. The first study focused on optimizing the production of swine manure-derived biochar to maximize phosphorus and nitrogen recovery while evaluating its potential of nutrient release. Building upon these findings, the second study investigated the competitive adsorption and desorption behavior of nutrients and enrofloxacin on the optimized biochar, aiming to assess its potential as a slow-release fertilizer while ensuring the retention of emerging contaminants. Finally, the third study evaluated the agronomic performance of phosphate-enriched biochar as a slow-release fertilizer for hybrid *Brachiaria* cv. Sabiá, assessing plant growth, nutrient uptake, and changes in soil chemical properties. Together, these studies provide an integrated assessment of biochar as a strategy for nutrient recovery from swine wastewater and its subsequent reuse in agriculture within a circular economy framework.

1.1 References

- Aarnink, A. J. ., & Ogink, N. W. . (2007). Environmental impact of daily removal of pig manure with a conveyer belt system. *International Symposium on Air Quality and Waste Management for Agriculture, 16-19 September 2007, Broomfield, Colorado*.
<https://doi.org/10.13031/2013.23906>
- Bolfe, É. L., Victoria, D. de C., Sano, E. E., Bayma, G., Massruhá, S. M. F. S., & de Oliveira, A. F. (2024). Potential for Agricultural Expansion in Degraded Pasture Lands in Brazil Based on Geospatial Databases. *Land 2024, Vol. 13, Page 200, 13(2)*, 200.
<https://doi.org/10.3390/LAND13020200>
- Cheng, D. L., Ngo, H. H., Guo, W. S., Liu, Y. W., Zhou, J. L., Chang, S. W., Nguyen, D. D., Bui, X. T., & Zhang, X. B. (2018). Bioprocessing for elimination antibiotics and hormones from swine wastewater. *Science of the Total Environment*, 621, 1664–1682.
<https://doi.org/10.1016/j.scitotenv.2017.10.059>
- Embrapa. (2026). *Estatísticas - Suínos - Embrapa Suínos e Aves - Portal Embrapa*.
<https://www.embrapa.br/web/suinos-e-aves/cias/estatisticas-suinos>
- FAO, F. and A. O. of the U. (2017). The future of food and agriculture: trends and challenges. In *The future of food and agriculture: trends and challenges* (Vol. 4, Issue 4).
www.fao.org/publications%0Ahttp://www.fao.org/3/a-i6583e.pdf%0Ahttp://siteresources.worldbank.org/INTARD/825826-1111044795683/20424536/Ag_ed_Africa.pdf%0Awww.fao.org/cfs%0Ahttp://www.jstor.org/stable/4356839%0Ahttps://ediss.uni-goettingen.de/bitstream/han
- He, M., Xu, Z., Hou, D., Gao, B., Cao, X., Ok, Y. S., Rinklebe, J., Bolan, N. S., & Tsang, D. C. W. (2022). Waste-derived biochar for water pollution control and sustainable development. *Nature Reviews Earth & Environment 2022 3:7, 3(7)*, 444–460.
<https://doi.org/10.1038/s43017-022-00306-8>
- Kunz, A., Amaral, A. C. do, & Steinmetz, R. L. R. (2022). Fundamentos da digestão anaeróbia, purificação do biogás, uso e tratamento do digestato (2nd ed.). Airton Kunz, Ricardo Luis Radis Steinmetz, André Cestonaro do Amaral (editores Técnicos).
https://doi.org/10.21452/978-85-93823-01-5.2019.01_1Mutimura, M., & Ghimire, S.

- (2021). Brachiaria Grass for Sustainable Livestock Production in Rwanda under Climate Change. *Handbook of Climate Change Management: Research, Leadership, Transformation, 1*, 195–211. https://doi.org/10.1007/978-3-030-57281-5_314/SAVE-RESEARCH
- Nardis, B. O., Santana Da Silva Carneiro, J., Souza, I. M. G. De, Barros, R. G. De, & Azevedo Melo, L. C. (2021). Phosphorus recovery using magnesium-enriched biochar and its potential use as fertilizer. *Archives of Agronomy and Soil Science*, 67(8), 1017–1033. <https://doi.org/10.1080/03650340.2020.1771699>
- Oliveira, P. A. V. de. (1993). Manual de manejo e utilização dos dejetos suínos. *Documentos / Embrapa*, 27, 188.
- ONU. (2024). *World Population Prospects 2024* (Issue 9). www.un.org/development/desa/pd/.
- Qambrani, N. A., Rahman, M. M., Won, S., Shim, S., & Ra, C. (2017). Biochar properties and eco-friendly applications for climate change mitigation, waste management, and wastewater treatment: A review. *Renewable and Sustainable Energy Reviews*, 79, 255–273. <https://doi.org/10.1016/j.rser.2017.05.057>
- Sajjadi, B., Zubatiuk, T., Leszczynska, D., Leszczynski, J., & Chen, W. Y. (2019). Chemical activation of biochar for energy and environmental applications: A comprehensive review. *Reviews in Chemical Engineering*, 35(7), 777–815. <https://doi.org/10.1515/revce-2018-0003>
- Sarmah, A. K., Meyer, M. T., & Boxall, A. B. A. (2006). A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment. *Chemosphere*, 65(5), 725–759. <https://doi.org/10.1016/J.CHEMOSPHERE.2006.03.026>
- Shakoor, M. B., Ye, Z. L., & Chen, S. (2021). Engineered biochars for recovering phosphate and ammonium from wastewater: A review. *Science of The Total Environment*, 779, 146240. <https://doi.org/10.1016/J.SCITOTENV.2021.146240>
- Spiller, M., Moretti, M., De Paepe, J., & Vlaeminck, S. E. (2022). Environmental and economic sustainability of the nitrogen recovery paradigm: Evidence from a structured literature review. *Resources, Conservation and Recycling*, 184(March), 106406.

<https://doi.org/10.1016/j.resconrec.2022.106406>

USDA, U. S. D. of A. (2024). *PSD Online*. PSD Online. <https://apps.fas.usda.gov/psdonline/app/index.html#/app/advQuery>

Walsh, M., Schenk, G., & Schmidt, S. (2023). Realising the circular phosphorus economy delivers for sustainable development goals. *Npj Sustainable Agriculture* 2023 1:1, 1(1), 2-. <https://doi.org/10.1038/s44264-023-00002-0>

Wang, R., Feng, F., Chai, Y., Meng, X., Sui, Q., Chen, M., Wei, Y., & Qi, K. (2019). Screening and quantitation of residual antibiotics in two different swine wastewater treatment systems during warm and cold seasons. *Science of the Total Environment*, 660, 1542–1554. <https://doi.org/10.1016/j.scitotenv.2019.01.127>

Zhou, L., Liang, M., Zhang, D., Niu, X., Li, K., Lin, Z., Luo, X., & Huang, Y. (2024). Recent advances in swine wastewater treatment technologies for resource recovery: A comprehensive review. *Science of The Total Environment*, 924, 171557. <https://doi.org/10.1016/J.SCITOTENV.2024.171557>

2. RESEARCH HYPOTHESES

The following hypotheses were formulated based on current knowledge and the existing research gaps concerning nutrient recovery, slow-release fertilization, and the environmental safety of biochar application:

Hypothesis 1 – Biochar optimization enhances its phosphorus and nitrogen adsorption capacity while enabling the gradual desorption of these nutrients, allowing its use as a slow-release fertilizer;

Hypothesis 2 – Nutrient-loaded biochar acts as a slow-release fertilizer, while enrofloxacin remains strongly adsorbed, exhibiting low desorption;

Hypothesis 3 – Nutrient-loaded biochars improve the agronomic performance of crops compared with soil without biochar application and with conventional fertilization.

3. OBJECTIVES

3.1. General objective

To evaluate biochars derived from swine manure for nutrient recovery from wastewater and their application as slow-release fertilizers, considering the retention of emerging contaminants and agronomic performance.

3.2. Specific objectives

- To optimize the production of biochars derived from swine manure in terms of activating agents, activator ratios, and carbonization temperatures to maximize phosphorus and nitrogen recovery and evaluate their nutrient release potential;
- To evaluate the competitive adsorption and desorption behavior of nutrients and enrofloxacin on the optimized swine manure-derived biochar, assessing its potential as a slow-release fertilizer;

- To evaluate the agronomic performance of phosphate-enriched swine manure-derived biochar as a slow-release fertilizer for hybrid *Brachiaria* cv. Sabiá.

4. THESIS STRUCTURE

Based on the hypotheses and specific objectives, the structure of the thesis is presented in Table 4-1.

Table 4-1. Thesis structure

Chapter 1	
Hypothesis	Specific objective
• Biochar optimization enhances its phosphorus and nitrogen adsorption capacity while enabling the gradual desorption of these nutrients, allowing its use as a slow-release fertilizer;	• To optimize the production of biochars derived from swine manure to maximize phosphorus and nitrogen recovery and evaluate their nutrient release potential;
Chapter 2	
Hypothesis	Specific objective
• Nutrient-loaded biochar acts as a slow-release fertilizer, while enrofloxacin remains strongly adsorbed, exhibiting low desorption.	• To evaluate the competitive adsorption and desorption behavior of nutrients and enrofloxacin on the optimized swine manure-derived biochar, assessing its potential as a slow-release fertilizer.
Chapter 3	
Hypothesis	Specific objective
• Nutrient-loaded biochars improve the agronomic performance of crops compared with soil without biochar application and with conventional fertilization.	• To evaluate the agronomic performance of phosphate-enriched swine manure-derived biochar as a slow-release fertilizer for hybrid <i>Brachiaria</i> cv. Sabiá.

5. CHAPTER 1 - BIOCHAR FROM SWINE MANURE: AN ALTERNATIVE FOR NUTRIENT RECOVERY AND SLOW-RELEASE FERTILIZATION¹

Abstract

The production of swine manure (SM) biochar was optimized to improve nutrient recovery. SM was activated with KOH, HCl, or MgCl₂ at different ratios (1:2 and 1:3, w/v) and carbonized at 400, 600, and 800 °C. Results showed that MgCl₂-activated biochar at 800 °C (3:1) showed enhanced production (84,9%) and the highest phosphate adsorption (2.93 mg g⁻¹) and ammonium adsorption (1.27 mg g⁻¹). Adsorption followed Langmuir isotherm for phosphate ($q_m = 67.56 \text{ mg g}^{-1}$) and Freundlich for ammonium ($q_m = 17.48 \text{ mg g}^{-1}$). Adsorption kinetics indicated that phosphate uptake was best described by the Elovich model ($R^2 = 0.99$), while ammonium followed pseudo-second-order kinetics ($R^2 = 0.90$), suggesting distinct but predominantly chemisorption-controlled mechanisms. Desorption tests showed limited solubility of phosphate in water and partial ammonium release, supporting the use of biochar as a slow-release fertilizer. Overall, MgCl₂-activated biochar at 800 °C proved to be the most effective condition, combining high adsorption capacity with nutrient release potential, highlighting its value for sustainable nutrient recovery in agriculture.

Keywords: pig manure biochar; MgCl₂-modified biochar; phosphate and ammonium recovery; slow-release fertilizer.

5.1. Introduction

Pork is the most consumed meat worldwide, with a global production of approximately 116.45 million tons in 2024–2025¹. This large-scale production generates significant amounts of waste, as swine farming produces between 1.31 and 3.6 kg of manure per animal per day^{2,3}. Swine manure is rich in bioavailable nutrients and is commonly applied to agricultural soils as a fertilizer. However, its continuous use can lead to eutrophication of water bodies, nitrogen volatilization, microbiological contamination, and soil accumulation of potentially toxic metals (e.g. Zn and Cu) and antibiotics⁴. Therefore, it is important to find alternative ways to recover nutrients.

¹ This chapter is based on an article published in ACS Omega. DOI: <https://doi.org/10.1021/acsomega.5c12363>.

Thermochemical conversion of animal manure into biochar reduces environmental risks, as the high temperatures involved in the process reduces the bioavailability of metals, eliminates pathogens and organic micropollutants deactivate, organic contaminants while minimizing nutrient leaching ⁴. Moreover, biochar exhibits favorable adsorption characteristics, enabling the retention of nutrients from nutrient-rich solutions and wastewaters and offers low cost due to the organic matter used as raw material ⁵. After nutrient adsorption, biochar can be reused as a soil amendment or slow-release fertilizer, contributing to sustainable nutrient recycling and reducing environmental impacts ⁶.

The physicochemical properties of biochar can vary depending on the raw material, heating rate, temperature, residence time, and the type of reactor used for production ⁷. Furthermore, the activation process can be applied to improve the porous structure of carbon-based materials, such as volume and specific surface area ⁸. Chemical activation is the most common method for modifying biochars, in which chemical agents are used to impregnate the material before or after heat treatment ⁹. Acids, bases, and salts (AlCl_3 , MgCl_2) metal oxides (MgO , Fe_2O_3) can be used in the process ¹⁰.

In this context, several studies have investigated strategies to enhance nutrient recovery using modified biochars. However, most of these investigations examine the process within a narrow scope, typically focusing on the adsorption of a single nutrient ¹¹. Other studies have assessed the simultaneous removal of nitrogen and phosphorus; however, these investigations generally rely on a single activation route ¹² or a fixed pyrolysis temperature, without emphasizing the nutrient desorption process, which could enable their subsequent use as fertilizers ¹³. In addition, few studies investigate nutrient desorption, but focusing on only one nutrient ¹⁴ or using biochars with one activating agent ¹⁵. Understanding these complex interactions is essential for developing efficient nutrient recovery strategies and producing biochar suitable for agricultural reuse as a slow-release fertilizer, which, to date, has not been reported in the literature.

Therefore, this study aimed to evaluate swine manure as an alternative source for nutrient recovery. Specifically, it sought to optimize the preparation of swine manure-derived biochars for nitrogen and phosphorus removal by assessing different activating agents, activator ratios, and carbonization temperatures. In addition, the adsorption capacity, adsorption kinetics, and nutrient release potential of the optimized biochar were evaluated.

5.2. Materials and methods

5.2.1. Biochar production

Swine manure (SM) was collected from a pig farm at the Federal University of Viçosa, Minas Gerais, Brazil. The material was oven-dried at 65 °C for 48 h, then ground and sieved to a particle size of 10–60 mesh (See Table S2). Chemical activation was performed by impregnating the SM with the activating agent in the desired proportion (Table 5-1). The mixtures were dried at 80 °C for 24 h and 105 °C for 3 h, according to the methodology adapted from Li et al.¹⁶. For biochar production, both pristine or impregnated SM samples were placed in porcelain crucibles, which were covered to limit O₂ flow and allowing for the partial release of volatiles during pyrolysis¹⁴. The crucibles were placed in a muffle furnace (10 °C min⁻¹) and held for 1 h at the temperature assigned to each treatment. Subsequently, the biochars were stirred in 0.1 mol L⁻¹ HCl solution for 30 min and washed eight times with 500 mL of warm water (50 ± 2 °C) to remove both activating agent and organic matter residues¹⁷. Finally, the samples were dried at 65 °C for 24 h and sieved to 20-115 mesh to ensure homogeneity.

The biochar production conditions were optimized, considering three variables: i) activating agent: KOH (3 mol L⁻¹), HCl (3 mol L⁻¹) and MgCl₂ (3 mol L⁻¹); ii) activating agent ratio: 1:2 and 3:1 (mL of solution: g of dry manure); iii) carbonization temperature (400, 600 and 800 °C) (Table 5-1). The concentrations employed follow the proposals of Nardis et al.¹⁴ e Li et al.¹⁶, in order to optimize the magnesium (Mg) content for phosphorus adsorption.

Table 5-1: Experimental design for optimizing biochar production

Nomenclature	Activating agent	Ratio	Temperature (°C)	Final pH*
BC-400	-	-	400	7.54 (± 0.04)
BC-600	-	-	600	7.42 (± 0.03)
BC-800	-	-	800	7.9 (± 0.01)
K-1	KOH	1:1	400	9.00 (± 0.03)
K-2	KOH	3:1	400	9.25 (± 0.29)
K-3	KOH	1:1	600	10.38 (± 0.08)
K-4	KOH	3:1	600	9.1 (± 0.25)
K-5	KOH	1:1	800	10.74 (± 0.10)
K-6	KOH	3:1	800	8.88 (± 0.13)
Cl-1	HCl	1:1	400	7.26 (± 0.06)
Cl-2	HCl	3:1	400	6.56 (± 0.09)
Cl-3	HCl	1:1	600	7.26 (± 0.42)
Cl-4	HCl	3:1	600	6.78 (± 0.37)
Cl-5	HCl	1:1	800	7.06 (± 0.18)
Cl-6	HCl	3:1	800	7.35 (± 0.27)
Mg-1	MgCl ₂	1:1	400	9.58 (± 0.18)
Mg-2	MgCl ₂	3:1	400	10.82 (± 0.08)
Mg-3	MgCl ₂	1:1	600	11.05 (± 0.06)
Mg-4	MgCl ₂	3:1	600	11.29 (± 0.11)
Mg-5	MgCl ₂	1:1	800	10.33 (± 0.17)
Mg-6	MgCl ₂	3:1	800	10.53 (± 0.02)

*pH after 24 hours of agitation with ammonium phosphate in the optimization test.

The biochar yield (Y) was calculated after washing the materials, using the following equation¹⁸:

$$Y(\%) = \frac{M_b}{M_s} * 100 \quad \text{Eq. (1)}$$

Where, M_b is the dry mass of biochar produced and M_s is the initial dry mass of biomass.

5.2.2. Optimization of biochar production for nutrient removal

The response used to evaluate the best conditions for biochar production was the removal of phosphate and ammonia. For this purpose, 0.200 g of each biochar was placed in 125 mL Erlenmeyer flasks and 50.00 mL of ammonium phosphate solution (50 mg L⁻¹) was added. The initial pH was adjusted to 7.2 ($\pm$ 0.2). The mixtures were agitated at 120 rpm for 24 h⁵. Afterwards, suspensions were filtered (0.45 μ m) and analyzed for phosphate and ammonia by colorimetric methods (see Section 2.6).

The adsorption capacity (q_e) of the different biochar materials was calculated by mass balance, as expressed by Equation 2.

$$q_e(\text{mg g}^{-1}) = \frac{V(C_i - C_e)}{m} \quad \text{Eq. (2)}$$

Characterization of biochar

The Swine manure was characterized for ash content, elemental and mineral composition. Characterization of the optimized biochar and SM included determination of BET specific surface area (S_{BET}), pore volume, pore diameter, pH at the point of zero charge (pH_{PZC}), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM). The optimized biochar was selected for isotherm and kinetic experiments.

5.2.3. Batch adsorption experiments

5.2.3.1. Adsorption kinetics

For adsorption kinetic analyses, optimized biochars and 200 mg L⁻¹ solutions of P-phosphate (KH₂PO₄) or N-ammonia (NH₄Cl) were added to a 125 mL Erlenmeyer flask at a solid-to-solution ratio of 4 g L⁻¹. The flasks were agitated and samples were collected at predetermined time intervals (0, 1, 5, 15, 30, 60, 180, 300, 480, 720, and 1,440 min). The samples were immediately filtered (0.45 µm), and the P-phosphate and N-ammonia concentrations were analyzed, as described in Section 2.6. Kinetic models (Table 5-2) were used to estimate adsorption rates and to support interpretation of adsorption mechanisms and adsorbent performance. The pseudo-first order (PFO) and pseudo-second order (PSO) and Elovich models were fitted to the experimental data ¹⁹.

Table 5-2: Models applied to describe adsorption kinetics.

Model	Equation	Model parameters
PFO	$q_t = q_e (1 - e^{-K_1 t})$	- q_t (mg g ⁻¹): amount of nutrient adsorbed onto the adsorbent per unit mass at time t ; - q_e (mg g ⁻¹): amount of nutrient adsorbed onto the adsorbent per unit mass at equilibrium;
PSO	$q_t = \frac{q_e^2 K_2 t}{1 + q_e K_2 t}$	- t (min): time; - K_1 (min ⁻¹): Pseudo-1st order constant; - K_2 (g mg ⁻¹ min ⁻¹): Pseudo-2nd order constant;
Elovich	$q_t = \frac{1}{b_E} \ln(1 + a_E b_E t)$	- a_E : initial sorption rate; - b_E (g mg ⁻¹): desorption constant;

5.2.3.2. Adsorption isotherms

For adsorption isotherm analyses, solutions of P-phosphate (KH₂PO₄) at concentrations of 10–350 mg L⁻¹ or N-ammonia (NH₄Cl) at concentrations of 10–300 mg L⁻¹ were added to a 125 mL Erlenmeyer flask at a solid-to-solution ratio of 4 g L⁻¹. The flasks were agitated for 24 h to ensure equilibrium. After filtration (0.45 µm), the solutions were analyzed for P-PO₄ e N-

NH₄, as described Section 2.6. The Langmuir, Freundlich and Temkin models (Table 5-3) were fitted to the experimental data ¹⁹.

Table 5-3: Models applied to adsorption isotherm.

Model	Equation	Model parameters
Langmuir	$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$	- $q_{\max}$ (mg g⁻¹): maximum sorption capacity; - q_e (mg g⁻¹): adsorption capacity at equilibrium; - C_e (mg L⁻¹): solution equilibrium concentration; - K_L (L mg⁻¹): Langmuir constant;
Freundlich	$q_e = K_F C_e^{1/n}$	- K_F ((mg g⁻¹) (mg L⁻¹)^(-1/n)): Freundlich constant; - n: constant related to the adsorption strength of adsorbent; - R (8.314 J.mol⁻¹.K⁻¹): universal gas constant; - T (K): absolute temperature;
Temkin	$q_e = \frac{RT}{b_T} \ln(A_T C_e)$	- A_T (L.mg⁻¹): Temkin equilibrium constant; - b_T (J.mol⁻¹) represents adsorption energy.

5.2.4. Volatilization

NH₃ volatilization from biochars was evaluated. Samples of 0.100 g of biochar and 25.00 mL of NH₄Cl solution (5, 100, and 200 mg L⁻¹) were added to 120 mL penicillin vials, then sealed with rubber stoppers and aluminum seal. After 24 hours of agitation (190 rpm), 40 mL of headspace gas was collected and immersed in H₃BO₃ to captured NH₃. The trapped NH₃ was measured as N-NH₄⁺ using a colorimetric method and the N-NH₄⁺ standards were prepared by using 1% H₃BO₃ matrix ²⁰. Control assays were performed under the same conditions but without biochar addition. This experiment was done in duplicate and at room temperature (~25 °C).

5.2.5. Desorption Test

A desorption study was carried out to evaluate the potential of biochar as a slow-release fertilizer. A batch experiment was conducted in 125 mL Erlenmeyer flasks containing 50 mL of extractant solutions and 0.200 g of biochar previously saturated with ammonium phosphate (1.2 g L⁻¹). A 2 mol L⁻¹ KCl solution was used as extractant for NH₄⁺ recovery¹⁵; Mehlich-I (0.025

mol L⁻¹ H₂SO₄ + 0.05 mol L⁻¹ HCl) and 2% citric acid solution for ortho-P, and deionized water was employed for both nutrients¹⁴. The flasks were agitated at room temperature for 24 hours, and after filtration (0.45 µm), the remaining concentrations of P-PO₄ e N-NH₄ were analyzed. Controls, without the saturation step, were conducted to evaluate the inherent release of phosphorus and nitrogen from the material.

5.2.6. Statistical analysis

Biochar production yield (Y) and adsorption capacity (q_e) data obtained in the optimization test were subjected to normality analysis using the Shapiro-Wilk test and homogeneity of variances analysis using the Bartlett test, followed by analysis of variance (ANOVA). The means were compared using the Tukey test with a 5% significance level. The statistical analysis was performed using R software, version 4.5.0.

5.2.7. Analytical methods

Ash content was determined using the standard method ASTM D1762-84²¹. FTIR spectra were performed on a VARIAN 660 FTIR instrument equipped with a GladiATR. A carbon sample was added to the diamond crystal of the GladiATR and spectral readings were taken for the 4000 to 400 cm⁻¹ range. For X-ray diffraction (XRD) analysis, measurements were conducted using a diffractometer (Bruker D8-Discover, Germany) equipped with a copper tube and Goebel mirror, using Ni-filtered Cu-Kα radiation (λ = 1.5418 Å). Scanning was performed at a rate of 0.05° s⁻¹ over a 2θ range of 5° to 90°. The MATCH software (v.3.8.3.151, trial version) was used to identify XRD peaks, bands, and spectral signatures.

To determine the point of zero charge (pH_{PZC}), 30 mL of a 0.01 M NaCl solution were prepared in several flasks, and the initial pH of each was adjusted between 2 and 12. Subsequently, 0.15 g of the optimized biochar produced at 800 °C and activated with MgCl₂ (3:1) was added to each flask. After 24 h agitation, the final pH values were recorded. The pH_{PZC} was identified as the intersection point between the pH_{final} *versus* pH_{initial} curve and the bisector line²².

The optimized biochar and swine manure were chemically analyzed. Total phosphorus was determined by the colorimetric method after nitroperchloric digestion. Total nitrogen was measured by the Semi-Micro-Kjeldahl method²³. Specific surface area was determined using

a Nova 600 Series equipment (Anton Paar). The analysis was performed based on N₂ adsorption-desorption isotherms, using the Brunauer, Emmett and Teller (BET) method to determine the surface area, and the Barrett-Joyner-Halenda (BJH) method to evaluate the pore size distribution.

Scanning electron microscopy (SEM) images were obtained using JEOL equipment (JSM-6010LA), with a resolution of 4 nm (with a 20 kV beam). The samples were pre-treated with gold metallization (Quorum Q150R S Metallizer).

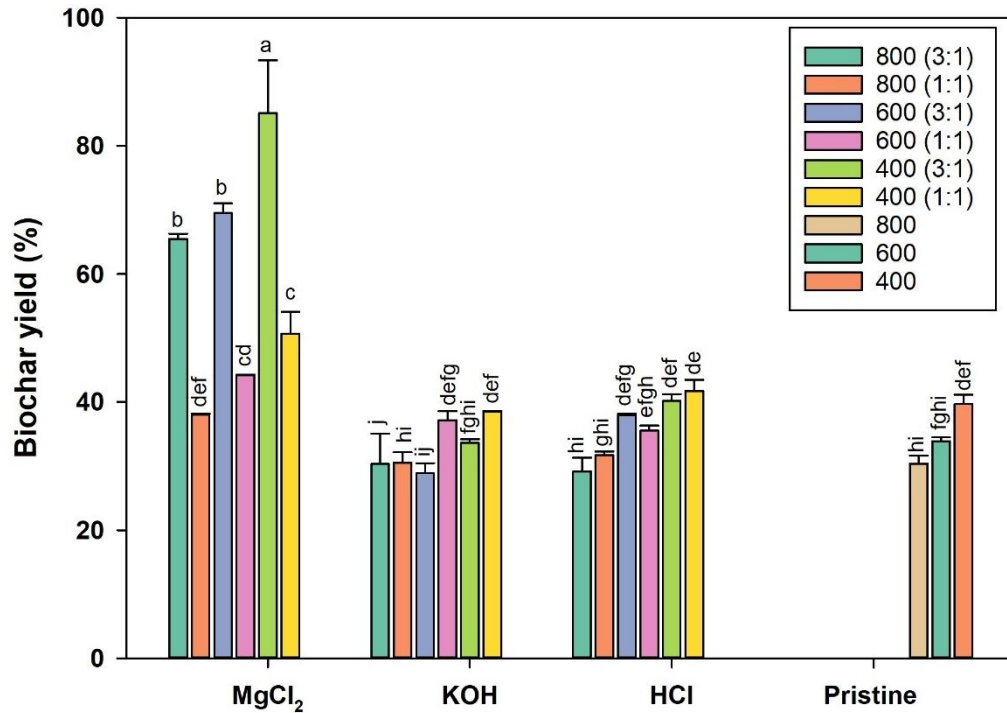
Nutrient concentrations (ammonium and phosphate ions) were measured colorimetrically. The N-NH₄⁺ content was determined by Hood-Nowotny et al. method²⁴ and the ortho-P content was determined by the ascorbic acid method²³.

5.3. Results and discussion

5.3.1. Influence of preparation conditions on biochar yield

Biochar yield results are shown in Figure 5-1. Biochar yield decreased as the pyrolysis temperature increased for all activating agents. Lower pyrolysis temperatures resulted in higher biochar yields because thermal degradation and volatilization of organic matter were less extensive, leading to reduced mass loss²⁵. The use of MgCl₂ enhanced the biochar yield, which can be attributed to its ability to inhibit depolymerization reactions. Furthermore, increasing the MgCl₂ concentration resulted in higher yields, likely due to the reduction in non-condensable gas production²⁶. In contrast, biochars activated with KOH and HCl exhibited lower yields, being statistically equal to or lower than those of the corresponding unmodified biochars. These results can be attributed to the higher efficiency of these agents in removing volatile matter¹⁰, promoting a reduction in biochar yield.

Figure 5-1: Biochar yield (%) of swine manure biochars prepared under different conditions.



Legend: Means followed by the same letter do not differ at the 5% level (Tukey test)

5.3.2. Effect of preparation conditions on nutrients removal

The adsorption results for phosphate and ammonium by the different biochars are presented in Tables 5-4 and 5-5.

Table 5-4: Adsorption capacity (mg g^{-1}) of phosphorus (P-PO_4^{3-}) of modified swine manure biochars (HCl, KOH, MgCl_2) produced at 400, 600 and 800 °C. Average ($\pm$ standard deviation)

Activating agent	Ratio	Temperature (°C)		
		400	600	800
HCl	1:1	-2.34* ($\pm$ 0.00) Cbb	-1.61* ($\pm$ 0.10) Bbb	-1.16* ($\pm$ 0.05) Abc
	3:1	-1.98* ($\pm$ 0.04) Cac	-1.15* ($\pm$ 0.09) Bac	-0.60* ($\pm$ 0.02) Aac
KOH	1:1	0.48 ($\pm$ 0.01) Aba	-3.30* ($\pm$ 0.18) Cbc	-0.06* ($\pm$ 0.01) Bbb
	3:1	2.71 ($\pm$ 0.02) Aaa	1.45 ($\pm$ 0.02) Bab	2.73 ($\pm$ 0.03) Aab
MgCl_2	1:1	0.64 ($\pm$ 0.06) Bba	2.55 ($\pm$ 0.13) Aba	2.59 ($\pm$ 0.02) Aba
	3:1	2.25 ($\pm$ 0.00) Bab	2.83 ($\pm$ 0.01) Aaa	2.93 ($\pm$ 0.05) Aaa

Values followed by the same uppercase letter within temperature levels, lowercase letters within ratio levels, and lowercase letters in italics within activating agent levels do not differ significantly according to Tukey's test at a

5% significance level. *The negative values result from the release of mineral phosphorus present in the biochars, as shown in Table S1.

Table 5-5: Adsorption capacity (mg g^{-1}) of nitrogen (N-NH_4^+) of modified swine manure biochars (HCl, KOH, MgCl_2) produced at 400, 600 and 800 °C. Average ($\pm$ standard deviation)

Activating agent	Ratio	Temperature (°C)		
		400	600	800
HCl	1:1	1.07 ($\pm$ 0.04) <i>Aaa</i>	0.27 ($\pm$ 0.02) <i>Bab</i>	0.35 ($\pm$ 0.03) <i>Bac</i>
	3:1	0.10 ($\pm$ 0.01) <i>Bbc</i>	0.31 ($\pm$ 0.03) <i>ABab</i>	0.52 ($\pm$ 0.03) <i>Aab</i>
KOH	1:1	0.57 ($\pm$ 0.12) <i>Bab</i>	0.97 ($\pm$ 0.05) <i>Aaa</i>	0.77 ($\pm$ 0.00) <i>ABab</i>
	3:1	0.39 ($\pm$ 0.03) <i>Bab</i>	0.68 ($\pm$ 0.08) <i>Aba</i>	0.41 ($\pm$ 0.01) <i>Bbb</i>
MgCl_2	1:1	0.57 ($\pm$ 0.06) <i>Cbb</i>	0.89 ($\pm$ 0.02) <i>Baa</i>	1.51 ($\pm$ 0.29) <i>Aaa</i>
	3:1	0.79 ($\pm$ 0.13) <i>Baa</i>	0.69 ($\pm$ 0.04) <i>Bba</i>	1.27 ($\pm$ 0.08) <i>Aba</i>

Values followed by the same uppercase letter within temperature levels, lowercase letters within ratio levels, and lowercase letters in italics within activating agent levels do not differ significantly according to Tukey's test at a 5% significance level.

The preparation conditions significantly influenced the adsorption of both nutrients. For phosphate, the MgCl_2 -activated biochar at a 3:1 ratio prepared at 800 °C exhibited the highest adsorption. In contrast, unactivated biochars and those activated with HCl exhibited greater phosphorus release compared to their adsorption capacity ($C_e > C_o$, Equation 2), resulting in negative adsorption values, as confirmed by release test in deionized water (see Supplementary Material, Table S1). Negative phosphorus (P-PO_4^{3-}) removal rates were also found by Ji et al.⁵ and Luo et al.¹². KOH-activated biochars exhibited variable phosphorus adsorption, with positive values comparable to MgCl_2 -treated biochars in some treatments and negative values in others.

Regarding ammonium, the highest adsorption was observed for MgCl_2 -activated biochars at a 1:1 ratio prepared at 800 °C (54% efficiency). HCl-activated biochars and unactivated showed the lowest adsorption, while KOH-activated biochars exhibited intermediate performance. Considering both phosphate and ammonium, the MgCl_2 -activated biochar at a 3:1 ratio and produced at 800 °C was therefore selected for subsequent experiments.

5.3.3. Characterization

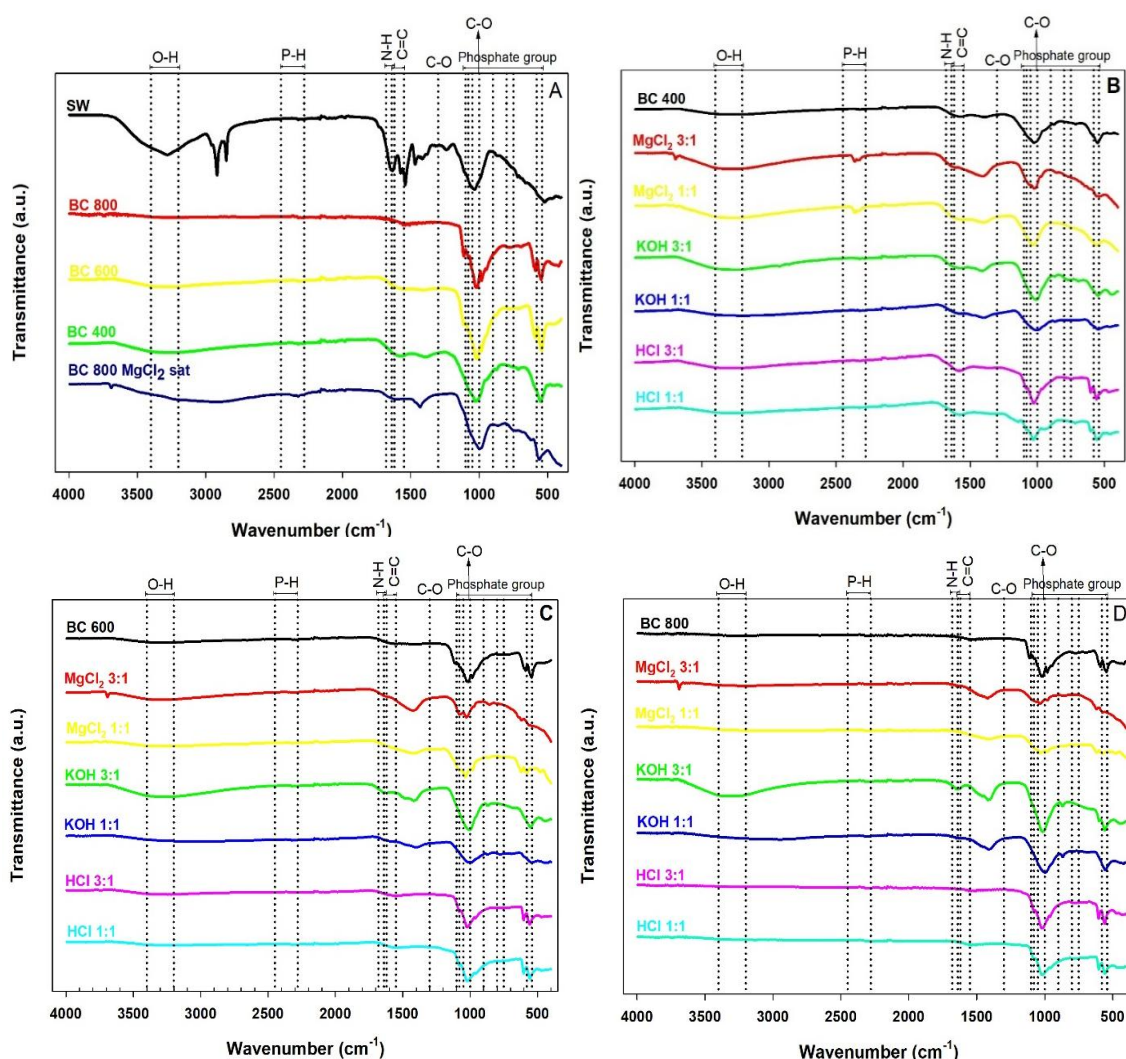
The raw swine manure was characterized prior to biochar production. Proximate analysis was performed to determine moisture, volatile matter, and ash contents, which were 5.67%, 69.20%, and 26.50%, respectively (see Table S2). The relatively high ash content reflects the presence of inorganic constituents typical of swine manure. Elemental and mineral composition of the raw material was assessed by energy-dispersive X-ray spectroscopy (EDS),

revealing the presence of C, O, N, P, K, and Ca (see Figure S3). This mineral-rich matrix is a characteristic feature of swine manure, as supported by literature ¹².

Fourier transform infrared spectroscopy (FTIR) was used to identify the main functional groups present in swine manure biochars before and after chemical modifications (Figure 5-2).

Legend: (A) SM and unmodified biochars (400–800 °C), including MgCl_2 -saturated biochar; (B–D) activated biochars at 400, 600 and 800 °C.

Figure 5-2: FTIR spectra of raw swine manure (SM) and derived biochars produced at 400, 600 and 800 °C, before and after chemical activation (MgCl_2 , KOH, HCl; 1:1 and 3:1).



FTIR spectra (Figures 5-2, A–D) show the structural evolution of swine manure (SM) into biochars, as well as the effects of chemical activation. In SM (Figure 5-2, A), a broad band is observed at $\sim 3400 \text{ cm}^{-1}$, attributed to hydroxyls (O–H), in addition to signals at 2920 and 2854 cm^{-1} (C–H of aliphatic bonds), 1640–1550 cm^{-1} (N–H and C=O of amines and

carboxylic acids) and phosphate groups ²⁷. In pyrolyzed biochars, especially at 800 °C, these bands decrease in intensity or disappear, indicating more intense carbonization and a reduction of surface oxygenated groups.

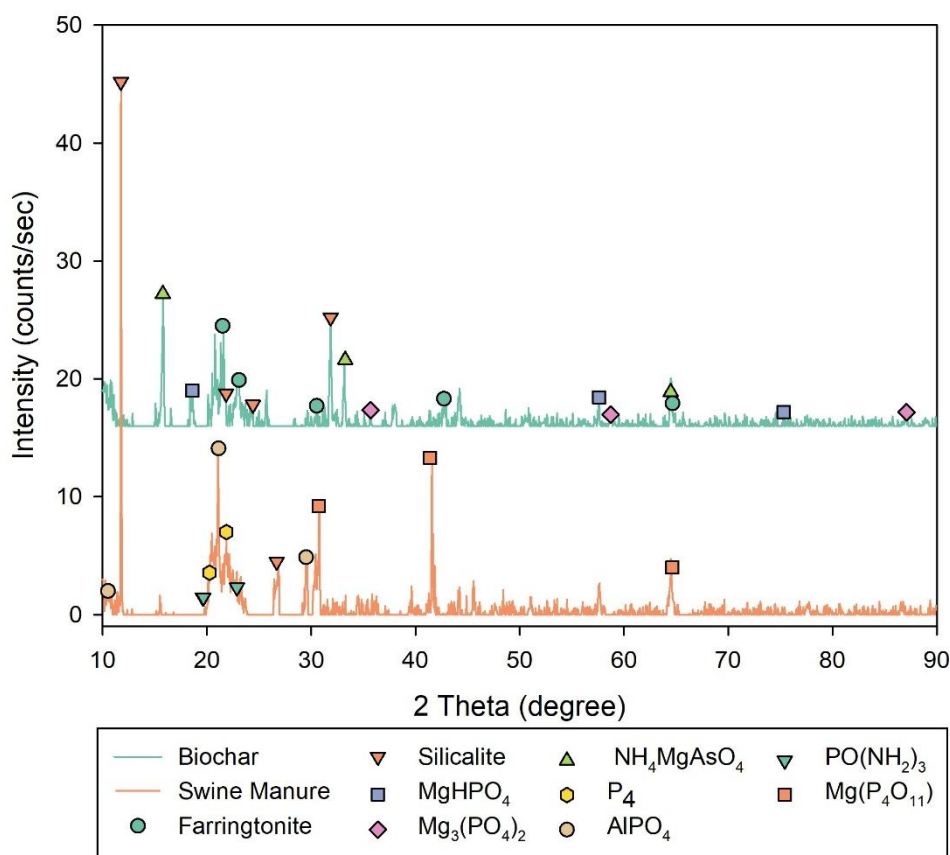
Among the activated materials (Figures 5-2, B–D), treatments with MgCl₂, especially in a 3:1 ratio, showed greater intensity in the 1000–500 cm⁻¹ region, associated with C–O and P–O vibrations, suggesting phosphorus stabilization in the biochar matrix ^{28,29}. Activation with KOH also intensified bands at 1100–1000 cm⁻¹, attributed to oxygenated structures (ethers, phenols), in addition to the presence of carboxylate group stretching (~1420 cm⁻¹), indicating the formation of carboxylic acid salts at intermediate temperatures (400–600 °C) ²⁷. On the other hand, biochars activated with HCl showed spectra with lower intensity of functional groups, consistent with the removal of compounds during acid activation.

The spectrum of MgCl₂ biochar (3:1, 800 °C) saturated with ammonium phosphate (Figure 5-2, A) showed an increase in the band at ~1040 cm⁻¹, characteristic of phosphate ^{28,29}, corroborating the adsorption data. In the case of activation with HCl, the reduction of functional groups and the final pH of the optimization (Table 5-1) close to neutrality restricts the formation of precipitates, which may justify the lower adsorption efficiency. In biochars activated with KOH, there may be a reduction in the concentration of the main exchangeable cations (Mg²⁺, Ca²⁺, Na⁺ and K⁺), due to their solubilization in the KOH solution ¹⁰. This decrease limits the availability of active sites for ion exchange reactions, which may contribute to the lower efficiency and variability observed in the adsorption of phosphorus and ammonia in some KOH treatments.

In MgCl₂-activated biochars, the MgCl₂ deposited on the biomass is decomposed into MgO at high temperatures during pyrolysis ¹⁰. In aqueous solutions, H⁺ is consumed by MgO, causing the increase in pH of the medium observed at the end of the optimization. Under high pH conditions, the precipitation of calcium phosphates and the generation of soluble mineral phases based on potassium, magnesium, or nitrogen can contribute significantly to phosphorus sorption mechanisms ¹⁴.

The XRD pattern of the swine manure and MgCl₂-modified biochar produced at 800 °C are presented in Figure 5-3.

Figure 5-3: XRD patterns of swine manure and saturated Mg-modified biochar

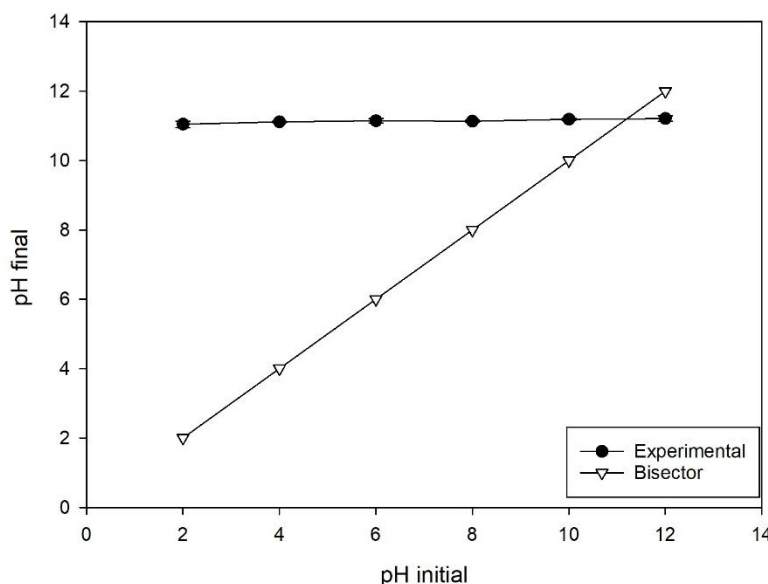


SM revealed the presence of crystalline peaks associated mainly with silicalite (SiO₂), aluminum phosphate, magnesium ultraphosphate (MgP₄O₁₁), and phosphoric triamide (PO(NH₂)₃). In turn, the saturated biochar exhibited phosphate crystals, such as farringtonite, magnesium phosphate (Mg₃(PO₄)₂), newberyite (MgHPO₄·3H₂O), and Arsenstruvite (NH₄MgAsO₄·6H₂O). Moreover, the predominance of silicalite indicates that a portion of the mineral matrix remained thermally stable after high-temperature carbonization. These findings support a dual mechanism for nutrient retention: (i) adsorption of phosphate and ammonium onto oxygenated functional groups and Mg-enriched surface sites, followed by (ii) localized precipitation of crystalline Mg–P–N phases.

The 800 MgCl₂ 3:1 biochar obtained a pH_{PZC} equal to 11.2 (Figure 5-4). The point of zero charge (PZC) of an adsorbent is that at which the pH value corresponds to a net surface charge equal to zero³⁰. Thus, in solutions with a pH higher than the pH_{PZC}, the surface charge is negative and the adsorption of cations is favored, while at pHs lower than the pH_{PZC}, the surface charge is positive and the adsorption of anions is favored. Phosphorus has the ionic form H₂PO₄²⁻ predominant between pH 7 and 12³¹. In this context, the adsorption of

phosphorus would be favored by the electrostatic attraction within the pH range found in the optimization (10.53) (Table 5-1).

Figure 5-4: pH at the point of zero charge of Mg-modified biochar



The chemical characterization data for biochar and swine manure are presented in Table 5-6. The natural phosphorus found in biochar increased compared to swine manure, attributed to the increased concentration of P during pyrolysis, since it is not a volatile element ⁴. Furthermore, the phosphorus content measured in saturated biochar reflected both the inherent phosphorus originally present in the material and the phosphorus subsequently adsorbed during the saturation step. In contrast, the total nitrogen content of the biochar decreased compared with the precursor material. This loss of nitrogen is attributable to thermal decomposition pathways that produce volatile N-species (e.g., NH₃, HCN and HNCO), whose relative yields depend strongly on pyrolysis temperature, heating rate and feedstock N-chemistry ³².

Table 5-6: Chemical characterization of swine manure (SM), biochar (BC 800 MgCl₂ 3:1), and saturated biochar (S BC 800 MgCl₂ 3:1). Mean ± standard deviation

Parameter	SM	BC 800 MgCl ₂ 3:1	S BC 800 MgCl ₂ 3:1
Total P (mg g ⁻¹)	28.96 ± 1.30	33.34 ± 4.79	86.96±11.72
Total N (mg kg ⁻¹)	49.77 ± 2.14	10.23 ± 0.80	6.25±0.31

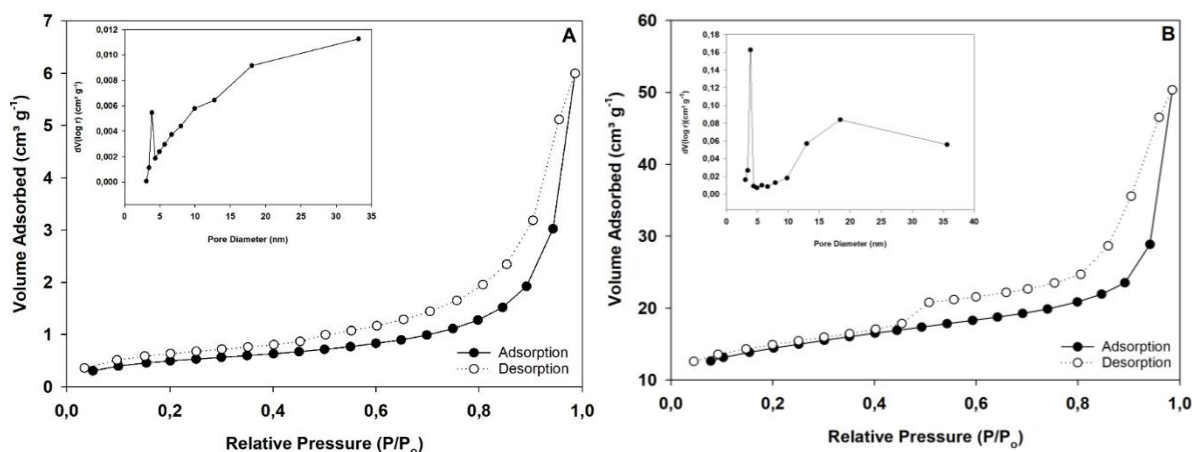
The results of the pore structure analysis are presented in Table 5-7 and Figure 5-5. The thermal treatment at 800 °C with MgCl₂ activation promoted a 25% increase in surface area compared to the SM. Furthermore, the pore volume was seven times greater in the modified

biochar compared to the SM, indicating a lighter and more porous material. In addition, both isotherms were classified as type IVa, indicating mesoporous materials. In fact, the average pore diameter was 3.8 nm for both samples, a value that falls within the mesopore range³³. However, the pore distribution (BJH-Desorption-dV(logd)) and the presence of hysteresis in the isotherm suggest a greater presence of macropores in the SM, while in the biochar there is a structure of meso- and micropores³³. In summary, the data demonstrate that activation with MgCl_2 , combined with pyrolysis at 800°C , was effective in generating a material with a high surface area and a highly porous structure.

Table 5-7: Porosity and surface area properties of SM and BC 800/ MgCl_2 3:1.

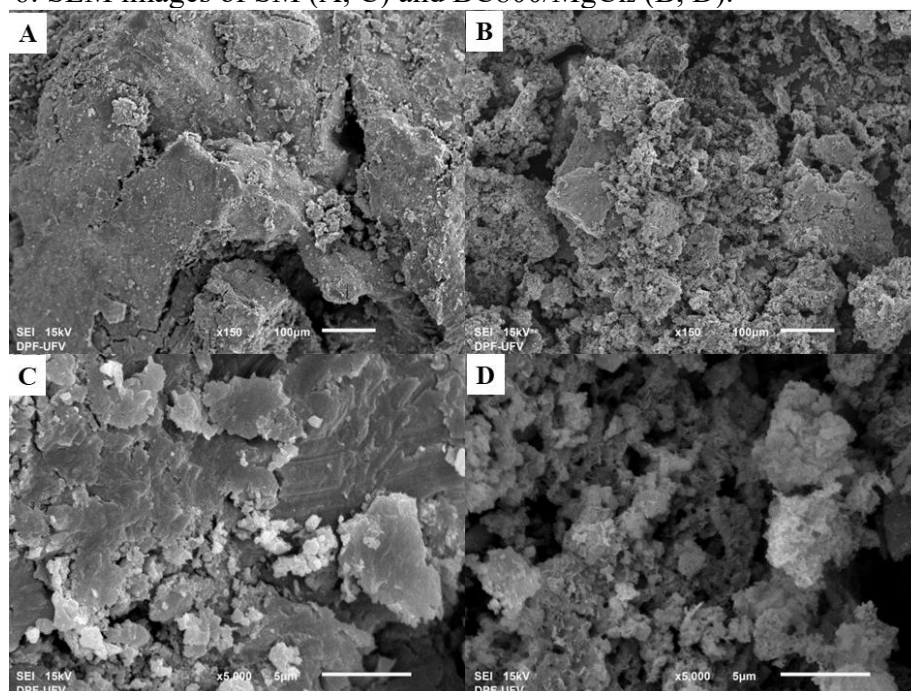
Parameter	Swine Manure	BC 800 °C MgCl_2
BET surface area ($\text{m}^2 \text{g}^{-1}$)	1.83	46.85
Microporous area ($\text{m}^2 \text{g}^{-1}$)	0.20	24.41
Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.0079	0.0573
Average pore diameter (nm)	3.85	3.88

Figure 5-5: N_2 adsorption/desorption isotherms for (A) SM - swine manure, (B) BC 800 MgCl_2 3:1 - biochar modified with MgCl_2 (3M) in a 3:1 ratio, produced at 800°C



The surface morphology of optimized biochar and swine manure was observed using SEM analysis, with images presented in Figure 5-6. The morphological analysis of swine manure revealed a predominantly compact and relatively smooth surface. In contrast, the biochar activated with MgCl_2 and produced at 800°C showed a fragmented surface with smaller particles.

Figure 5-6: SEM images of SM (A, C) and BC800/MgCl₂ (B, D).

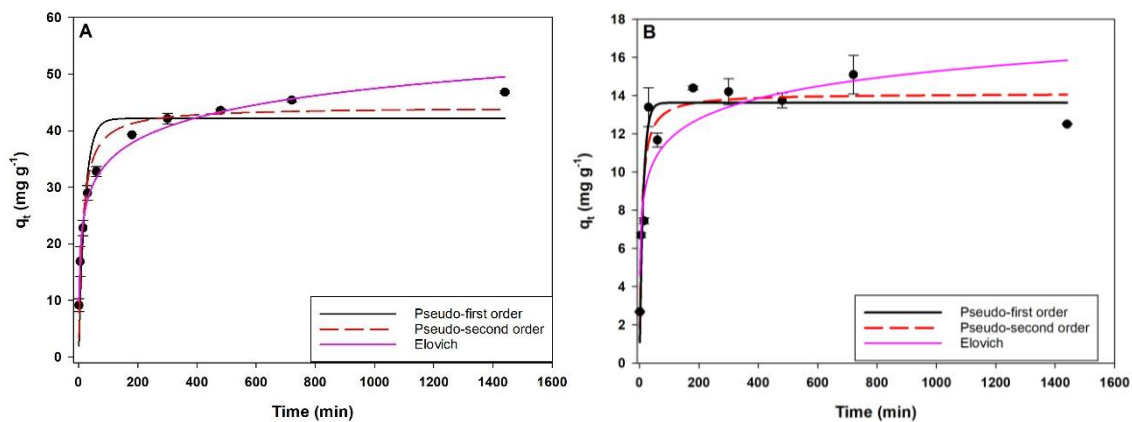


5.3.2. Adsorption kinetics

The adsorption kinetics of phosphate (P-PO_4^{3-}) and ammonium (N-NH_4^+) ions on BC 800 MgCl_2 (3:1) biochar was evaluated using pseudo-first order (PFO), pseudo-second order (PSO) and Elovich models (Figure 5-7) (Table 5-8). For phosphorus, the Elovich model provided the best fit to the experimental data ($R^2 = 0.99$), suggesting that the adsorption of phosphate occurs on a highly heterogeneous surface¹⁹. The initial adsorption rate (a_E) for P was $26.01 \text{ mg g}^{-1} \text{ h}^{-1}$, while the low desorption constant ($b_E = 0.18 \text{ g mg}^{-1}$) indicates that the phosphate ions are strongly retained.

Table 5-8: Phosphate and ammonia kinetic parameters for BC 800 MgCl₂ 3:1 biochar.

Model	Parameters	Adsorbate	
		P-PO ₄	N-NH ₄
PPO	q_e (mg g ⁻¹)	42.15	13.63
	K_1 (h ⁻¹)	0.048	0.083
	R^2	0.858	0.867
PSO	q_e (mg g ⁻¹)	44.17	14.12
	K_2 (g(mg h) ⁻¹) ⁻¹	0.002	0.011
	R^2	0.94	0.90
Elovich	a_E	26.01	28.78
	b_E	0.18	0.64
	R^2	0.99	0.78

Figure 5-7: Phosphate (A) and ammonia (B) adsorption kinetics of BC 800 MgCl₂ 3:1 biochar.

For ammonium (N–NH₄⁺), the Elovich model showed a higher b_E (0.64), indicating a less stable adsorption and the lower R^2 for ammonium (0.78), suggesting a more uniform interaction compared to phosphate. In turn, the PSO model showed the highest correlation ($R^2=0.90$), indicating that the rate-limiting step is predominantly governed by chemisorption³⁴. Although the adsorption rate constant (K_2) was higher for ammonium (0.0105 g mg⁻¹ h⁻¹), indicating faster adsorption, phosphate showed a higher retention capacity. These results highlight the potential of MgCl₂-modified biochar as an effective adsorbent for the simultaneous removal of nutrients in aqueous solutions.

5.3.3. Adsorption isotherm

The adsorption isotherms of P-PO_4^{3-} and N-NH_4^+ onto the BC 800 MgCl_2 3:1 biochar were evaluated using the Langmuir and Freundlich models (Figure 5-8) (Table 5-9). For phosphorus, the Langmuir model showed the best fit to the experimental data ($R^2 = 0.97$), indicating that adsorption occurs predominantly as monolayer coverage on a homogeneous surface³⁵. The maximum adsorption capacity (q_m) estimated by the model was 67.56 mg g^{-1} , and the Langmuir constant (K_L) was 0.37 L mg^{-1} , reflecting the affinity of the biochar for phosphate ions³⁶. The q_m value is within the range reported in the literature for Mg-modified feedstocks: $27.3 - 138 \text{ mg g}^{-1}$ for lignocellulosic materials^{37,38}, and 50 mg g^{-1} for sewage sludge³⁹ and $0.86 - 324.17 \text{ mg g}^{-1}$ for swine manure-derived biochars^{5,14}. Differences in q_m between studies are often attributable to feedstock composition, the nature and amount of the activating/loading activating agent, impregnation protocol, and pyrolysis parameters (temperature, heating rate, residence time).

Figure 5-8: Phosphate (A) and ammonia (B) adsorption isotherms of biochar BC800 MgCl_2 3:1.

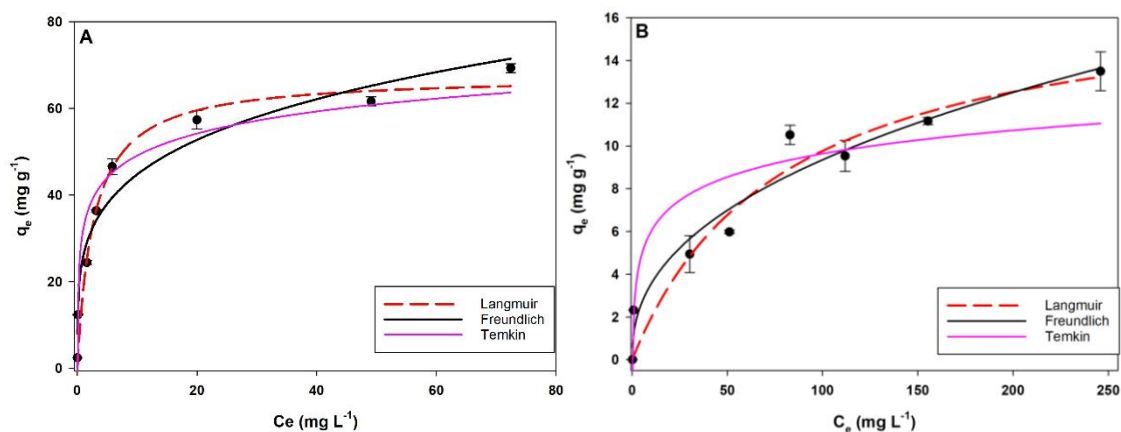


Table 5-9: Phosphate and ammonia isotherm parameters for BC 800 MgCl₂ 3:1 biochar.

Model	Parameters	Adsorbate	
		P-PO ₄	N-NH ₄
Langmuir	q_m (mg g ⁻¹)	67.56	17.48
	K_L (L mg ⁻¹)	0.37	0.0126
	R^2	0.97	0.9436
Freundlich	K_F ((mg g ⁻¹) (mg L ⁻¹) ^(-1/n))	26.01	1.35
	$1/n$	0.2362	0.42
	R^2	0.96	0.95
Temkin	A_T (L.mg ⁻¹)	79.99	4.5608
	b_T (J.mol ⁻¹)	337.305	1574.41
	R^2	0.9397	0.8468

In contrast, the maximum adsorption capacity for N–NH₄⁺ was substantially lower than that observed for phosphorus ($q_m = 17.48$ mg g⁻¹), and the Langmuir constant (K_L) was 0.0126 L mg⁻¹, indicating weaker affinity for the active sites. q_m values were between 1.54⁵ – 50 mg g⁻¹³⁷. In this case, the Freundlich model provided a better fit ($R^2 = 0.9549$) compared with the Langmuir model ($R^2 = 0.9436$). The Freundlich constant (K_F) was 1.35, confirming the lower adsorption capacity for ammonium relative to phosphate. The $1/n$ value, related to surface heterogeneity and adsorption intensity, was higher for ammonium ($1/n = 0.42$), suggesting lower reversibility and greater heterogeneity of the adsorption sites^{36,40}.

Temkin model was also applied to investigate the interaction potential between the adsorbates and the biochar. For phosphorus, the Temkin constant (b_T) of 337.30 J mol⁻¹. This relatively low value for the heat of adsorption is characteristic of physical adsorption or weak electrostatic interactions between the phosphate anions and the magnesium-functionalized surface. Furthermore, the high equilibrium binding constant ($A_T = 79.99$ L mg⁻¹) indicates a strong initial affinity⁴⁰ of the biochar for P–PO₄³⁻ ions, corroborating the high K_L value obtained in the Langmuir model.

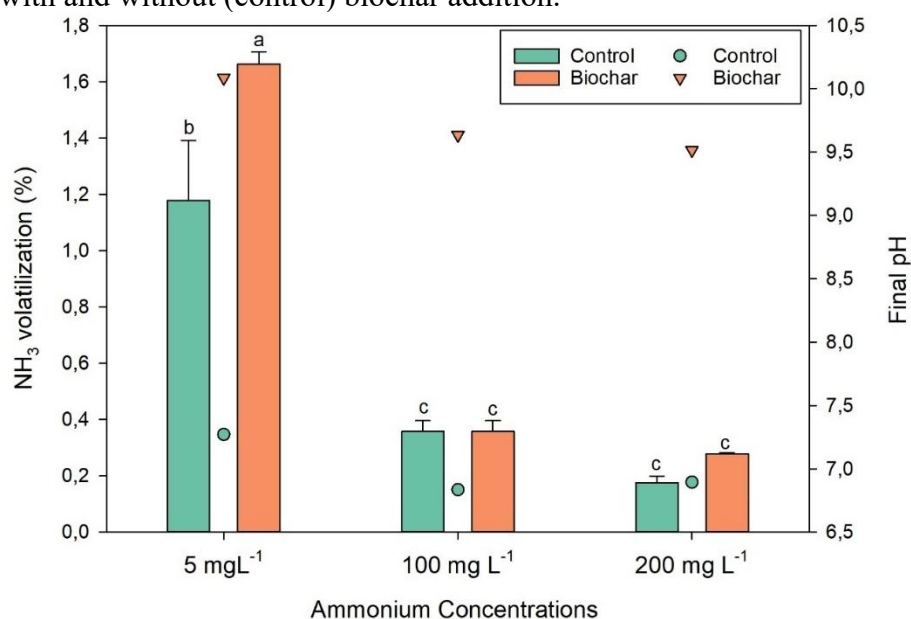
For ammonium, the Temkin model presented the lowest correlation among the three models ($R^2 = 0.8468$). The calculated b_T value was 1574.41 J mol⁻¹, which is higher than that observed for phosphorus, suggesting that although the total capacity for nitrogen is lower, the change in adsorption heat during the process is more pronounced for ammonium ions.

Additionally, the A_T value for ammonium (4.56 L mg^{-1}) was approximately 17 times lower than that of phosphate, further confirming the weaker affinity of the active sites for N-NH_4^+ .

5.3.4. Volatilization

The results of ammonia volatilization are shown in Figure 5-9. Volatilization measurements indicated low NH_3 losses across treatments ($<1.8\%$ of initial N), but statistical analysis showed a significant difference between biochar and control only at the lowest ammonium concentration (5 mg L^{-1} ; $p < 0.05$). At 100 and 200 mg L^{-1} , volatilization rates did not differ significantly between biochar-treated and control samples ($p > 0.05$).

Figure 5-9: Ammonia volatilization (%) and final pH at different ammonium concentrations in treatments with and without (control) biochar addition.



Legend: Bars represent mean values ($\pm$ SD). Different letters above the bars indicate significant differences between treatments at the same ammonium concentration according to Tukey's test ($p < 0.05$). Points indicate the final pH of each treatment.

The concentration-dependent pattern can be explained by two complementary mechanisms. First, the solutions containing biochar exhibited higher final pH values (9.51–10.08), which shifts the $\text{NH}_4^+ \rightleftharpoons \text{NH}_3$ equilibrium toward free NH_3 and can enhance volatilization under dilute conditions. Second, at higher ammonium concentrations ($100\text{--}200 \text{ mg L}^{-1}$) the biochar favors formation of less volatile species (e.g., surface-associated Mg-phosphate/struvite-like phases), reducing the fraction available for conversion to NH_3 ⁴¹. Taken

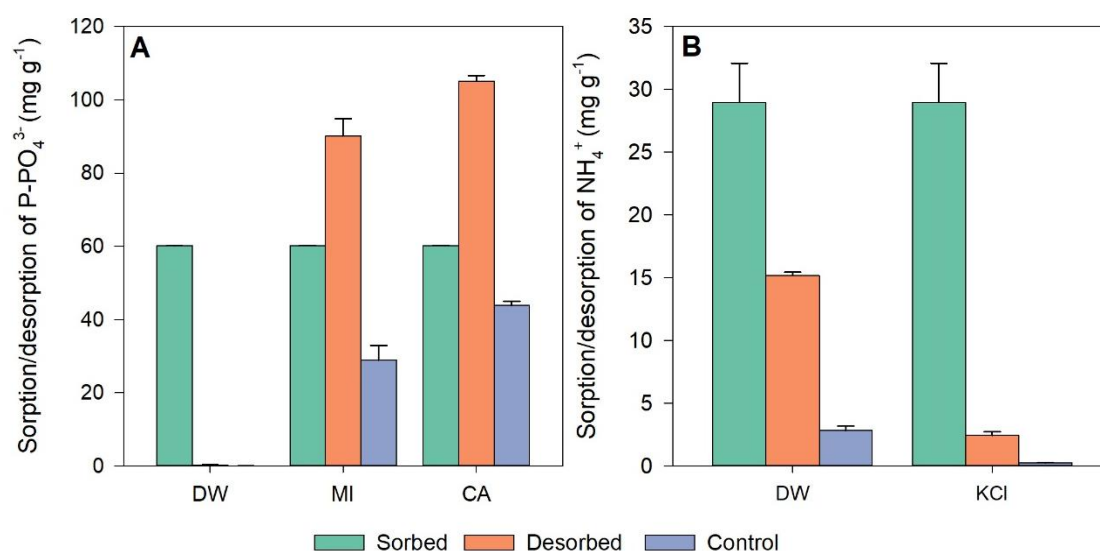
together, these processes explain why volatilization differences are significant only at the lowest concentration.

Banik et al.¹⁵ reported NH_3 losses between 0.006 and 1.9% in experiments with biochars, while control treatments showed higher emissions (up to 4.5%). In their study, the lower volatilization in the presence of biochar was associated with microbial activity and localized pH. Importantly, the absolute volatilization losses were small in all cases; indicating that the majority of nitrogen removal observed in the adsorption assays is attributable to uptake by the biochar rather than gaseous losses.

5.3.5. Desorption

The desorption analysis of phosphorus and nitrogen from MgCl_2 -modified biochar highlights the potential of these materials as slow-release fertilizers. Phosphorus desorption (extraction) was performed using deionized water, 2% citric acid, and Mehlich-1 solution (Figure 5-10).

Figure 5-10: Desorption (%) of phosphorus (A) and ammonium ion (B) using different extractants.



Legend: DW: deionized water, M1: Mehlich-1, CA: 2% citric acid, and KCl: 2 M KCl. Controls treatments were performed without the saturation step.

Water-soluble P represents the fraction readily available for plant uptake and is easily leached in sandy soils or fixed in clayey soils rich in Fe and Al oxides. The P extracted with Mehlich-1 and citric acid reflects the chemically soluble species potentially available to plants through rhizosphere exudates⁴². Negligible recovery in water indicates that phosphorus is

retained possibly through precipitation with magnesium or stable electrostatic interactions. In contrast, Mehlich-1 and citric acid desorption exceeded 100%, indicating not only the release of previously adsorbed phosphorus but also the dissolution of structural P from the biochar matrix under acidic conditions. This result can be attributed to the nature of the chemical interactions involved in adsorption, indicating that in these materials, phosphorus was predominantly adsorbed through electrostatic interactions or reversible ion exchange.

Ammonium ion (NH_4^+) desorption exhibited greater release in deionized water than in 2 M KCl solution. This result suggests that nitrogen is retained mainly through chemical mechanisms, such as precipitation in the form of struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) or interaction with magnesium phosphates. During KCl extraction, K^+ competes with NH_4^+ for exchangeable sites on the biochar surface; therefore, the low NH_4^+ release indicates that only a small fraction of the nitrogen was retained by ion exchange. A low desorption of NH_4^+ may also occur when adsorption takes place through oxygen-containing functional groups on the biochar surface rather than through ion exchange or physisorption¹⁵. The partial solubilization observed in water suggests that a fraction of these precipitates—particularly surface-associated or poorly crystallized forms—may dissolve under low ionic strength conditions⁴³. This result indicates a gradual nitrogen supply consistent with the concept of a slow-release fertilizer. Furthermore, the low desorption observed in KCl reinforces the potential of biochar to reduce nutrient losses through leaching.

5.4. Conclusions

The production of biochar from swine manure proved to be a promising strategy for nutrient recovery and environmental impact mitigation. Among the evaluated conditions, the biochar activated with MgCl_2 at a 3:1 ratio and pyrolyzed at 800 °C exhibited the best performance. Adsorption kinetics indicated that phosphate uptake was best described by the Elovich model ($R^2 = 0.99$), while ammonium followed pseudo-second-order kinetics ($R^2 = 0.90$), suggesting distinct but predominantly chemisorption-controlled mechanisms. Isotherm analyses revealed a high maximum adsorption capacity for phosphate ($q_m = 67.56 \text{ mg g}^{-1}$; $R^2 = 0.97$, Langmuir model) and a lower capacity for ammonium ($q_m = 17.48 \text{ mg g}^{-1}$), better described by the Freundlich model ($R^2 = 0.95$). The underlying mechanisms involve chemical precipitation (formation of magnesium phosphates), and electrostatic interactions for phosphorus and ion exchange and struvite formation for ammonium. Finally, desorption assays

validated the material's slow-release potential, showing negligible phosphorus release in deionized water and a gradual release of nitrogen. Therefore, optimizing activation and carbonization with MgCl_2 at 800 °C represents a viable route for producing multifunctional biochars capable of integrating swine waste valorization with sustainable nutrient recovery in agricultural systems.

Supporting Information data for this work can be found in Appendix A.

5.5. References

- (1) USDA, U. S. D. of A. *Pork | USDA Foreign Agricultural Service*. <https://www.fas.usda.gov/data/production/commodity/0113000> (accessed 2025-10-21).
- (2) André J.A Aarnink; Nico W.M Ogink. Environmental Impact of Daily Removal of Pig Manure with a Conveyer Belt System. In *International Symposium on Air Quality and Waste Management for Agriculture, 16-19 September 2007, Broomfield, Colorado*; American Society of Agricultural and Biological Engineers: St. Joseph, MI, 2007. <https://doi.org/10.13031/2013.23906>.
- (3) Oliveira, P. A. V. de. Manual de Manejo e Utilização Dos Dejetos Suínos. *Doc. / Embrapa* **1993**, No. 27, 188.
- (4) Rathnayake, D.; Schmidt, H.; Leifeld, J.; Mayer, J.; Epper, C. A.; Bucheli, T. D.; Hagemann, N. Biochar from Animal Manure: A Critical Assessment on Technical Feasibility, Economic Viability, and Ecological Impact. *GCB Bioenergy* **2023**, *15* (9), 1078–1104. <https://doi.org/10.1111/gcbb.13082>.
- (5) Ji, S.; Zhang, F.; Yao, P.; Li, C.; Faheem, M.; Feng, Q.; Chen, M.; Wang, B. Optimization of Pig Manure-Derived Biochar for Ammonium and Phosphate Simultaneous Recovery from Livestock Wastewater. *Environ. Sci. Pollut. Res.* **2023**, *30* (34), 82532–82546. <https://doi.org/10.1007/s11356-023-28092-w>.
- (6) Wang, C.; Luo, D.; Zhang, X.; Huang, R.; Cao, Y.; Liu, G.; Zhang, Y.; Wang, H. Biochar-Based Slow-Release of Fertilizers for Sustainable Agriculture: A Mini Review. *Environ. Sci. Ecotechnology* **2022**, *10*, 100167. <https://doi.org/10.1016/J.ESE.2022.100167>.
- (7) Qambrani, N. A.; Rahman, M. M.; Won, S.; Shim, S.; Ra, C. Biochar Properties and Eco-Friendly Applications for Climate Change Mitigation, Waste Management, and Wastewater Treatment: A Review. *Renew. Sustain. Energy Rev.* **2017**, *79*, 255–273. <https://doi.org/10.1016/j.rser.2017.05.057>.
- (8) Gupta, V. K.; Ali, I. Water Treatment for Inorganic Pollutants by Adsorption Technology. In *Environmental Water*; Elsevier, 2013; pp 29–91. <https://doi.org/10.1016/B978-0-444-59399-3.00002-7>.
- (9) Bonilla-Petriciolet, A.; Mendoza-Castillo, D. I.; Reynel-Ávila, H. E. *Adsorption Processes for Water Treatment and Purification*; Bonilla-Petriciolet, A., Mendoza-

- Castillo, D. I., Reynel-Ávila, H. E., Eds.; Springer International Publishing: Cham, 2017. <https://doi.org/10.1007/978-3-319-58136-1>.
- (10) Sajjadi, B.; Zubatiuk, T.; Leszczynska, D.; Leszczynski, J.; Chen, W. Y. Chemical Activation of Biochar for Energy and Environmental Applications: A Comprehensive Review. *Rev. Chem. Eng.* **2019**, *35* (7), 777–815. <https://doi.org/10.1515/revce-2018-0003>.
 - (11) He, L.; Wang, D.; Wu, Z.; Li, S.; Lv, Y. Co-Pyrolysis of Pig Manure and Magnesium-Containing Waste Residue and Phosphorus Recovery for Planting Feed Corn. *J. Water Process Eng.* **2022**, *49*, 103146. <https://doi.org/10.1016/j.jwpe.2022.103146>.
 - (12) Luo, L.; Wang, G.; Shi, G.; Zhang, M.; Zhang, J.; He, J.; Xiao, Y.; Tian, D.; Zhang, Y.; Deng, S.; Zhou, W.; Lan, T.; Deng, O. The Characterization of Biochars Derived from Rice Straw and Swine Manure, and Their Potential and Risk in N and P Removal from Water. *J. Environ. Manage.* **2019**, *245* (May), 1–7. <https://doi.org/10.1016/j.jenvman.2019.05.072>.
 - (13) Wu, L.; Xu, D.; Li, B.; Wu, D.; Yang, H. Enhanced Removal Efficiency of Nitrogen and Phosphorus from Swine Wastewater Using MgO Modified Pig Manure Biochar. *J. Environ. Chem. Eng.* **2024**, *12* (1), 111793. <https://doi.org/10.1016/j.jece.2023.111793>.
 - (14) Nardis, B. O.; Franca, J. R.; Carneiro, J. S. da S.; Soares, J. R.; Guilherme, L. R. G.; Silva, C. A.; Melo, L. C. A. Production of Engineered-Biochar under Different Pyrolysis Conditions for Phosphorus Removal from Aqueous Solution. *Sci. Total Environ.* **2022**, *816*. <https://doi.org/10.1016/j.scitotenv.2021.151559>.
 - (15) Banik, C.; Bakshi, S.; Andersen, D. S.; Laird, D. A.; Smith, R. G.; Brown, R. C. The Role of Biochar and Zeolite in Enhancing Nitrogen and Phosphorus Recovery: A Sustainable Manure Management Technology. *Chem. Eng. J.* **2023**, *456* (December 2022), 141003. <https://doi.org/10.1016/j.cej.2022.141003>.
 - (16) Li, R.; Wang, J. J.; Zhou, B.; Awasthi, M. K.; Ali, A.; Zhang, Z.; Lahori, A. H.; Mahar, A. Recovery of Phosphate from Aqueous Solution by Magnesium Oxide Decorated Magnetic Biochar and Its Potential as Phosphate-Based Fertilizer Substitute. *Bioresour. Technol.* **2016**, *215*, 209–214. <https://doi.org/10.1016/J.BIORTECH.2016.02.125>.
 - (17) Huang, H.; Tang, J.; Gao, K.; He, R.; Zhao, H.; Werner, D. Characterization of KOH Modified Biochars from Different Pyrolysis Temperatures and Enhanced Adsorption of Antibiotics. *RSC Adv.* **2017**, *7* (24), 14640–14648. <https://doi.org/10.1039/C6RA27881G>.
 - (18) Tay, T.; Ucar, S.; Karagöz, S. Preparation and Characterization of Activated Carbon from Waste Biomass. *J. Hazard. Mater.* **2009**, *165* (1–3), 481–485. <https://doi.org/10.1016/J.JHAZMAT.2008.10.011>.
 - (19) Wang, Y.; Wang, C.; Huang, X.; Zhang, Q.; Wang, T.; Guo, X. Guideline for Modeling Solid-Liquid Adsorption: Kinetics, Isotherm, Fixed Bed, and Thermodynamics. *Chemosphere* **2024**, *349*, 140736. <https://doi.org/10.1016/J.CHEMOSPHERE.2023.140736>.
 - (20) Bakshi, S.; Banik, C.; Laird, D. A.; Smith, R.; Brown, R. C. Enhancing Biochar as Scaffolding for Slow Release of Nitrogen Fertilizer. *ACS Sustain. Chem. Eng.* **2021**, *9* (24), 8222–8231. <https://doi.org/10.1021/acssuschemeng.1c02267>.

- (21) ASTM D 1762-84. Standard Test Method for Chemical Analysis of Wood Charcoal. *ASTM Int.* **2011**, *84* (Reapproved 2007), 1–2. <https://doi.org/10.1520/D1762-84R21.2>.
- (22) Akkari, I.; Graba, Z.; Bezzi, N.; Merzeg, F. A.; Bait, N.; Ferhati, A. Raw Pomegranate Peel as Promise Efficient Biosorbent for the Removal of Basic Red 46 Dye: Equilibrium, Kinetic, and Thermodynamic Studies. *Biomass Convers. Biorefinery* **2023**, *13* (9), 8047–8060. <https://doi.org/10.1007/s13399-021-01620-9>.
- (23) APHA; American Public Health; American Water Works; Federation, W. E. *Standard Methods for the Examination of Water and Wastewater*, 24th ed.; American Public Health Association; American Water Works Association; Water Environment Federation: Washington, DC, 2022. <https://doi.org/10.2105/SMWW.2882.002>.
- (24) Hood-Nowotny, R.; Umana, N. H.-N.; Inselbacher, E.; Oswald- Lachouani, P.; Wanek, W. Alternative Methods for Measuring Inorganic, Organic, and Total Dissolved Nitrogen in Soil. *Soil Sci. Soc. Am. J.* **2010**, *74* (3), 1018–1027. <https://doi.org/10.2136/sssaj2009.0389>.
- (25) Mariyam, S.; Alherbawi, M.; Pradhan, S.; Al-Ansari, T.; McKay, G. Biochar Yield Prediction Using Response Surface Methodology: Effect of Fixed Carbon and Pyrolysis Operating Conditions. *Biomass Convers. Biorefinery* **2023**, *14* (22), 28879–28892. <https://doi.org/10.1007/S13399-023-03825-6/FIGURES/5>.
- (26) Silva, L. D.; Lira, T. S.; Xavier, T. P.; Barrozo, M. A. S.; Dantas, S. C.; Silvério, B. C.; Santos, K. G. Effect of Temperature and MgCl₂ Concentration on the Catalytic Pyrolysis of Malt Waste Using Response Surface Methodology. *ChemistrySelect* **2022**, *7* (21). <https://doi.org/10.1002/slct.202200663>.
- (27) Barbosa, L. C. de A. Espectroscopia No Infravermelho Na Caracterização de Compostos Orgânicos. *Universidade Federal de Viçosa*. Ed. UFV: Viçosa/MG 2007, p 189.
- (28) Bekiaris, G.; Peltre, C.; Jensen, L. S.; Bruun, S. Using FTIR-Photoacoustic Spectroscopy for Phosphorus Speciation Analysis of Biochars. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2016**, *168*, 29–36. <https://doi.org/10.1016/J.SAA.2016.05.049>.
- (29) Coates, J. Interpretation of Infrared Spectra, A Practical Approach. *Encycl. Anal. Chem.* **2000**. <https://doi.org/10.1002/9780470027318.A5606>.
- (30) Park, J.; Regalbuto, J. R. A Simple, Accurate Determination of Oxide PZC and the Strong Buffering Effect of Oxide Surfaces at Incipient Wetness. *J. Colloid Interface Sci.* **1995**, *175* (1), 239–252. <https://doi.org/10.1006/jcis.1995.1452>.
- (31) de Magalhães, L. F.; da Silva, G. R.; Peres, A. E. C. Zeolite Application in Wastewater Treatment. *Adsorpt. Sci. Technol.* **2022**, 1–26. <https://doi.org/10.1155/2022/4544104>.
- (32) Hansson, K. M.; Samuelsson, J.; Tullin, C.; Åmand, L. E. Formation of HNCO, HCN, and NH₃ from the Pyrolysis of Bark and Nitrogen-Containing Model Compounds. *Combust. Flame* **2004**, *137* (3), 265–277. <https://doi.org/10.1016/J.COMBUSTFLAME.2004.01.005>.
- (33) Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87* (9–10), 1051–1069. <https://doi.org/10.1515/pac-2014-1117>.

- (34) Qiu, H.; Lv, L.; Pan, B. C.; Zhang, Q. J.; Zhang, W. M.; Zhang, Q. X. Critical Review in Adsorption Kinetic Models. *J. Zhejiang Univ. Sci. A* **2009**, *10* (5), 716–724. <https://doi.org/10.1631/jzus.A0820524>.
- (35) Serafin, J.; Dziejarski, B. Application of Isotherms Models and Error Functions in Activated Carbon CO₂ Sorption Processes. *Microporous Mesoporous Mater.* **2023**, *354*, 112513. <https://doi.org/10.1016/j.micromeso.2023.112513>.
- (36) Do, D. D. *Fundamentals of Diffusion and Adsorption in Porous Media*; Imperial College Press: London, 1998; Vol. 2. https://doi.org/10.1142/9781860943829_0007.
- (37) Biswas, B.; Adhikari, S.; Jahromi, H.; Ammar, M.; Baltrusaitis, J.; Torbert, A.; Linhoss, J.; Lamba, J. Magnesium Doped Biochar for Simultaneous Adsorption of Phosphate and Nitrogen Ions from Aqueous Solution. *Chemosphere* **2024**, *358*, 142130. <https://doi.org/10.1016/J.CHEMOSPHERE.2024.142130>.
- (38) Pinto, M. de C. E.; da Silva, D. D.; Gomes, A. L. A.; dos Santos, R. M. M.; de Couto, R. A. A.; de Novais, R. F.; Constantino, V. R. L.; Tronto, J.; Pinto, F. G. Biochar from Carrot Residues Chemically Modified with Magnesium for Removing Phosphorus from Aqueous Solution. *J. Clean. Prod.* **2019**, *222*, 36–46. <https://doi.org/10.1016/j.jclepro.2019.03.012>.
- (39) Elkhilfi, Z.; Lahori, A. H.; Shahib, I. I.; Iftikhar, J.; Wang, S.; He, L.; Meili, L.; Gendy, E. A.; Sharma, P.; Chen, Z. Comparative Assessment of Phosphate Adsorption Properties and Mechanisms on Mg/Al-Engineered Sewage Sludge Biochar in Aqueous Solution. *J. Water Process Eng.* **2023**, *56*, 104443. <https://doi.org/10.1016/J.JWPE.2023.104443>.
- (40) Mane, V. S.; Deo Mall, I.; Chandra Srivastava, V. Kinetic and Equilibrium Isotherm Studies for the Adsorptive Removal of Brilliant Green Dye from Aqueous Solution by Rice Husk Ash. *J. Environ. Manage.* **2007**, *84* (4), 390–400. <https://doi.org/10.1016/j.jenvman.2006.06.024>.
- (41) Cai, G.; Ye, Z. long. Concentration-Dependent Adsorption Behaviors and Mechanisms for Ammonium and Phosphate Removal by Optimized Mg-Impregnated Biochar. *J. Clean. Prod.* **2022**, *349*, 131453. <https://doi.org/10.1016/J.JCLEPRO.2022.131453>.
- (42) Li, H.; Shen, J.; Zhang, F.; Clairotte, M.; Drevon, J. J.; Le Cadre, E.; Hinsinger, P. Dynamics of Phosphorus Fractions in the Rhizosphere of Common Bean (*Phaseolus Vulgaris* L.) and Durum Wheat (*Triticum Turgidum Durum* L.) Grown in Monocropping and Intercropping Systems. *Plant Soil* **2008**, *312* (1–2), 139–150. <https://doi.org/10.1007/s11104-007-9512-1>.
- (43) Le Corre, K. S.; Valsami-Jones, E.; Hobbs, P.; Parsons, S. A. Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review. *Crit. Rev. Environ. Sci. Technol.* **2009**, *39* (6), 433–477. <https://doi.org/10.1080/10643380701640573>.

6. CHAPTER 2 - SWINE MANURE-BIOCHAR: POTENTIAL AS A SLOW-RELEASE BIOFERTILIZER AND ANTIBIOTIC REMOVAL²

Abstract

This study evaluated swine manure-derived biochar as a multifunctional material for nutrient recovery and immobilization of enrofloxacin (ENR), a veterinary antibiotic commonly detected in livestock wastewater. Biochars were produced under different conditions: activating agent - potassium hydroxide (KOH), hydrochloric acid (HCl), and magnesium chloride (MgCl₂)-, impregnation ratio (1:1 and 3:1) and pyrolysis temperature (400, 600 and 800 °C). The MgCl₂-modified biochar produced at 800 °C (3:1) exhibited the best performance for ammonium and phosphate removal. In single-analyte tests the material reached phosphate (60.1 mg g⁻¹), ammonium (28.9 mg g⁻¹) and ENR (39.5 mg g⁻¹) uptake. Multicomponent experiments showed high phosphate removal (100%) and ammonium removal (93%) attributed to an ideal stoichiometry for struvite formation, whereas ENR uptake decreased due to competition for metal-rich sites and alkaline speciation. Desorption assays showed high nutrient release (150% P and 40% N) and minimal ENR desorption (<7%). A theoretical mass-balance indicates that 317 m³ of digestate can be treated per tonne of produced biochar, with 86 kg P recovered. Overall, Mg-modified swine-manure biochar is a promising route for nutrient recycling and contaminant mitigation.

Key-words: Swine Manure Biochar, Nutrient Recovery, enrofloxacin removal.

6.1. Introduction

Pig farming generates large volumes of Swine Waste (SW) rich in nutrients such as nitrogen and phosphorus, as well as pollutants like antibiotics (Nagarajan et al., 2019). In this context, anaerobic digestion (AD) is a suitable and widely used alternative for the treatment of SW. The resulting effluent, known as digestate, remains rich in bioavailable nutrients. Owing to this composition, the agricultural application of swine waste is common practice as a source of nutrients and organic matter that enhances both crop productivity and quality (Kunz et al., 2019).

² This chapter is based on an article published in Revista Engenharia Sanitária e Ambiental. DOI: <https://doi.org/10.1590/S1413-4152031S107>

However, the repeated application of animal waste to agricultural soils can result in several environmental concerns, including nutrient leaching, eutrophication of water bodies, nitrogen volatilization, microbiological contamination of soils, and high transportation costs (Rathnayake et al., 2023). Additionally, enrofloxacin (ENR), a fluoroquinolone-class antibiotic developed for veterinary use, is commonly detected in animal waste (Wang et al., 2019). In that respect, anaerobic digestion (AD) shows limited efficiency in antibiotic removal, with a reduction rate of approximately 55%. After AD, enrofloxacin concentrations can still range between 1,050 and 550 $\mu\text{g L}^{-1}$ (Wang et al., 2019). The presence of antibiotics in the environment can impair microalgae growth, lead to bioaccumulation in aquatic organisms, and promote the proliferation of antibiotic resistance genes (ARGs) within ecosystems (Cheng et al., 2018).

In this context, the biochar has garnered significant attention due to its favorable adsorption properties, which could provide benefits for nutrient recovery as well as antibiotic retention. The main properties of the biochar include its high specific surface area, well-developed porosity, and the low cost of its organic feedstocks (Ji et al., 2023). The physicochemical characteristics of biochar are influenced by several factors, such as the type of feedstock, heating rate, pyrolysis temperature, residence time, and the reactor design used during its production. Furthermore, activation processes—particularly chemical activation—are often employed to enhance the porous structure and surface functionality of carbon-based materials (Sajjadi et al., 2019). Nevertheless, the application of nutrient-enriched biochar is envisaged as a more controlled fertilizer source. However, the combined effects of carbonization temperature and different chemical activators on the adsorption and desorption capacity for both nutrients and enrofloxacin remain underexplored and warrant further investigation.

Therefore, producing biochar from pig manure offers several advantages, including: i) valorization of the main waste generated in pig farming ii) high nutrient adsorption capacity (Ji et al., 2023), and iii) the ability to adsorb undesirable contaminants such as enrofloxacin (Chowdhury et al., 2019). Moreover, some studies have investigated the use of nutrient-saturated biochars as slow-release fertilizers (Banik et al., 2023; Nardis et al., 2022). However, to ensure the safe agricultural application of biochar, it is essential to assess both the adsorption and desorption behaviors of residual contaminants present in the effluent, particularly antibiotics like enrofloxacin.

In this context, this study aimed to evaluate the viability of swine manure biochar as a slow-release fertilizer. The specific objectives were: i) to evaluate the nutrient adsorption capacity (phosphate and ammonium) in terms of biochar preparation conditions (temperature, type of activating agent, and activator ratio); ii) to evaluate the adsorption and desorption of nutrients and enrofloxacin on biochar; iii) to characterize adsorption behavior for nutrients and enrofloxacin in competitive (multicomponent) systems and iii) to assess practical scalability through a theoretical mass-balance scenario. This approach aligns with circular economy principles and addresses critical challenges in nutrient recovery and emerging contaminant mitigation.

6.2. Material and methods

6.2.1. Preparation of biochar

The dried Swine Manure (SM) (65 °C for 48 hours), was ground and sieved between 10–60 mesh. Activation was carried out by immersing the SM in the activating agent, following the ratio established for each treatment. The mixtures were then dried at 80 °C for 24 hours and at 105 °C for 3 hours, adapted from Li et al. (2016). The pyrolysis process was conducted in a muffle furnace (10 °C min⁻¹), maintained for 1 hour at the target temperature. Finally, the biochars were stirred for 30 minutes in a 0.1 mol L⁻¹ HCl solution, washed with 8 L of deionized water (50 ± 2 °C), and dried at 65 °C for 24 hours.

The biochar production conditions were optimized considering three variables: i) activating agent: KOH (3 mol L⁻¹), HCl (3 mol L⁻¹), and MgCl₂ (3 mol L⁻¹) ii) activating ratio - 1:1 and 3:1 (mL solution: g manure); and iii) pyrolysis temperature (400, 600 and 800 °C). The concentration was defined to optimize the performance of magnesium (Mg) in phosphorus removal (Li et al., 2016).

The biochar yield (R_m) was calculated after washing, according to equation 1.

$$R_m(\%) = \frac{M_b}{M_s} * 100 \quad (1)$$

Where, M_b is the dry mass of biochar produced and M_s is the initial dry mass of biomass.

6.2.2. Batch adsorption/desorption tests

Adsorption and desorption assays were conducted in batch mode using 125 mL Erlenmeyer flasks placed on an orbital incubator shaker operated at 190 rpm and maintained at room temperature (25 ± 2 °C). For all experiments, the adsorption capacity (q_e , mg g⁻¹) was calculated by mass balance according to Equation 2:

$$q_e(\text{mg g}^{-1}) = \frac{V(C_i - C_e)}{m} \quad (2)$$

Where, V is the solution volume (L); C_i is the initial concentration of adsorbate (mg L⁻¹); C_e is the concentration of adsorbate at equilibrium (mg L⁻¹); m is the amount of adsorbent.

Removal efficiency (%) was calculated as $(C_i - C_e)/C_i \times 100$, whereas adsorption capacity (Q_e) was expressed in mg g⁻¹.

6.2.3. Adsorption capacity of swine manure biochars produced under different conditions

The removal of phosphate and ammonia was used to evaluate the best conditions for biochar production. 0.2 g of each biochar was added to 50 mL of ammonium phosphate solution (50 mg L⁻¹). After 24 h, the remaining concentration of phosphate and ammonium after filtration (0.45 µm) was determined via colorimetric methods (See section Analytical methods) and the best-performing material was select for further tests (Ji et al., 2023). Characterization of the selected biochar and SM included pH at the point of zero charge (pH_{PZC}) and chemically analyzed for total phosphorus, total nitrogen and available Potassium (K) and magnesium (Mg).

The experimental data were subjected to analysis of variance (ANOVA) and the means were compared by Tukey's test at 5% significance. Statistical analyses were performed using R software, version 4.5.0.

6.2.4. Single-analyte adsorption of nutrients and ENR

The performance of the selected biochar (800 °C, MgCl₂ 3:1) was further evaluated for nutrients and ENR separately. This step also served as a formal saturation procedure to load the biochar with analytes for subsequent desorption studies. For nutrients, 0.2 g of biochar was added to 50 mL of ammonium phosphate solution (1.2 g L⁻¹) and agitated for 24 h. For ENR,

0.02 g of biochar was added to 20 mL of ENR solution (100 mg L^{-1}), agitated for 4 h. After the contact time, the suspensions were centrifuged and filtered ($0.45 \text{ }\mu\text{m}$). The filtrates were analyzed for phosphate and ammonium via colorimetric methods, while ENR concentrations were determined by UV-Vis spectrophotometry at 275 nm (Chowdhury et al., 2019). The saturated biochar was then recovered for the subsequent release assays.

6.2.5. Desorption assays

To assess the feasibility of using biochar as a slow-release fertilizer and its effectiveness in ENR immobilization, desorption assays were performed using the previously saturated materials. The saturated biochar was placed in contact with 50 mL of three extractants. Deionized water (DW) was used to simulate natural leaching in soils, representing the water-soluble and easily mobile fraction of the adsorbed compounds. Mehlich-1 (MI) solution ($0.025 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 0.05 \text{ mol L}^{-1} \text{ HCl}$) was selected to estimate the plant-available phosphorus and antibiotic fractions in the rhizosphere (Nardis et al., 2022). For ammonium, $2 \text{ mol L}^{-1} \text{ KCl}$ (potassium chloride) was used to replace exchangeable cations through ion-exchange mechanisms (Banik et al., 2023).

The percentage of desorbed P was calculated by dividing the desorbed by the adsorbed P amounts. Control assays were performed using unsaturated biochar subjected to the same extraction procedures to determine the contribution of the biochar matrix to the total release analytes. After 24 h of shaking, samples were filtered ($0.45 \text{ }\mu\text{m}$) and analyzed for ammonium, phosphate and ENR.

6.2.6. Competitive (multicomponent) adsorption tests

To evaluate the interaction between analytes, 0.10 g of biochar ($800 \text{ }^\circ\text{C}$, MgCl_2 3:1) was added to 50 mL of a multicomponent solution containing ammonium phosphate (50 mg L^{-1}) and ENR (200 mg L^{-1}). After contact (24 h), suspensions were filtered ($0.45\text{-}\mu\text{m}$) and the pH was measured. Residual concentrations of phosphate (P-PO_4^{3-}), ammonium (NH_4^+) and enrofloxacin were determined by the colorimetric methods (Chowdhury et al., 2019).

6.2.7. Mass balance and agronomic potential estimation

A theoretical mass balance was performed based on the experimental yield and adsorption data obtained in this study. The estimation considered a specific swine digestate scenario with concentrations of 189 mg L⁻¹ for P-PO₄³⁻ and 962 mg L⁻¹ for N-NH₄⁺ (Kunz et al., 2019) and 500 µg L⁻¹ for ENR (Wang et al., 2019).

The volume of wastewater capable of being treated per tonne of biochar (V_e , m³) was calculated, according to Equation 3.

$$V_e = \frac{q_e \times m_{BC}}{C_i} \quad (3)$$

Where q_e is the adsorption capacity of the biochar (mg g⁻¹), m_{BC} is the applied mass of biochar (1 tonne or 10⁶ g), and C_i is the influent concentration (mg L⁻¹).

The mass of phosphorus recovered was converted to its agronomic equivalent as P₂O₅ using a conversion factor of 2.29, and further compared with the nutrient content of commercial Single Superphosphate (SSP), considering 18% of P₂O₅.

6.2.8. Analytical methods

Nutrient concentrations (ammonium and phosphate ions) were measured colorimetrically. The N-NH₄⁺ content was determined by the method of Hood-Nowotny et al. (2010) and the ortho-P content was determined by the ascorbic acid method (APHA et al., 2022).

The pH of the point of zero charge (pH_{PCZ}) was determined by preparing 30 mL of 0.01 M NaCl solution in several flasks with pH adjusted to the desired values (2 to 12). An amount of 0.15 g of 800 MgCl₂ 3:1 biochar was added to each flask. The mixture was stirred for 24 h and the final pH was recorded. Specific surface area was determined using a Nova 600 Series equipment (Anton Paar). The analysis was performed based on N₂ adsorption-desorption isotherms, using the Brunauer, Emmett and Teller (BET) (Brunauer et al., 1938) method to determine the surface area, and the Barrett-Joyner-Halenda (BJH) method to evaluate the pore size distribution (Barrett et al., 1951).

The selected biochar and swine manure were analyzed for total phosphorus was determined by the colorimetric method after nitroperchloric digestion and total nitrogen was measured by the Semi-Micro-Kjeldahl method, both following the procedures described by APHA et al. (2022). Potassium (K) and magnesium (Mg) analyses were performed by atomic

absorption after desorption for 24 hours and 190 rpm using Mehlich-1 (MI) for K and 1 M KCl for Mg (Guimarães et al., 1999).

6.3. Results and discussion

6.3.1. Preparation of biochar

The yield results demonstrated the significant influence of the type of activating agent, the pyrolysis temperature and the proportion used, as shown in Figure 6-1.

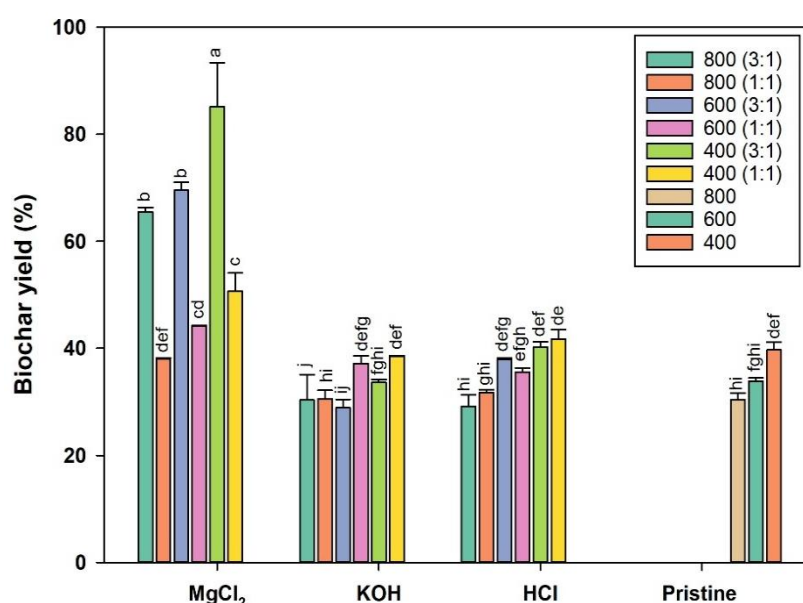


Figure 6-1 Biochar yield (%) for biochars derived from swine manure with different preparation conditions.

The treatments indicated by the same letter do not differ at the 5% significance level by the Tukey test. Pristine is the unmodified biochar

In general, yield decreases with increasing temperature. Low-temperature pyrolysis favors the formation of a greater amount of biochar, as primary reactions predominate and the decomposition of larger compounds does is reduced (Silva et al., 2022). Furthermore, the use of MgCl₂ increased the biochar yield, attributed to the activating agent's ability to reduce depolymerization reactions (Silva et al., 2022). On the other hand, biochars activated with KOH and HCl showed lower yields. These results can be attributed to the greater efficiency of these agents in removing volatile matter and the formation of porosity (Sajjadi et al., 2019), leading to a significant reduction in yield.

6.3.2. Influence of production conditions on biochar adsorption capacity

The optimization of the biochar preparation conditions was done based on the adsorption capacity of each biochar in relation to phosphate and ammonium ion (Figure 6-2).

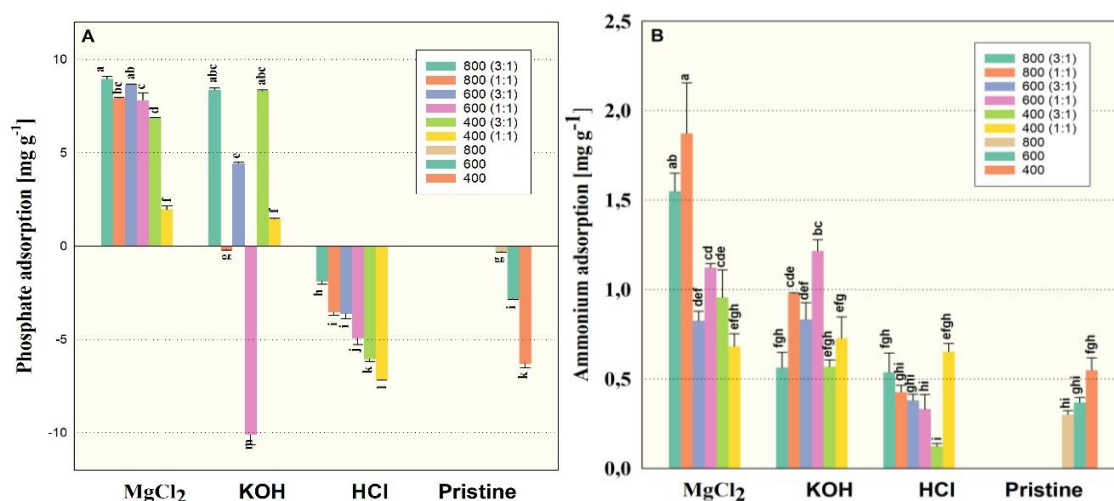


Figure 6-2 Phosphate (A) and Ammonia (B) adsorption for biochars derived from swine manure with different preparation conditions.

The treatments indicated by the same letter do not differ at the 5% significance level by the Tukey test.

Phosphorus and ammonium adsorption were significantly influenced by the biochar preparation conditions. The highest phosphorus adsorption efficiency (99%) was achieved by the biochar produced at 800 °C and modified with MgCl₂ at a 3:1 ratio (Figure 6-2, a). In contrast, both raw and HCl-modified biochars exhibited phosphorus release, resulting in negative adsorption values. For ammonium, the biochar produced at 800 °C and modified with MgCl₂ at a 1:1 ratio showed the highest adsorption efficiency (55%), but it did not differ statistically from the 800 °C biochar modified at a 3:1 ratio (Figure 6-2, b). Treatments without chemical modification or those modified with HCl consistently demonstrated lower adsorption capacities, regardless of the carbonization temperature or activation ratio applied.

Indeed, MgCl₂ deposited on the biomass during activation decomposes into MgO at high pyrolysis temperatures, thereby increasing the number of adsorption sites and enhancing mass transfer (Sajjadi et al., 2019). Additionally, biochar produced at elevated temperatures typically exhibits greater surface area, enhanced microporosity, increased hydrophobicity, and improved anion exchange capacity (Ji et al., 2023), contributing to phosphorus adsorption. In this sense, given the higher efficiency of BC 800 °C MgCl₂ 3:1 biochar for adsorption of phosphorus and ammonia, this biochar was selected for the next steps.

6.3.2. Biochar characterization

The biochar produced at 800 °C with MgCl_2 (3:1) exhibited a pH_{PZC} of 11.2 (Figure 6-3).

Overall, the evaluated models showed good agreement with the experimental data, with RRMSE values below 10% and coefficients of determination (R^2) above 0.96 for most treatments. The only exceptions were A12D1 and A12D5 fitted with the first-order model, which exhibited RRMSE values exceeding 10%. Based on the AIC, for which lower values indicate superior predictive performance (Zhan et al., 2023), the Cone model provided the best fit for most MA treatments. In contrast, the modified Gompertz model exhibited the best performance for the control. The cumulative methane production curves together with the selected models for each treatment are presented in Fig. 2.

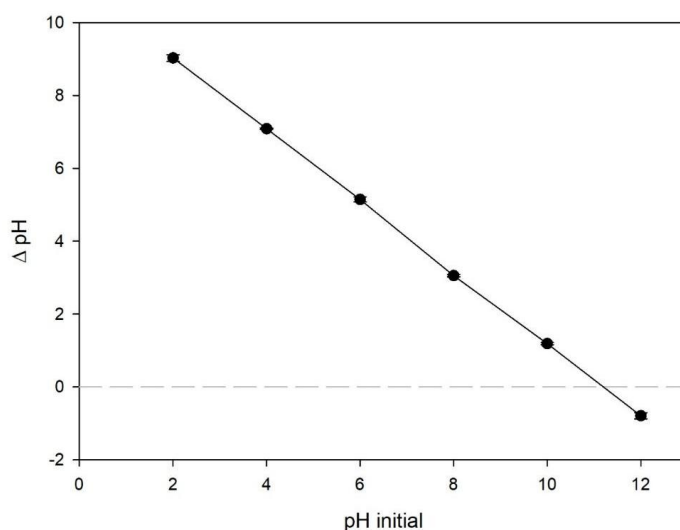


Figure 6-3 pH of the point of zero charge of 800 MgCl_2 (3:1) biochar

The point of zero charge (pH_{PZC}) is the pH at which the adsorbent surface has no net charge (Park & Regalbuto, 1995). In solutions with a pH higher than pH_{PZC} , the surface charge is negative and the adsorption of cations is favored, while at pHs lower than pH_{PZC} , the surface charge is positive and the adsorption of anions is favored (Sajjadi et al., 2019).

The pore structure analysis results are presented in Table 6-1. The biochar prepared at 800 °C with MgCl_2 (3:1) activation showed 25% increase in surface area compared to the SM.

The average pore diameter was 3.8 nm for both samples, a value that falls within the mesopore range, with higher presence of microporous area in biochar in comparison to SM.

Table 6-1: Porosity and surface area properties of SM and BC 800/MgCl₂ 3:1.

Parameter	Swine Manure	BC 800 °C MgCl ₂
BET surface area (m ² g ⁻¹)	1.83	46.85
Microporous area (m ² g ⁻¹)	0.20	24.41
Average pore diameter (nm)	3.85	3.88

The chemical characterization data for biochar and swine manure are presented in Table 6-2. Phosphorus content in the unmodified (33.34 mg g⁻¹) and MgCl₂-modified biochars (86.96 mg g⁻¹) increased relative to that in the SM (28.96 mg g⁻¹), attributed to its increasing concentration during pyrolysis, as it is not a volatile element (Rathnayake et al., 2023). Furthermore, the phosphorus content measured in the saturated biochar reflected both the inherent phosphorus originally present in the material and the phosphorus subsequently adsorbed during the saturation step. Nitrogen decreased in biochars by 79%-87%, due to its rapid decomposition into ammonia and subsequent volatilization during pyrolysis (Rathnayake et al., 2023). Similarly, potassium decreased in biochars more than 95%, likely due to its volatilization at high temperatures during pyrolysis. (Rathnayake et al., 2023). The magnesium was 20-10 times more available in Mg-modified biochar than SM. Magnesium (Mg) is an essential plant nutrient that plays a key role in the activation of enzymes involved in respiration, photosynthesis, and the synthesis of DNA and RNA (Taiz, 2017).

Table 6-2: Chemical characterization of swine manure (SM), biochar (BC 800 MgCl₂ 3:1), and saturated biochar (S BC 800 MgCl₂ 3:1).

Parameter	SM	BC-MgCl ₂ 3:1	S BC- MgCl ₂ 3:1
Total P (mg g ⁻¹)	28.96 ± 1.30	33.34 ± 4.79	86.96±11.72
Total N (mg kg ⁻¹)	49.77 ± 2.14	10.23 ± 0.80	6.25±0.31
Available K (mg g ⁻¹)	1.89 ± 0.16	0.069 ± 0.03	0.0555±0.037
Available Mg (mg kg ⁻¹)	257.83 ± 8.54	5151.09 ± 648.57	2576.87±131.69

Values represent mean ± standard deviation

6.3.3. Adsorption tests

Adsorption and desorption data are presented in the Figure 6-4. The adsorption capacities were 60.1 mg g^{-1} (99% efficiency) for phosphate and 28.9 mg g^{-1} (53% efficiency) for ammonium. The final pH of the working solution of ammonium phosphate was 10.53, which indicates that the surface of the biochar would be positively charged. Phosphorus has ionic forms according to pH. $\text{H}_2\text{PO}_4^{2-}$ is predominant at pH between 7 and 12 (Ji et al., 2023). In this sense, alkaline solution would be beneficial for the adsorption of phosphorus by electrostatic attraction.

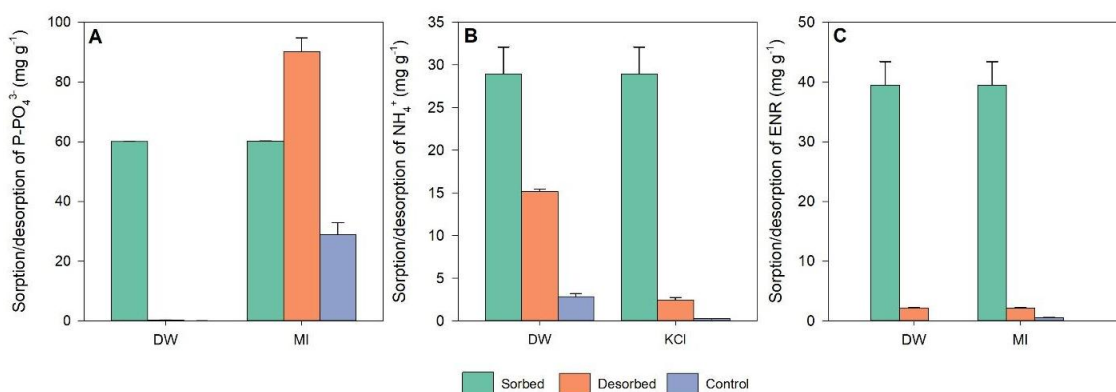


Figure 6-4 Sorption and desorption of (A) phosphorus (P-PO_4^{3-}), (B) ammonium (NH_4^+) and (C) enrofloxacin (ENR) by swine-manure biochar.

Extractants: DW = deionized water; MI = Mehlich-1 solution ($0.025 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 0.05 \text{ mol L}^{-1} \text{ HCl}$); KCl = KCl 2 mol L^{-1} . Bars represent mean $\pm$ standard deviation. Control refers to unsaturated biochar tested under the same conditions.

For nitrogen, the functional groups on the biochar surface are the main removal pathway (Ji et al., 2023). Furthermore, struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) precipitation can occur in the presence of Mg, NH_4^+ and PO_4^{3-} at pH above 7.5 (Le Corre et al., 2009).

The adsorption capacity of the biochar was then tested for enrofloxacin, reaching 39.5 mg g^{-1} (60% efficiency). This result is comparable to that reported by Chowdhury et al. (2019), who found a maximum adsorption of 44 mg g^{-1} (60% efficiency). In this case, the final pH on ENR solution after adsorption test were higher than 9.6. Thus, the ENR molecule was deprotonated (ENR^-) during part of the adsorption experiment ($\text{pK}_{a1} = 5.88$ and $\text{pK}_{a2} = 7.74$) (Jiménez-Lozano et al., 2002). Despite electrostatic attraction contribution under these conditions, other mechanisms such as π - π stacking, hydrophobic interactions, and hydrogen bonding remain active and contribute significantly to ENR adsorption (Kar et al., 2024).

In the desorption study, phosphorus desorption in water (DW) was negligible, whereas Mehlich-1 (MI) extracted 90.1 mg g^{-1} . This value corresponds to 150% of the phosphorus previously adsorbed (60.1 mg g^{-1}). This recovery rate is attributed to the combined release of the adsorbed phosphate and the indigenous phosphorus from the biochar matrix, as the control experiment with unsaturated biochar confirmed a contribution of 28.9 mg g^{-1} . The high extraction by MI suggests that phosphorus was primarily retained through the formation of mineral precipitates, such as magnesium phosphates, rather than simple electrostatic interactions. The acidic nature of the MI extractant promoted the dissolution of these structural mineral phases, which explains the recovery of both adsorbed and matrix-bound phosphorus.

Regarding ammonium (NH_4^+), the greater release in deionized water (15.18 mg g^{-1} , 43%) compared to KCl (2.44 mg g^{-1} , 8.3%) suggests that a significant fraction was held by relatively weaker interactions. The lower recovery in the salt solution indicates that a fraction of the nitrogen was likely incorporated into more stable chemical structures or complex precipitates (e.g., struvite) during the process, which were not readily displaced by K^+ ions through ion-exchange mechanisms. For ENR, desorption in both water (2.17 mg g^{-1} , 6.5%) and MI (2.13 mg g^{-1} , 6.4%) was low, while the release from the control biochar was negligible (0.5 mg g^{-1} , 1.7%), indicating that the antibiotic was strongly immobilized and remained stable within the biochar matrix, with minimal interference from indigenous components.

6.3.3. Competitive adsorption in multicomponent systems

To evaluate competitive interactions among nutrients and ENR in complex matrices, multicomponent adsorption assays were conducted. The results indicated that in the multicomponent batch (Figure 6-5), phosphate (100%, $q_e = 18 \text{ mg g}^{-1}$) and ammonium (93%, $q_e = 6 \text{ mg g}^{-1}$) were removed with high efficiencies. Phosphate exhibited the highest removal, consistent with the electrostatic attraction at final pH of the prepared multicomponent solution ($10 < \text{pH}_{\text{PZC}}$) and complexation Mg–phosphate phases at alkaline solution.

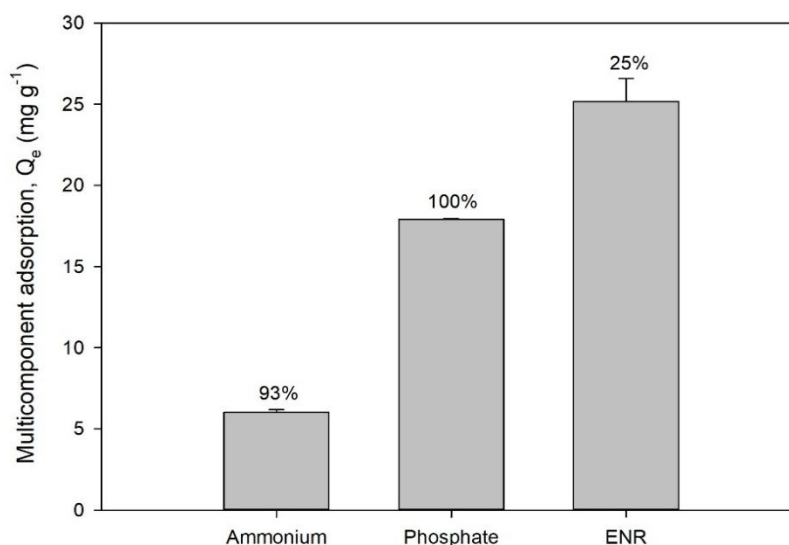


Figure 6-5: Multicomponent adsorption capacities (q_e) of ammonium, phosphate, and enrofloxacin by Mg-modified biochar.

Bars represent mean q_e (mg g⁻¹) values and the percentages above the bars indicate removal efficiency. Error bars show standard deviation.

Interestingly, ammonium removal was significantly higher in the multicomponent system than in the single-analyte and optimization assays. The presence of enrofloxacin (ENR) and phosphate as anionic species at the operational pH facilitates the formation of ternary complexes, even though electrostatic repulsion typically hinders the direct adsorption of cationic ammonium (NH_4^+) onto a positively charged surface. These organic and inorganic ligands may act as electrostatic bridges, neutralizing surface repulsion and providing secondary binding sites for NH_4^+ , thereby promoting a synergistic 'ion-bridging' mechanism (Ötöker & Akmechmet-Balcioğlu, 2005).

In turn, ENR removal was limited in the multicomponent system (25% efficiency, $q_e = 25 \text{ mg g}^{-1}$), compared to the single-solute tests (60% efficiency). Similar competitive behavior has been reported for fluoroquinolones in the presence of phosphate (Zhu et al., 2020). Under alkaline conditions, phosphate forms complexes on the surface of biochar, occupying a portion of the active sites (Zhu et al., 2020). Furthermore, the biochar surface becomes less positively charged with increasing concentration of adsorbed phosphate (Zhu et al., 2020). Therefore, the electrostatic repulsion between the negatively charged phosphate on the biochar surface and the anionic ENR molecule may be a mechanism inhibiting ENR adsorption in the presence of phosphate. Thus, the Mg-modified biochar performed well in absorbing nutrients, especially phosphorus. Furthermore, the saturated material is also capable of releasing nutrients, while the antibiotic exhibited more stable adsorption, with minimal desorption.

6.3.4. Use of swine manure in the treatment of swine wastewater

The application of swine manure MgCl_2 -modified (3:1) biochar may contribute to circular economy within agricultural activity, while also increasing its economic attractiveness for farmers due to agricultural reuse of the recovered nutrients. To assess the scalability of this approach, the volume of wastewater capable of being treated per ton of biochar (V_e) was determined using Equation 3 (Table 6-3 and Figure 6-6).

Table 6-3: Mass balance parameters and estimated wastewater treatment capacity per ton of Mg-modified biochar.

Compound	C (mg L ⁻¹)	q_e (mg g ⁻¹)	V_e (m ³ ton ⁻¹)
N-NH ₄ ⁺	962	28.9	30
P-PO ₄ ³⁻	189	60	317.5
Enrofloxacin	0.5	25	50,000

The estimation of treatable volume (V_e) was based on the adsorption capacities (q_e) values obtained from single-solute saturation assays for P and N. These experiments also were designed to reach the saturation of biochar; thus, these values reflect the maximum recovery potential of the biochar when exposed to high nutrient loads typical of raw swine wastewater. Conversely, for ENR, the multicomponent capacity (q_e) was utilized to ensure a conservative and safer estimate, accounting for the observed competition with phosphate.



Figure 6-6: Biochar-Assisted Treatment of Swine Wastewater

Ammoniacal nitrogen presented the lowest treatable volume (30 m³ ton⁻¹), thus acting as the limiting factor for the biochar's treatment capacity of the swine digestate. However, the total

nitrogen content measured in the saturated biochar (6.25 mg kg^{-1} , Table 6-2) was lower than the nitrogen removal during the adsorption assays ($q_e=29 \text{ mg g}^{-1}$), indicating that the nitrogen captured by the biochar was subsequently lost through volatilization during the drying process. In this regard, a nitrogen pretreatment step is recommended before the adsorption process. Technologies such as air stripping, nitrification-denitrification, anammox processes, or membrane separation could be integrated into the treatment train. However, the selection of the most suitable method must be based on a comprehensive assessment of several factors, including the farm's scale of operation, technical feasibility, and economic viability (Qin et al., 2023).

By reducing the initial nitrogen load, the treatable volume would be extended to the phosphorus saturation limit ($317 \text{ m}^3 \text{ ton}^{-1}$), representing a 10-fold increase in material efficiency. This process would recover 86 kg of P (or 200 kg P_2O_5), as measured in the chemical characterization (Table 6-2). This phosphorus load corresponds to approximately 1.1 tons of commercial Single Superphosphate (SSP) fertilizer, representing a significant economic offset for the producer. In turn, the highest treatable volume was for ENR ($50,000 \text{ m}^3$), due to its low concentration in digestate. In that case, the material will be harvested for fertilizer use long before its antibiotic removal capacity is exhausted. Therefore, the final product acts as a Phosphorus-rich organomineral fertilizer (8.7% P), which also ensures environmental safety by immobilizing pharmaceutical contaminants like enrofloxacin. However, testing in dynamic systems and with real or more complex effluents is still needed to understand the interactions between solutes.

6.4. Conclusions

This study demonstrated that MgCl_2 -modified swine-manure biochar (800°C , 3:1) exhibited high adsorption capacity for both phosphorus (60 mg g^{-1}), ammonium (29 mg g^{-1}) and enrofloxacin (39.5 mg g^{-1}). Furthermore, high nutrient desorption was observed - 150% of phosphorus and 40% of nitrogen - and low release of enrofloxacin (only 6%). Multicomponent test showed high nutrient removal attributed to struvite formation and secondary binding, whereas ENR uptake decreased due to competition for metal-rich sites and alkaline speciation. A mass-balance assessment indicates that biochar can recover meaningful phosphorus amounts (86 kg P per tonne of biochar) and treat 317 m^3 of digestate per tonne of biochar. This result indicates the potential use of biochar as a slow-release fertilizer, without the antibiotic being

available. Thus, the optimized swine-manure biochar represents a sustainable and effective strategy for nutrient recycling and environmental protection in integrated agricultural systems.

6.5. References

- APHA, American Public Health, American Water Works, & Federation, W. E. (2022). Standard Methods for the Examination of Water and Wastewater. In *Standard Methods for the Examination of Water and Wastewater* (24th ed.). American Public Health Association; American Water Works Association; Water Environment Federation. <https://doi.org/10.2105/SMWW.2882.002>
- Banik, C., Bakshi, S., Andersen, D. S., Laird, D. A., Smith, R. G., & Brown, R. C. (2023). The role of biochar and zeolite in enhancing nitrogen and phosphorus recovery: A sustainable manure management technology. *Chemical Engineering Journal*, 456(December 2022), 141003. <https://doi.org/10.1016/j.cej.2022.141003>
- Barrett, E. P., Joyner, L. G., & Halenda, P. P. (1951). The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *Journal of the American Chemical Society*, 73(1), 373–380. <https://doi.org/10.1021/ja01145a126>
- Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*, 60(2), 309–319. <https://doi.org/10.1021/ja01269a023>
- Cheng, D. L., Ngo, H. H., Guo, W. S., Liu, Y. W., Zhou, J. L., Chang, S. W., Nguyen, D. D., Bui, X. T., & Zhang, X. B. (2018). Bioprocessing for elimination antibiotics and hormones from swine wastewater. *Science of the Total Environment*, 621, 1664–1682. <https://doi.org/10.1016/j.scitotenv.2017.10.059>
- Chowdhury, S., Sikder, J., Mandal, T., & Halder, G. (2019). Comprehensive analysis on sorptive uptake of enrofloxacin by activated carbon derived from industrial paper sludge. *Science of the Total Environment*, 665, 438–452. <https://doi.org/10.1016/j.scitotenv.2019.02.081>
- Guimarães, P. T. G., Alvarez, V. H., & Ribeiro, A. C. (1999). 5 Aproximacao. *Recomendações Para o Uso de Corretivos e Fertilizantes Em Minas Gerais - 5ª Aproximação*, 13–20. <https://www.google.com.br/webhp?sourceid=chrome-instant&ion=1&espv=2&ie=UTF-8#q=recomendações para o uso de corretivos e fertilizantes em minas gerais>
- Hood-Nowotny, R., Umana, N. H.-N., Inselbacher, E., Oswald- Lachouani, P., & Wanek, W.

- (2010). Alternative Methods for Measuring Inorganic, Organic, and Total Dissolved Nitrogen in Soil. *Soil Science Society of America Journal*, 74(3), 1018–1027. <https://doi.org/10.2136/sssaj2009.0389>
- Ji, S., Zhang, F., Yao, P., Li, C., Faheem, M., Feng, Q., Chen, M., & Wang, B. (2023). Optimization of pig manure-derived biochar for ammonium and phosphate simultaneous recovery from livestock wastewater. *Environmental Science and Pollution Research*, 30(34), 82532–82546. <https://doi.org/10.1007/s11356-023-28092-w>
- Jiménez-Lozano, E., Marqués, I., Barrón, D., Beltrán, J. L., & Barbosa, J. (2002). Determination of pKa values of quinolones from mobility and spectroscopic data obtained by capillary electrophoresis and a diode array detector. *Analytica Chimica Acta*, 464(1), 37–45. [https://doi.org/10.1016/S0003-2670\(02\)00435-X](https://doi.org/10.1016/S0003-2670(02)00435-X)
- Kar, S., Mandal, T., & Halder, G. (2024). Sorptive and microbial remediation of fluoroquinolone enrofloxacin laden water: A holistic review on approaches, contrivances, hindrances and perspectives. *Process Safety and Environmental Protection*, 188, 877–904. <https://doi.org/10.1016/J.PSEP.2024.05.099>
- Kunz, A., Steinmetz, R. L. R., & Amaral, A. C. do. (2019). Fundamentos da digestão anaeróbia, purificação do biogás, uso e tratamento do digestato. In *Journal of Chemical Information and Modeling* (Vol. 53, Issue 9). Sbera: Embrapa Suínos e Aves. <https://doi.org/10.21452/978-85-93823-01-5.2019.01>
- Le Corre, K. S., Valsami-Jones, E., Hobbs, P., & Parsons, S. A. (2009). Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review. *Critical Reviews in Environmental Science and Technology*, 39(6), 433–477. <https://doi.org/10.1080/10643380701640573>
- Li, R., Wang, J. J., Zhou, B., Awasthi, M. K., Ali, A., Zhang, Z., Lahori, A. H., & Mahar, A. (2016). Recovery of phosphate from aqueous solution by magnesium oxide decorated magnetic biochar and its potential as phosphate-based fertilizer substitute. *Bioresource Technology*, 215, 209–214. <https://doi.org/10.1016/J.BIORTECH.2016.02.125>
- Nagarajan, D., Kusmayadi, A., Yen, H. W., Dong, C. Di, Lee, D. J., & Chang, J. S. (2019). Current advances in biological swine wastewater treatment using microalgae-based processes. *Bioresource Technology*, 289(June), 121718. <https://doi.org/10.1016/j.biortech.2019.121718>
- Nardis, B. O., Franca, J. R., Carneiro, J. S. da S., Soares, J. R., Guilherme, L. R. G., Silva, C. A., & Melo, L. C. A. (2022). Production of engineered-biochar under different pyrolysis conditions for phosphorus removal from aqueous solution. *Science of the Total*

- Environment*, 816. <https://doi.org/10.1016/j.scitotenv.2021.151559>
- Ötör, H. M., & Akmeahmet-Balcioğlu, I. (2005). Adsorption and degradation of enrofloxacin, a veterinary antibiotic on natural zeolite. *Journal of Hazardous Materials*, 122(3), 251–258. <https://doi.org/10.1016/j.jhazmat.2005.03.005>
- Park, J., & Regalbuto, J. R. (1995). A Simple, Accurate Determination of Oxide PZC and the Strong Buffering Effect of Oxide Surfaces at Incipient Wetness. *Journal of Colloid and Interface Science*, 175(1), 239–252. <https://doi.org/10.1006/jcis.1995.1452>
- Qin, Y., Wang, K., Xia, Q., Yu, S., Zhang, M., An, Y., Zhao, X., & Zhou, Z. (2023). Up-concentration of nitrogen from domestic wastewater: A sustainable strategy from removal to recovery. *Chemical Engineering Journal*, 451(P3), 138789. <https://doi.org/10.1016/j.cej.2022.138789>
- Rathnayake, D., Schmidt, H., Leifeld, J., Mayer, J., Epper, C. A., Bucheli, T. D., & Hagemann, N. (2023). Biochar from animal manure: A critical assessment on technical feasibility, economic viability, and ecological impact. *GCB Bioenergy*, 15(9), 1078–1104. <https://doi.org/10.1111/gcbb.13082>
- Sajjadi, B., Zubatiuk, T., Leszczynska, D., Leszczynski, J., & Chen, W. Y. (2019). Chemical activation of biochar for energy and environmental applications: A comprehensive review. *Reviews in Chemical Engineering*, 35(7), 777–815. <https://doi.org/10.1515/revce-2018-0003>
- Silva, L. D., Lira, T. S., Xavier, T. P., Barrozo, M. A. S., Dantas, S. C., Silvério, B. C., & Santos, K. G. (2022). Effect of Temperature and MgCl₂ Concentration on the Catalytic Pyrolysis of Malt Waste Using Response Surface Methodology. *ChemistrySelect*, 7(21). <https://doi.org/10.1002/slct.202200663>
- Taiz, L. (2017). *Fisiologia e desenvolvimento vegetal* (6th ed.). Artmed. <https://doi.org/10.4324/9780429492556-8>
- Wang, R., Feng, F., Chai, Y., Meng, X., Sui, Q., Chen, M., Wei, Y., & Qi, K. (2019). Screening and quantitation of residual antibiotics in two different swine wastewater treatment systems during warm and cold seasons. *Science of the Total Environment*, 660, 1542–1554. <https://doi.org/10.1016/j.scitotenv.2019.01.127>
- Zhu, Y., Yang, Q., Lu, T., Qi, W., Zhang, H., Wang, M., Qi, Z., & Chen, W. (2020). Effect of phosphate on the adsorption of antibiotics onto iron oxide minerals: Comparison between tetracycline and ciprofloxacin. *Ecotoxicology and Environmental Safety*, 205, 111345. <https://doi.org/10.1016/J.ECOENV.2020.111345>

7. CHAPTER 3: AGRONOMIC PERFORMANCE OF SWINE MANURE BIOCHAR AS A SLOW-RELEASE FERTILIZER FOR HYBRID BRACHIARIA

Abstract

Nutrient losses from swine manure management represent an important environmental challenge, driving the development of technologies to nutrient recovery. This study evaluated the potential of a swine manure biochar as a slow-release fertilizer for hybrid *Brachiaria* cv. Sabiá over subsequent cultivation cycles. A greenhouse experiment was conducted in a randomized complete block design with five fertilization treatments: saturated biochar (BCS), unsaturated biochar (BC), swine manure (SM), mineral fertilization (C), and unfertilized soil (S). Phosphorus saturation increased the biochar P concentration by 2.6-fold, reducing the amount of biochar required to supply the same phosphorus dose. Overall, morphogenic analysis showed no differences between the fertilized treatments for the parameters analyzed. The biochar showed an intermediate aboveground biomass production; however, they produced a residual root biomass and a total biomass similar to the treatment C. BCS water productivity was comparable to the conventional mineral treatment in successive cycles. Furthermore, biochar treatments maintained high soil available P (15.4 mg dm^{-3}) and enhanced soil organic matter while regulating the uptake of potentially toxic elements like copper. These findings demonstrate that phosphorus-enriched swine manure biochar is a promising strategy for nutrient recovery and agricultural reuse, contributing to phosphorus recycling and sustainable tropical pasture production.

Keywords: Circular economy; hybrid *Brachiaria* cv. Sabiá; phosphorus availability;

7.1. Introduction

Fertilizer production uses energy and raw materials of fossil origin. Ammonia production by Haber-Bosch consumes more than 1% of the world's total energy and is responsible for 1.2% of anthropogenic CO₂ emissions (Spiller et al., 2022). Phosphorus (P) is an essential, non-substitutable nutrient for living organisms. However, natural P reserves, phosphate rock, are finite and are facing rapid depletion due to the intensive use of phosphate fertilizers in agricultural production (Walsh; Schenk; Schmidt, 2023). In Brazil, approximately 88% of fertilizers are imported, increasing the vulnerability of agricultural systems to external market fluctuations (ANDA, 2024). Therefore, there is an urgent need to develop technologies that allow for nutrient recovery and their safe reuse (Ahmed; Hayes, 2025).

Brazil stands out as the world's fourth-largest pork producer, with 5.6 million tonnes produced in 2025 (Embrapa, 2026), generating an average of approximately 5.8 kg of waste (manure + urine) animal⁻¹ day⁻¹ (Oliveira et al., 2016). Swine waste (SW) is characterized by high pollutant loads, typically containing 1000–30,000 mg L⁻¹ of COD, 400–2000 mg L⁻¹ of ammonium nitrogen (NH₄⁺-N), 600–2400 mg L⁻¹ of total nitrogen (TN), 50–300 mg L⁻¹ of total phosphorus (TP) (Zhou et al., 2024). However, inadequate management of agro-industrial residues and wastewater contributes to nutrient losses, leading to eutrophication of water bodies and subsequent ecological imbalances (Shakoor; Ye; Chen, 2021).

The conversion of animal manure into biochar through thermochemical processes has emerged as a sustainable strategy for waste management, reducing environmental risks by lowering metal bioavailability, eliminating pathogens, degrading organic contaminants, and minimizing nutrient leaching (Rathnayake et al., 2023). Furthermore, the application of biochar to the soil improve several properties, including increased water retention, enhanced carbon sequestration, reduced greenhouse gas emissions, and pollutant immobilization (Oliveira et al., 2017). Besides, the use of biochars as adsorbents has emerged as a promising strategy for capturing nutrients from liquid matrices and reintegrating them into the circular economy of plant nutrition (Nascimento et al., 2026; Shakoor; Ye; Chen, 2021).

In Brazilian, livestock production is predominantly based on pasture systems, which occupy approximately 21% of Brazil's total territory. However, nearly 60% of these pastures show some degree of degradation, largely due to inadequate soil fertility management and nutrient depletion (Bolfe et al., 2024; IBGE, 2025). *Brachiaria* species are among the most

widely cultivated tropical forage grasses and play a central role in Brazilian livestock production (Mutimura; Ghimire, 2021). However, forage productivity is frequently limited by phosphorus availability (Frontado et al., 2025).

In this scenario, nutrient-loaded biochars represent a promising alternative because they can simultaneously improve soil physical and chemical properties while supplying nutrients through gradual release (Banik et al., 2023; Nardis et al., 2021; Shakoor; Ye; Chen, 2021), contributing to pasture restoration and reducing dependence on imported mineral fertilizers. For example, phosphate-enriched poultry litter biochar increased *Urochloa brizantha* shoot biomass by approximately 11% compared with triple superphosphate while enhancing residual soil P availability (Lustosa Filho et al., 2020). However, information remains limited regarding the agronomic performance of nutrient-recovered Mg-modified swine manure biochar in perennial forage systems under successive cultivation cycles.

Therefore, we hypothesized that phosphate-saturated Mg-modified swine manure biochar could act as an effective slow-release fertilizer and soil amendment, sustaining forage production while improving soil fertility. Accordingly, this study aimed to evaluate the agronomic performance of phosphate-saturated Mg-modified swine manure biochar in comparison with mineral fertilizer and swine manure under successive cultivation cycles of hybrid *Brachiaria* cv. Sabiá. Specifically, the objectives were to: (i) evaluate forage growth dynamics, biomass production, and water productivity; (ii) assess nutrient uptake and plant nutritional status; and (iii) determine the effects of the different fertilization strategies on soil chemical properties.

7.2. Materials and methods

7.2.1. Biochar production and characterization

The biochar used in this study was prepared from swine manure modified with MgCl_2 (3 mol L^{-1}) at 3:1 (mL of solution: g of dry manure) and pyrolyzed at 800°C for 1 h. The selection of this material was based on prior adsorption assays (Nascimento et al., 2026) that compared different modifications and pyrolysis conditions. The MgCl_2 -modified biochar produced at 800°C stood out for exhibiting the highest adsorption capacities for phosphate (67.56 mg g^{-1}) and ammonium (17.48 mg g^{-1}). Furthermore, desorption assays demonstrated the gradual release of the adsorbed nutrients, reinforcing the potential of this material as a slow-release fertilizer, supporting its potential use as a nutrient-loaded biochar for agronomic

applications. Subsequently, a portion of the biochar was saturated using an ammonium phosphate solution (1.2 g L^{-1}) at a solid-to-liquid ratio of 4 g L^{-1} . After 24 h of agitation (190 rpm), the nutrient-loaded biochar was recovered, oven-dried (24 h, 65°C) and stored at 4°C until use in the biofertilizer experiment.

For characterization, the selected biochar and swine manure were analyzed for total P and total N. Total phosphorus was determined by the colorimetric method after nitroperchloric digestion and total nitrogen was measured by the Semi-Micro-Kjeldahl method, both following the APHA et al. (2022). Available P, K, and Mg were determined after extraction for 24 h at 190 rpm, using a solid-to-volume ratio of 1:250 (g mL^{-1}). P was quantified colorimetrically (APHA et al., 2022) after deionized water (DW) and Mehlich-1 (M1) solution ($0.025 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 0.05 \text{ mol L}^{-1} \text{ HCl}$) extraction (Guimarães; Alvarez; Ribeiro, 1999). Potassium (K) and magnesium (Mg) were measured by atomic absorption spectrometry after M1 and 1 mol L^{-1} KCl extraction, respectively (Guimarães; Alvarez; Ribeiro, 1999).

The point of zero charge (pH_{PZC}) was determined using the salt addition method. Briefly, 30 mL of 0.01 M NaCl solution with initial pH values ranging from 2 to 12 were prepared, and 0.15 g of biochar was added. After 24 h of agitation, the final pH was measured. The pH_{PZC} was obtained from the intersection between the $\text{pH}_i = \text{pH}_f$ (Akkari et al., 2023).

7.2.2. Biofertilizer experimental design

The performance of biochar as a slow-release fertilizer was evaluated using hybrid *Brachiaria* cv. Sabiá, a forage grass extensively cultivated in pasture systems across tropical environments. The study was performed in a greenhouse facility ($20^\circ45'14'' \text{ S}$, $42^\circ52'53'' \text{ W}$; 650 m altitude), over the period from September 2025 to January 2026. The cultivation was evaluated over four successive 31-day cycles, to assess the residual fertilization effect of the nutrient-loaded biochar. Specifically, the experimental period comprised standardization (Uni) (from Sep 3, 25), C1 (from Oct 8, 25), C2 (from Nov 11, 25), C3 (from Dec 12, 25). The experiment was carried out in a loam-textured soil, with the following characteristics: 4.23 pH (H_2O), 4.9 mg P dm^{-3} , 22 mg K dm^{-3} , $0.40 \text{ cmol}_c \text{ Ca}^{2+} \text{ dm}^{-3}$ and $0.14 \text{ cmol}_c \text{ Mg}^{2+} \text{ dm}^{-3}$, $0.89 \text{ cmol}_c \text{ Al}^{3+} \text{ dm}^{-3}$, $3.6 \text{ cmol}_c \text{ dm}^{-3}$ (H + Al), 0.52 dag kg^{-1} organic matter content, $4.9 \text{ mg P-rem L}^{-1}$. The liming calculation followed the base saturation method defined in the 5th approximation of Minas Gerais (Guimarães; Alvarez; Ribeiro, 1999).

The experiment was carried out in a randomized complete block design. Each treatment was arranged with five replicates, totalizing 25 pots (4 dm³) and five plants per pot after thinning. Based on prior biochar characterization, phosphate was selected as the reference chemical element (Kunz; Steinmetz; Amaral, 2019). Thus, fertilized treatments received the equivalent of 210 kg P₂O₅ ha⁻¹ throughout the experimental period., consisting of five phosphate fertilization strategies: (i) nutrient-saturated biochar (BCS); (ii) non-saturated biochar (BC); (iii) swine manure (SM); (iv) conventional mineral fertilization (C) applied as single superphosphate (15.3% P₂O₅), as positive control; and (v) unfertilized soil (S), as negative control. Urea (46% N) was used for N fertilization and KCl (58% K₂O) for K fertilization.

Regarding fertilization, nutrients were applied for soil fertility correction (100 kg N ha⁻¹; 120 kg P₂O₅ ha⁻¹ and 70 kg K₂O ha⁻¹) at crop establishment, based on soil analysis and crop requirements. Maintenance fertilization was carried out in each cycle (30 kg N ha⁻¹; 30 kg P₂O₅ ha⁻¹ and 30 kg K₂O ha⁻¹), in accordance with the methodology proposed by Kunz (2019) and fertilization requirements by (Guimarães; Alvarez; Ribeiro, 1999). Nitrogen and potassium were supplied in three doses throughout each cycle, whereas phosphorus was applied as a single dose at the beginning of each cycle. Irrigation was managed using a gravimetric approach, considering 90% of the soil field capacity and crop evapotranspiration (Nascimento et al., 2021).

7.2.3. Morphogenetic measurements

To evaluate the development of *Brachiaria* throughout the cycles, measurements of leaf blade and pseudostem length were performed on previously identified tillers (two per pot) using a graduated ruler. The length of fully expanded leaves was determined from the tip to the ligule. For expanding leaves, the ligule of the most recently fully expanded leaf was used as the reference point. In senescent leaves, length was defined as the distance between the ligule and the point up to which senescence had progressed. Pseudostem length was measured as the distance from the soil surface to the ligule of the youngest fully expanded leaf.

Based on the mean of growth data, the following morphogenetic variables were calculated according to Gomide and Gomide (2000):

- Number of live leaves (NLL): obtained before harvest by summing the number of expanding and expanded leaves per tiller.

- Leaf appearance rate (LAR, leaves tiller⁻¹ day⁻¹): calculated as the difference between the final and initial number of leaves per tiller, divided by the evaluation period.
- Stem elongation rate (SER, cm tiller⁻¹ day⁻¹): obtained from the difference between final and initial stem length, divided by the evaluation period and multiplied by the number.
- Leaf elongation rate (LER, cm tiller⁻¹ day⁻¹): calculated from the difference between final and initial leaf blade lengths, divided by the number of days of evaluation and adjusted by the number of tillers evaluated.
- Leaf senescence rate (LSR, cm tiller⁻¹ day⁻¹): determined by dividing the total length of senescent tissue at the end of the evaluation by the number of days in the period.

7.2.4. Biomass evaluation

Shoot fresh mass (SFM) and shoot dry mass (SDM) were determined at the end of each cultivation cycle. SFM comprised all aboveground plant biomass harvested above 15 cm height, including leaves and stems, and was measured using a precision digital scale, while the material below this height was left as residual biomass for the subsequent cycle. Subsequently, the harvested material was placed in paper bags, oven-dried at 65 °C for 72 h, and reweighed to obtain SDM.

At the end of the experiment, all remaining biomass was harvested. The plant material below 15 cm, namely residual biomass, was collected. The root system was isolated after washing over a 2 mm sieve. All fractions (residual and root biomass) were oven-dried at 65 °C for 72 h for dry mass determination.

7.2.5. Water consumption and water productivity

Water productivity (WP) was determined to evaluate the efficiency of biomass production in relation to the volume of water applied under the different fertilization strategies. WP (kg m⁻³) was calculated according to Equation (1) as the ratio between shoot dry mass and the total volume of water applied to each pot.

$$WP = \frac{SDM}{V_w} \quad (3)$$

Where: WP is water productivity (kg m^{-3}); SDM is shoot dry mass (kg pot^{-1}); and V_w is volume of water applied ($\text{m}^3 \text{pot}^{-1}$).

7.2.6. Soil chemical assessment

Soil samples were collected at the end of the experiment and analyzed for pH in H_2O (at a ratio of 1:2.5), available P, exchangeable K, Ca, Mg, and Al, potential acidity ($\text{H} + \text{Al}$), remaining phosphorus (P-rem). Soil organic matter was determined based on organic carbon content. All soil analysis was determined according Teixeira et al. (2017).

7.2.7. Plant chemical analysis

Plant nutrient analysis was performed to assess nutrient uptake and compare the nutritional performance of the different fertilization strategies. Thus, dried plant material was ground for the determination of nutrient concentrations (N, P, K, Mg, and Zn). Total phosphorus was determined by the colorimetric method after nitroperchloric digestion. Total nitrogen was measured by the Semi-Micro-Kjeldahl method (APHA et al., 2022). Potassium (K), magnesium (Mg) and Zinc analyses were performed by atomic absorption after nitroperchloric digestion.

7.2.8. Meteorological conditions

Variations in air temperature and relative humidity during hybrid *Brachiaria* cv. Sabiá grass cultivation are shown in Figure 7-1. Mean air temperature increased progressively from the standardization cycle (19.7°C) to C3 (23.3°C), with minimum values varying between 13.8°C to 18.6°C and maximum temperatures from 23.8°C to 28.3°C . Mean relative humidity ranged from 72.8% in the standardization cycle to 81.3% in C3, whereas minimum values ranged from 57.5% to 65.1% and maximum relative humidity ranged from 87.4% to 96.1% throughout the experimental period.

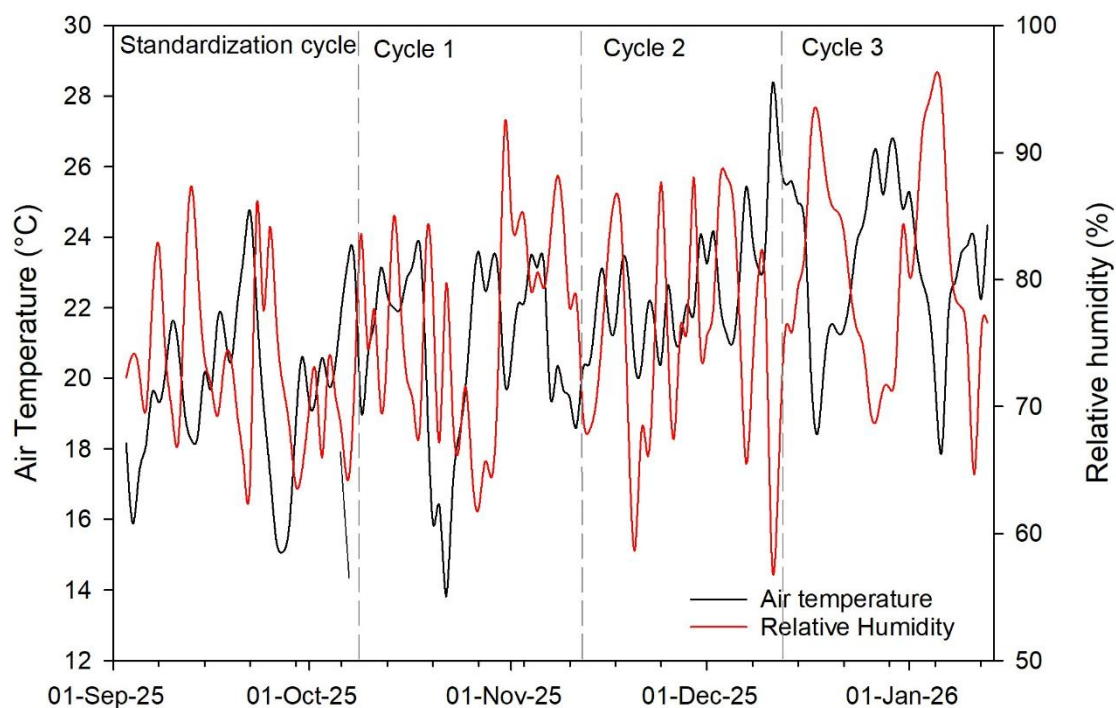


Figure 7-1. Daily mean air temperature and relative humidity throughout the experimental period.

7.2.9. Statistical Analysis

Normality of residuals were verified using the Shapiro–Wilk or Lilliefors tests and homogeneity of variances analysis using the O'Neill-Mathews test for single-factor analyses and by the Levene test for the factorial scheme, all at 5% significance level. Then, all data were subjected to analysis of variance (ANOVA), with 5% significance level in the F-test. When significant effects were detected, means were compared using Tukey's test at the 5% significance level. All statistical analyses were carried on R software, version 4.2.0.

7.3. Results and discussion

7.3.1. Biochar characterization

The chemical characterization of swine manure (SM), pristine biochar (BC 800 MgCl_2 3:1), and saturated biochar (S BC 800 MgCl_2 3:1) are presented in Table 7-1.

Table 7-1 Chemical characterization of swine manure (SM), biochar (BC 800 MgCl₂ 3:1), and saturated biochar (S BC 800 MgCl₂ 3:1).

Parameter	SM	BC 800 MgCl ₂ 3:1	S BC 800 MgCl ₂ 3:1
Total P (mg g ⁻¹)	28.96 ± 1.30	33.34 ± 4.79	86.96 ± 11.72
Total N (mg kg ⁻¹)	49.77 ± 2.14	10.23 ± 0.80	6.25 ± 0.31
Available P- DW (mg g ⁻¹)	8.85 ± 0.12	0.0036 ± 0.0003	0.32 ± 0.03
Available P- M1 (mg g ⁻¹)	25.80 ± 0.79	28.72 ± 4.09	99.50 ± 5.17
Available K (mg g ⁻¹)	1.89 ± 0.16	0.069 ± 0.03	0.0555 ± 0.037
Available Mg (mg kg ⁻¹)	257.8 ± 8.5	5151.1 ± 648.6	2576.9 ± 131.7

Values represent mean ± standard deviation. Available phosphorus was determined by extraction with deionized water (DW) and Mehlich-1 solution (M1).

Phosphorus (P) is one of the main nutrient present in biochar is due to its concentration during pyrolysis as organic matter is progressively volatilized (Rathnayake et al., 2023). The saturation process increased the total P concentration in BCS by approximately 2.6-fold compared with BC and by 3.0-fold compared with SM. Furthermore, Mehlich-1 (M1) extraction promotes the complete recovery of the phosphorus present in both biochars, suggesting that acidic conditions effectively solubilize both surface-adsorbed and matrix-bound phosphorus. In turn, the water P extraction was negligible, indicating that P is predominantly retained in less soluble forms, but potentially available to plants through the rhizosphere (Li et al., 2008). These findings support the potential of biochars to supply phosphorus for crop production.

Higher Mg content observed in the Mg-modified biochar (5151.09 mg kg⁻¹) reflects the effectiveness of the chemical activation. After nutrient loading, Mg content decreased to 2576.87 mg kg⁻¹, possibly due to the partial dissolution and release of loosely bound Mg species during the saturation step under continuous agitation. In contrast, total nitrogen (N) and available potassium (K) contents were lower in the biochar samples compared to SM, which can be attributed to nutrient losses and transformations during pyrolysis.

The biochar presented a pHPZC of 11.2, indicating that its surface remains positively charged in solutions with pH values below this threshold, which favors the electrostatic attraction of phosphate during the nutrient-loading process. Moreover, during pyrolysis, MgCl₂ deposited on the biomass surface is converted into MgO in MgCl₂-activated biochars. In aqueous environments, MgO can consume H⁺ ions, resulting in an increase in solution pH (Nardis et al., 2022). Overall, these physicochemical properties explain the high phosphate

adsorption/desorption capacity and alkaline behavior of the Mg-modified biochar, supporting its potential use as a phosphorus-enriched soil amendment for agricultural applications.

7.3.2. Morphogenetic Characteristics

Table 7-2 summarizes the morphogenetic characteristics of hybrid *Brachiaria* cv. Sabiá under the different fertilization strategies. These variables provide valuable information on plant growth dynamics and help identify management strategies aimed at maximizing plant–animal system efficiency (Gomide; Gomide; Paciullo, 2006).

Table 7-2 Morphogenetic characteristics of hybrid *Brachiaria* cv. Sabiá including number of live leaves (NLL), stem elongation rate (SER), leaf appearance rate (LAR), leaf elongation rate (LER), and leaf senescence rate (LSR) in different cycles.

Variable	Treatment	Cultivation Cycles		
		1	2	3
NLL	BCS	4.40±0.65 Aa	4.60 ±1.02 Aa	4.80 ±0.27 Aa
	BC	4.80 ±0.45 Aa	4.50 ±0.61 Aa	4.00 ±0.94 Aa
	C	4.40 ±0.42 Aa	4.60 ±1.08 Aa	4.60 ±0.42 Aa
	SM	4.80 ±0.27 Aa	4.50 ±0.61 Aa	5.10 ±0.74 Aa
	S	4.90 ±0.65 Aa	4.60 ±0.42 Aa	4.10 ±0.82 Aa
LAR (leaves tiller ⁻¹ d ⁻¹)	BCS	0.048 ±0.007 Ab	0.048 ±0.016 Aa	0.034 ±0.007 Aa
	BC	0.069±0.008 Aab	0.045 ±0.013 Ba	0.031 ±0.011 Ba
	C	0.052 ±0.013 Ab	0.048 ±0.022 Aa	0.034±0.007 Aa
	SM	0.061 ±0.00 Aab	0.042 ±0.008 Ba	0.044 ±0.007 ABa
	S	0.076 ±0.01 Aa	0.055 ±0.014 Ba	0.031 ±0.011 Ca
SER (cm tiller ⁻¹ d ⁻¹)	BCS	0.023 ±0.005 Ab	0.023 ±0.020 Aa	0.047 ±0.020 Aa
	BC	0.035 ±0.02 Ab	0.027 ±0.013 Aa	0.037 ±0.022 Aa
	C	0.035 ±0.023 Ab	0.038 ±0.028 Aa	0.053 ±0.024 Aa
	SM	0.030 ±0.015 Ab	0.034 ±0.030 Aa	0.061 ±0.032 Aa
	S	0.106 ±0.021 Aa	0.032 ±0.019 Ba	0.035 ±0.023 Ba
LER (cm tiller ⁻¹ d ⁻¹)	BCS	1.26 ±0.12 Ab	0.65 ±0.08 Ba	0.60 ±0.12 Ba
	BC	1.77 ±0.43 Aa	0.80 ±0.12 Ba	0.43 ±0.08 Ca
	C	1.14 ±0.36 Ab	0.68 ±0.15 Ba	0.53 ±0.20 Ba
	SM	1.26 ±0.24 Ab	0.71 ±0.08 Ba	0.68 ±0.19 Ba
	S	1.18 ±0.44 Ab	0.94 ±0.28 Aa	0.53 ±0.22 Ba
LSR (cm tiller ⁻¹ d ⁻¹)	BCS	0.50 ±0.21 Ba	0.31 ±0.09 Ba	1.71 ±0.40 Aa
	BC	0.64 ±0.35 Ba	0.41 ±0.11 Ba	1.44 ±0.30 Aa
	C	0.26 ±0.17 Ba	0.39 ±0.14 Ba	1.68 ±0.46 Aa
	SM	0.29 ±0.24 Ba	0.36 ±0.05 Ba	1.96 ±0.35 Aa
	S	0.19 ±0.08 Ba	0.48 ±0.23 Ba	1.77 ±0.32 Aa

Values represent mean ± standard deviation. Different lowercase letters indicate significant differences among treatments within the same cultivation cycle, whereas different uppercase letters indicate significant differences among cultivation cycles within the same treatment, according to the Tukey test ($p < 0.05$). Treatments: BCS = saturated biochar; BC = non-saturated biochar; C = conventional mineral fertilization; SM = swine manure; S = unfertilized soil.

The number of live leaves (NLL) remained uniform among treatments and cultivation cycles. According to Gastal and Lemaire (2015), the maintenance of a relatively constant number of live leaves reflects a dynamic equilibrium between leaf production and senescence, which is a characteristic feature of grasses growing under stable conditions. indicating that the balance between leaf appearance and senescence was maintained throughout the experiment.

Leaf appearance rate (LAR) showed a treatment effect only during the first cycle, with the unfertilized treatment presenting the highest value, whereas BC and SM exhibited intermediate values. Subsequently, LAR decreased in these treatments, and no significant differences among treatments were observed in C2 and C3. A similar response was observed for stem elongation rate (SER), which was higher in the unfertilized treatment during the first cycle and declined in the subsequent cycles, remaining comparable to the fertilized treatments. Among the fertilized treatments, SER remained comparatively low and stable.

The decline in LAR over successive cycles may be associated with the increase in pseudostem length. As the pseudostem elongates, emerging leaves must travel a greater distance before ligule exposure, reducing the apparent rate of leaf appearance (Gastal; Lemaire, 2015). In addition, excessive stem elongation reduces green leaf density and promotes the accumulation of senescent material within the canopy. Furthermore, the physical barriers formed by the stems may also limit leaf accessibility to grazing animals, reducing forage utilization efficiency (Gomide; Gomide; Paciullo, 2006).

Leaf elongation rate (LER) decreased over successive cultivation cycles, regardless of treatment. According to Gastal (2015), successive defoliation can leave older leaf tissues in the canopy, reducing photosynthetic activity and limiting regrowth in later cycles. In turn, Leaf senescence rate (LSR) increased in the third cycle for all treatments, regardless of fertilization strategy. This may have been due to more severe climatic factors such as increased temperature and decreased relative humidity at cycle 3 (Zhang et al., 2024).

7.3.3. Biomass production

The effects of fertilization strategies on shoot biomass production throughout the cultivation cycles are presented in Tables 7-3 and 7-4.

Table 7-3 Shoot fresh mass (g pot⁻¹) of hybrid *Brachiaria* cv. Sabiá under different fertilization strategies across cultivation cycles.

Treatment	Cultivation Cycles			
	Uni	1	2	3
BCS	9.49 ±4.63 Aa	8.55 ±2.71 Aa	3.81 ±1.60 Ba	3.32 ±1.07 Ba
BC	6.67 ±3.37 Aa	8.14 ±0.74 Aa	2.86 ±0.54 Ba	2.61 ±0.98 Ba
C	11.59 ±4.92 Aa	10.77 ±7.33 Aa	5.53 ±6.38 Ba	3.79 ±1.98 Ba
SM	10.23 ±3.14 Aa	9.55 ±3.4 Aa	3.89 ±2.14 Ba	4.50 ±2.18 Ba
S	0.01 ±0.02 Ab	0.87 ±0.92 Ab	0.79 ±0.48 Ab	0.59 ±0.27 Ab

Values are mean ± standard deviation. Uni = standardization cycle; C1–C3 = successive cultivation cycles. Different lowercase letters indicate significant differences among treatments within each cultivation cycle, whereas different uppercase letters indicate significant differences among cultivation cycles within each treatment, according to Tukey's test ($p < 0.05$). Treatments: BCS = saturated biochar; BC = non-saturated biochar; C = conventional mineral fertilization; SM = swine manure; S = unfertilized soil.

Table 7-4 Shoot dry mass (g pot⁻¹) of hybrid *Brachiaria* cv. Sabiá under different fertilization strategies across cultivation cycles.

Treatment	Cultivation Cycles			
	Uni	1	2	3
BCS	3.05 ±1.30 Aab	2.55 ±0.63 ABa	1.57 ±0.56 Ba	1.56 ±0.32 Ba
BC	1.80 ±1.17 ABb	2.54 ±0.2 Aa	1.30 ±0.17 Ba	1.29 ±0.43 Ba
C	3.84 ±1.05 Aa	2.88 ±1.08 ABa	1.83 ±1.4 Ba	1.69 ±0.8 Ba
SM	3.34 ±0.92 Aa	2.88 ±0.83 ABa	1.79 ±0.9 Ba	2.25 ±0.94 ABa
S	0.01 ±0.01 Ac	0.27 ±0.3 Ab	0.32 ±0.17 Ab	0.23 ±0.1 Ab

Values are mean ± standard deviation. Uni = standardization cycle; C1–C3 = successive cultivation cycles. Different lowercase letters indicate significant differences among treatments within each cultivation cycle, whereas different uppercase letters indicate significant differences among cultivation cycles within each treatment, according to Tukey's test ($p < 0.05$). Treatments: BCS = saturated biochar; BC = non-saturated biochar; C = conventional mineral fertilization; SM = swine manure; S = unfertilized soil.

Shoot dry and fresh mass showed comparable response patterns throughout the experiment, except for the standardization cycle (Uni). Plant growth was very limited in the unfertilized control in all harvests ($p < 0.05$). During the Uni cycle, C and SM resulted in higher biomass production, which may be associated with the greater initial nutrient availability provided by both materials. In contrast, BC showed the lowest production among the fertilized treatments, whereas BCS showed intermediate production. This response may be associated with the higher water-extractable P fraction in BCS (Table 7-1), reflecting a greater potential for rapid phosphorus release compared to BC. In the subsequent harvests (C1–C3), fertilized

treatments did not differ significantly in either dry or fresh mass. Within treatments, shoot biomass generally decreased over successive cycles, corroborating the reductions observed in morphogenetic traits throughout the experimental period.

Biomass accumulation and distribution are presented in Figures 7-2 and 7-3.

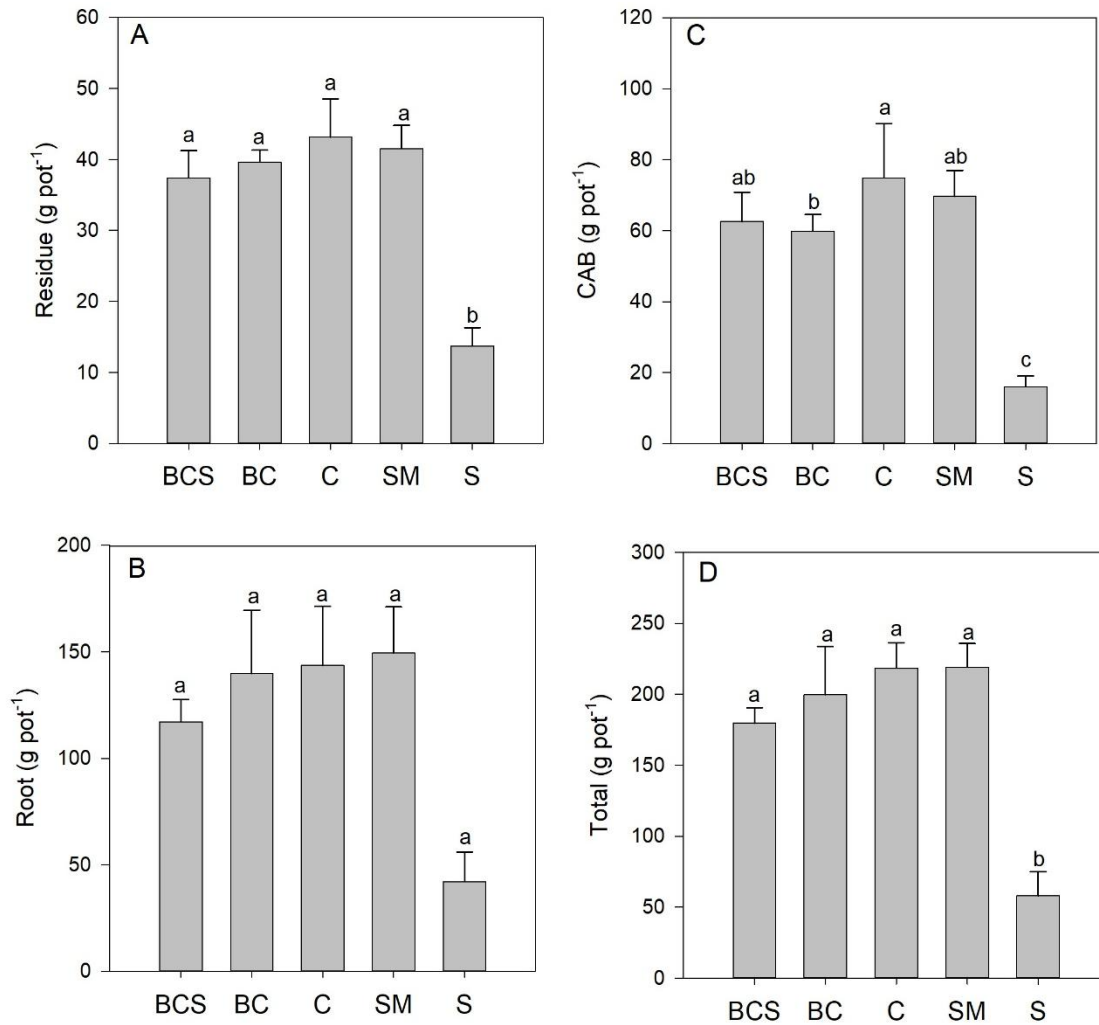


Figure 7-2. Residual biomass, root biomass, cumulative aboveground biomass (CAB), and total biomass on a fresh-mass basis of hybrid *Brachiaria* cv. Sabiá under different fertilization strategies.

Values are presented as mean $\pm$ standard deviation. Different lowercase letters indicate significant differences among treatments according to Tukey's test at the 5% significance level ($p < 0.05$). Treatments: BCS = saturated biochar; BC = non-saturated biochar; C = conventional mineral fertilization; SM = swine manure; S = unfertilized soil.

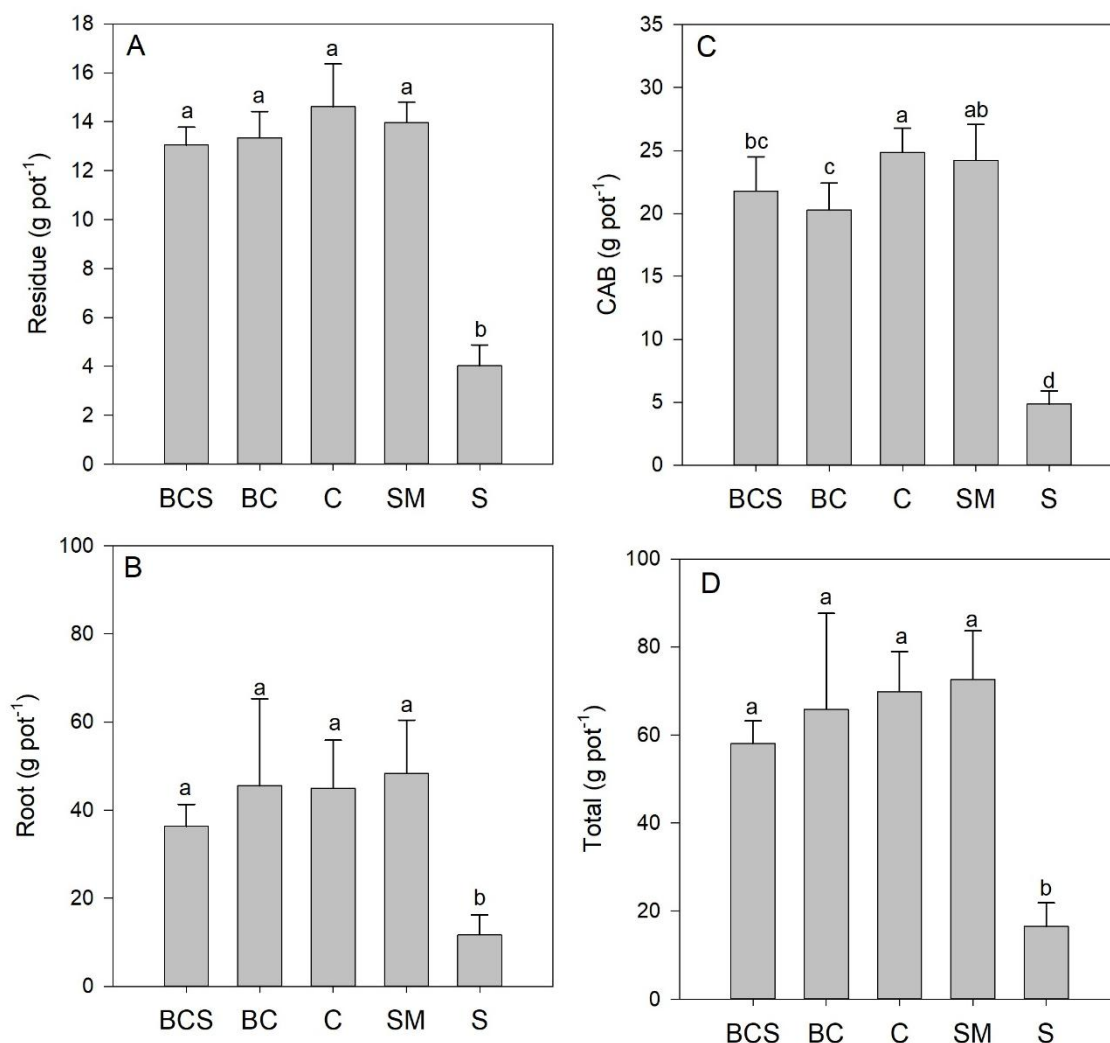


Figure 7-3. Residual biomass, root biomass, cumulative aboveground biomass (CAB), and total biomass on a dry-mass basis of hybrid *Brachiaria* cv. Sabiá under different fertilization strategies.

Values are presented as mean $\pm$ standard deviation. Different lowercase letters indicate significant differences among treatments according to Tukey's test at the 5% significance level ($p < 0.05$). Treatments: BCS = saturated biochar; BC = non-saturated biochar; C = conventional mineral fertilization; SM = swine manure; S = unfertilized soil.

The unfertilized treatment (S) showed the lowest values for all biomass components on both dry and fresh bases, highlighting the importance of nutrient supply for both above- and belowground growth. Among the fertilized treatments, no significant differences were observed for residue, root or total biomass in either dry or fresh mass. Cumulative aboveground biomass (CAB) showed similar patterns on both dry and fresh bases, with mineral fertilization (C) and SM exhibited the highest values. Compared with C, BC showed reductions of 18% in dry mass and 20% in fresh mass, whereas BCS showed intermediate performance, with reductions of 12% and 16% in dry and fresh mass, respectively. Overall, S produced 73–81% less CAB than the fertilized treatments.

The effects of biochar on crop yield are influenced by several factors, including feedstock type, pyrolysis temperature, application rate, crop species and soil type (Joseph et al., 2021). In the present study, biochar fertilization outperformed the unfertilized control. This response may be attributed to the higher nutrient content of the swine-manure-derived biochar, consistent with findings reported by Ye et al. (2020) for biochars derived from animal and human wastes. The authors also observed greater yield responses when biochar was applied along with N sources, at rates $> 100 \text{ kg N ha}^{-1}$ which is consistent with the fertilization strategy adopted in this study.

Regarding biochars, the adsorptive capacity allows for the reduction of P concentration in wastewater and the return of nutrients to agriculture (Joseph et al., 2021). Although CAB tended to be lower in the biochar treatments than in C, this difference was mainly associated with the standardization cycle (Uni). In the successive harvests (C1- C3), BCS did not differ significantly from the mineral treatment (Table 7-4). Furthermore, total biomass did not differ significantly among nutrient sources, indicating that BCS can sustain competitive forage production over the long term.

7.3.4. Water Consumption and Productivity Performance

The data on water consumption (WC) and water productivity (WP) are presented in Tables 7-5.

Table 7-5 Water consumption (WC in L pot^{-1}) and water productivity (WP in kg m^{-3}) of hybrid *Brachiaria* cv. Sabiá cultivated under different fertilization strategies over successive cultivation cycles.

Var.	Treat.	Cultivation Cycles			
		Uni	1	2	3
WC (L pot^{-1})	BCS	3.62 $\pm$ 0.28 ABb	3.54 $\pm$ 0.22 ABa	3.73 $\pm$ 0.13 Aa	3.32 $\pm$ 0.54 Ba
	BC	3.24 $\pm$ 0.33 Bc	3.87 $\pm$ 0.14 Aa	3.87 $\pm$ 0.11 Aa	3.35 $\pm$ 0.09 Ba
	C	3.99 $\pm$ 0.21 Aa	3.74 $\pm$ 0.08 ABa	3.94 $\pm$ 0.12 Aa	3.42 $\pm$ 0.13 Ba
	SM	3.86 $\pm$ 0.25 Aab	2.37 $\pm$ 0.2 Ca	3.87 $\pm$ 0.11 Aa	3.46 $\pm$ 0.08 Ca
	S	2.48 $\pm$ 0.13 Cd	3.57 $\pm$ 0.56 Ab	2.87 $\pm$ 0.19 Bb	2.77 $\pm$ 0.11 BCb
WP (kg m^{-3})	BCS	0.83 $\pm$ 0.32 Aab	0.72 $\pm$ 0.16 ABb	0.36 $\pm$ 0.15 Ba	0.47 $\pm$ 0.38 Ba
	BC	0.53 $\pm$ 0.28 ABb	0.66 $\pm$ 0.07 Ab	0.34 $\pm$ 0.05 Bab	0.37 $\pm$ 0.18 ABa
	C	0.96 $\pm$ 0.25 Aa	0.78 $\pm$ 0.15 ABb	0.47 $\pm$ 0.37 Ba	0.50 $\pm$ 0.24 Ba
	SM	0.86 $\pm$ 0.2 ABab	1.24 $\pm$ 0.41 Aa	0.46 $\pm$ 0.24 Ca	0.65 $\pm$ 0.29 BCa
	S	0.003 $\pm$ 0.005 Ac	0.07 $\pm$ 0.08 Ac	0.11 $\pm$ 0.06 Ab	0.08 $\pm$ 0.04 Ab

Values are mean $\pm$ standard deviation. Different lowercase letters indicate significant differences among treatments within the same cultivation cycle, whereas different uppercase letters indicate significant differences among cultivation cycles within each treatment, according to Tukey's test ($p < 0.05$). Treatments: BCS = saturated biochar;

BC = non-saturated biochar; C = conventional mineral fertilization; SM = swine manure; S = unfertilized soil. Uni = standardization cycle

WC followed a pattern similar to that observed for shoot dry mass. The fertilized treatments showed higher water consumption than the unfertilized control throughout the experiment, likely due to their greater vegetative growth and biomass accumulation. During the standardization cycle, mineral fertilization exhibited the highest WC values, whereas SM showed intermediate values. BCS showed higher consumption than BC, probably due to the greater biomass production. In the subsequent cycles, no significant differences were observed among the different phosphorus sources.

Treatments C, SM, and BCS maintained comparable WP values for most of the cultivation period, whereas BC showed lower WP at the beginning of the experiment (Uni and C1). These results suggest that BCS enabled water productivity comparable to mineral fertilization. This performance may be related to the low application rates used in this study (1.8 g pot^{-1} for BCS and 4.7 g pot^{-1} for BC), nutrients supplied by biochar and the additional N fertilization. According to Gao et al. (2020), high biochar application rates may increase the C:N ratio and promote N immobilization, which can reduce crop yield and WP. In addition, N fertilization rates in the range of $100\text{--}200 \text{ kg ha}^{-1}$ and nutrient-supplying capacity of biochar have been reported to improve WP, reinforcing the importance of nutrient availability for plant performance.

In turn, the lower efficiency for BC may be related to the lower nutritional availability of the material, as previously discussed, causing an initial reduction in biomass production and thus leading to a decrease in water productivity. Moreover, the well-watered conditions maintained throughout the experiment may have limited the expression of biochar effects on WP, as these responses are generally enhanced under water deficit conditions (Hou et al., 2023; Liu et al., 2021).

7.3.5. Soil chemical properties

Soil pH (Table 7-6) raised with the application of unsaturated biochar (BC) soil pH above the unfertilized control (S) and stood out alongside conventional fertilization (C) as the treatments with the highest soil pH. This response highlights the inherent liming potential of biochar. On the other hand, phosphate saturation in BCS markedly suppressed this alkalizing capability, reducing soil pH.

Biochar treatments (BC and BCS) maintained the highest levels of available phosphorus in the soil, comparable to the mineral fertilizer (Table 7-6). This response may be related to the enhanced phosphate retention capacity of biochar and the high P desorption, as demonstrated with M1 extraction. The unfertilized control showed the lowest value, reflecting continuous depletion during plant growth. In turn, the soil fertilized with SM showed an intermediate concentration of available P, while maintaining biomass production and nutrient uptake comparable to other fertilized treatments.

The concentration of extractable Mg was higher in the soil with BC, probably due to the chemical modification with $MgCl_2$ for biochar production. In BCS, the Mg content decreased after the saturation process, reducing its presence in the soil. The incorporation of Mg cations into the biochar structure may promote electrostatic interactions with phosphate anions and the precipitation of Mg-phosphate groups on the biochar surface, allowing the gradual release of P and maintaining P availability in the soil (Nardis et al., 2022; Nascimento et al., 2026).

Furthermore, the Mg content is related to the Ca concentration. Ca is preferentially retained at soil exchange sites due to its smaller hydrated ionic radius compared with Mg. Therefore, the presence of Mg reduces the availability of Ca to interact with phosphate ions in solution (Manimel Wadu et al., 2013). In soil after cultivation, the SM treatment showed the highest extractable Ca concentration, thereby increasing the precipitation of Ca-phosphates that are less soluble than Mg-phosphates (Manimel Wadu et al., 2013). This chemical mechanism likely contributed to the intermediate available phosphorus content observed in the SM-treated soil at the end of the experiment.

Regarding soil potassium (K) dynamics, exchangeable K levels at the end of the experiment did not differ significantly among any of the treatments (Table 7-6). The similar soil K levels suggest that K supply was sufficient to maintain adequate soil K availability regardless of the fertilizer source. Moreover, the reduced biomass production observed in the unfertilized treatment (Table 7-4) may have contributed to maintaining residual soil K levels comparable to fertilized treatments.

Soil organic matter (SOM) was significantly enhanced in all organic-amended units (BCS, BC, and SM) relative to the unfertilized control. In biochar-amended soils, this response may be associated with the input of recalcitrant carbon and with a possible reduction in the mineralization of native SOM, whereas swine manure likely contributed through the addition of more labile organic compounds (Joseph et al., 2021).

Table 7-6 Soil characterization after plant cultivation with different fertilizer treatments.

Treat.	pH	P (mg dm ⁻³)	K (mg dm ⁻³)	Ca (cmol _c dm ⁻³)	Mg (cmol _c dm ⁻³)	H+Al (cmol _c dm ⁻³)	SOM (dag kg ⁻¹)	Prem (mg L ⁻¹)
initial	4.23	4.9	22	0.40	0.14	3.6	0.52	4.9
BCS	6.47 ±0.13 d	15.40 ±3.19 a	20.60 ±1.14 a	2.73 ±0.09 b	0.67 ±0.01 cd	1.20 ±0.07 a	0.69 ±0.09 a	28.02 ±2.31 a
BC	7.16 ±0.25 a	20.62 ±11.6 a	22.20 ±4.71 a	2.14 ±0.16 d	1.94 ±0.33 a	0.28 ±0.23 c	0.67 ±0.13 a	22.96 ±0.72 b
C	6.99 ±0.12 ab	17.18 ±3.42 a	22.00 ±1.00 a	2.41 ±0.10 c	1.18 ±0.03 b	0.90 ±0.07 b	0.46 ±0.19 ab	27.72 ±0.56 a
SM	6.50 ±0.09 cd	10.78 ±1.50 ab	19.20 ±1.64 a	3.18 ±0.12 a	0.55 ±0.09 d	1.32 ±0.11 a	0.68 ±0.03 a	29.00 ±0.83 a
S	6.78 ±0.05 bc	1.82 ±0.16 b	20.80 ±4.66 a	2.48 ±0.08 c	0.79 ±0.03 c	0.94 ±0.05 b	0.35 ±0.12 b	29.48 ±1.86 a

Values are presented as mean ± standard deviation. Different lowercase letters within the same column indicate significant differences among treatments according to Tukey's test ($p < 0.05$). Treatments: BCS = phosphate-saturated Mg-modified biochar; BC = non-saturated Mg-modified biochar; C = conventional mineral fertilization; SM = swine manure; S = unfertilized soil. SOM = soil organic matter; Prem = remaining phosphorus.

7.3.6. Leaf nutrient content

Leaf nutrient concentrations and nutrient uptake are shown in Table 7-7 and 7-8, respectively.

Table 7-7 Chemical composition of the shoot biomass of hybrid *Brachiaria* cv. Sabiá cultivated under different fertilization strategies.

Treat	P total (g kg ⁻¹)	N (g kg ⁻¹)	K (g kg ⁻¹)	Mg (g kg ⁻¹)	Cu (mg kg ⁻¹)	Zn (mg kg ⁻¹)
BCS	0.24 ± 0.07 a	6.41 ± 1.61 a	14.00 ± 1.83 a	6.99 ± 0.7 a	1.84 ± 0.44 b	21.18 ± 6.66 ab
BC	0.24 ± 0.11 a	4.92 ± 1.13 a	13.62 ± 1.46 a	7.59 ± 0.54 a	1.81 ± 0.45 b	12.15 ± 1.98 b
C	0.27 ± 0.05 a	5.46 ± 0.69 a	13.49 ± 2.38 a	7.52 ± 2.05 a	1.53 ± 0.43 b	19.66 ± 5.85 ab
SM	0.25 ± 0.08 a	7.44 ± 0.99 a	13.72 ± 1.04 a	5.94 ± 0.56 ab	4.14 ± 0.74 a	19.8 ± 4.66 ab
S	0.07 ± 0.01 b	5.54 ± 1.55 a	15.82 ± 1.49 a	4.18 ± 0.62 b	5.08 ± 0.48 a	23.2 ± 4.67 a

Values represent mean ± standard deviation. Different lowercase letters indicate significant differences among treatments according to the Tukey test ($p < 0.05$). Treatments: BCS = saturated biochar; BC = non-saturated biochar; C = conventional mineral fertilization; SM = swine manure; S = unfertilized soil. P total = total phosphorus; N = total nitrogen; K = potassium; Mg = magnesium; Cu = copper; Zn = zinc.

Table 7-8 Nutrient uptake by hybrid *Brachiaria* cv. Sabiá under different fertilization strategies.

Treat.	P (mg pot ⁻¹)	N (mg pot ⁻¹)	K (mg pot ⁻¹)	Mg (mg pot ⁻¹)	Cu (μg pot ⁻¹)	Zn (mg pot ⁻¹)
BCS	3.46 ± 1.24 a	90.83 ± 23.96 ab	197.67 ± 26.27 a	99.13 ± 13.59 a	2.59 ± 0.51 b	0.30 ± 0.08 ab
BC	3.44 ± 1.39 a	71.37 ± 14.69 b	200.10 ± 32.57 a	110.77 ± 4.61 a	2.65 ± 0.69 b	0.18 ± 0.03 bc
C	4.29 ± 0.70 a	88.97 ± 13.61 ab	216.56 ± 14.39 a	122.28 ± 35.64 a	2.49 ± 0.76 b	0.32 ± 0.11 a
SM	4.00 ± 1.14 a	121.24 ± 22.28 a	222.85 ± 24.18 a	96.01 ± 5.01 a	6.74 ± 1.45 a	0.32 ± 0.09 a
S	0.30 ± 0.03 b	22.79 ± 4.43 c	67.25 ± 13.69 b	17.80 ± 4.78 b	2.14 ± 0.29 b	0.10 ± 0.02 c

Values represent mean ± standard deviation. Different lowercase letters indicate significant differences among treatments according to the Tukey test ($p < 0.05$). Treatments: BCS = saturated biochar; BC = non-saturated biochar; C = conventional mineral fertilization; SM = swine manure; S = unfertilized soil. P total = total phosphorus; N = total nitrogen; K = potassium; Mg = magnesium; Cu = copper; Zn = zinc.

The phosphorus concentration in *Brachiaria* leaves reflected the phosphorus supply provided by the different treatments. No significant differences were observed among the fertilized treatments, whereas the unfertilized control showed the lowest P content. This suggests that the phosphorus recovered and loaded onto biochar was effectively taken up by the plants, with performance comparable to mineral fertilization.

Nitrogen concentrations in leaves were similar across treatments, whereas SM treatment resulted in the highest nitrogen uptake. This was likely due to a greater nitrogen content compared to the other sources (Table 7-1). Biochar treatments showed an uptake comparable to the mineral treatment, while S exhibit the lowest value.

Potassium concentrations did not differ among treatments. Likewise, K uptake was comparable among all fertilized treatments, whereas the unfertilized control showed

significantly lower values. This result suggests that K supply was sufficient to meet plant requirements in all fertilized treatments.

Magnesium concentrations were highest in BCS, BC, and C, whereas SM exhibited intermediate values. In turn, Mg uptake did not differ among fertilized treatments, suggesting that Mg acquisition remained adequate under all fertilization strategies. In the unfertilized control, the concentration of Mg and Mg-uptake showed reduced due to reduced biomass production.

Copper concentration and uptake were higher in the SM treatment, likely due to the Cu input provided by swine manure, since this element is commonly used as a feed additive in pig production. However, Cu availability can interfere with plant nutrient uptake and translocation, impair root elongation, and negatively affect root cell membrane permeability (Fageria, 2000). In contrast, BC, BCS, and C showed lower Cu concentrations and uptake. In the biochar treatments, this response may be associated with the retention of Cu by the biochar matrix, which can reduce its availability for plant uptake (Sui et al., 2023). In the C treatment, a dilution effect may have reduced foliar micronutrient concentration due to high biomass production, whereas the unfertilized control exhibited relatively high Cu concentrations in plant tissues due to a concentration effect (Jarrell; Beverly, 1981).

Leaf Zn concentration was highest in the unfertilized control (S) ($p < 0.05$), while its total uptake was the lowest. This can be attributed to a concentration effect caused by the reduced biomass production (Jarrell; Beverly, 1981). The lower Zn concentration and intermediate uptake observed in BC may be associated with the higher soil pH induced by the non-saturated biochar, which likely reduced Zn solubility and plant uptake. In addition, Zn retention by the biochar matrix may have further limited its availability to the crop. Conversely, BCS, C and SM showed intermediate zinc concentrations and higher uptake, reflecting a reduced dilution effect (Jarrell; Beverly, 1981).

Overall, these results suggest that Mg-modified swine manure biochar possesses adsorptive properties capable of recovering phosphorus from phosphate-rich aqueous solutions. Furthermore, the nutrient-loaded biochar supported forage biomass production comparable to mineral fertilization, while maintaining adequate phosphorus availability and reducing soil-available copper. This approach contributes to circular economy strategies by transforming swine manure into a value-added agricultural input, with potential benefits for nutrient recycling and reduced dependence on mineral fertilizers. Nevertheless, further studies are

needed to evaluate the economic feasibility and large-scale implementation and other forage characteristics, such as crude protein content and palatability.

7.4. Conclusions

This study demonstrates that biochar derived from swine manure and modified with magnesium chloride is a highly promising alternative for nutrient recovery and sustainable agriculture. The biochars showed an intermediate initial shoot biomass production, resulting in lower cumulative aboveground biomass. However, the root, residual, and total biomass remained statistically equal to the treatment with mineral fertilization. Furthermore, the application of biochars significantly enhanced soil chemical properties by maintaining high levels of available phosphorus, increasing soil organic matter. Leaf chemical analysis showed that biochars provided phosphorus bioavailability, while restricted the bioavailability and uptake of potentially toxic elements such as copper, ensuring safe plant nutrition. Although both biochars showed similar agronomic performance, the saturation process enables the removal of phosphorus from effluents, while increasing the phosphorus concentration in the material and consequently reducing the application rate by approximately 2.6-fold compared to unsaturated biochar. Therefore, recycling swine manure residues into engineered biochars represents an efficient circular strategy to reduce dependence on imported mineral fertilizers, mitigate environmental degradation, and support tropical pasture management.

7.5. References

- AHMED, Mysha; HAYES, Michael. Waste to resource: A review of nitrate and phosphate removal from agricultural runoff using recycled byproducts. **Journal of Agriculture and Food Research**, v. 24, p. 102371, 1 Dec. 2025.
- AKKARI, Imane *et al.* Raw pomegranate peel as promise efficient biosorbent for the removal of Basic Red 46 dye: equilibrium, kinetic, and thermodynamic studies. **Biomass Conversion and Biorefinery**, v. 13, n. 9, p. 8047–8060, 2023.
- ANDA. **Pesquisa Setorial - ANDA**. Disponível em: <http://anda.org.br/pesquisa_setorial/>. Acesso em: 3 jan. 2025.
- APHA *et al.* **Standard Methods for the Examination of Water and Wastewater**. 24. ed. Washington, DC: American Public Health Association; American Water Works Association; Water Environment Federation, 2022.
- BANIK, Chumki *et al.* The role of biochar and zeolite in enhancing nitrogen and phosphorus

recovery: A sustainable manure management technology. **Chemical Engineering Journal**, v. 456, n. December 2022, p. 141003, 2023.

BOLFE, Édson Luis *et al.* Potential for Agricultural Expansion in Degraded Pasture Lands in Brazil Based on Geospatial Databases. **Land** **2024**, Vol. 13, Page 200, v. 13, n. 2, p. 200, 6 Feb. 2024.

EMBRAPA. **Estatísticas - Suínos - Embrapa Suínos e Aves - Portal Embrapa**. Disponível em: <<https://www.embrapa.br/web/suinos-e-aves/cias/estatisticas-suinos>>. Acesso em: 14 sep. 2026.

FAGERIA, V. D. Journal of Plant Nutrition: Preface. **Journal of Plant Nutrition**, v. 23, n. 11–12, p. 37–41, 2000.

FRONTADO, Néstor Eduardo Villamizar *et al.* Phosphorus Use Efficiency: Morphogenetic and Productive Responses of *Brachiaria decumbens* Genotypes (Syn: *Urochloa decumbens*). **Grasses** **2025**, Vol. 4, Page 20, v. 4, n. 2, p. 20, 14 May 2025.

GASTAL, François; LEMAIRE, Gilles. Defoliation, Shoot Plasticity, Sward Structure and Herbage Utilization in Pasture: Review of the Underlying Ecophysiological Processes. **Agriculture** **2015**, Vol. 5, Pages 1146–1171, v. 5, n. 4, p. 1146–1171, 25 Nov. 2015.

GOMIDE, C. A. M.; GOMIDE, José Alberto; PACIULLO, D. S. C. Morfogênese como ferramenta para o manejo de pastagens. **43ª Reunião Anual da SBZ**, p. 457–478, 2006.

GOMIDE, Carlos Augusto Miranda; GOMIDE, José Alberto. Morfogênese de cultivares de *Panicum maximum* jacq. **Revista Brasileira de Zootecnia**, v. 29, n. 2, p. 341–348, Mar. 2000.

GUIMARÃES, Paulo Tácito G.; ALVAREZ, Victor Hugo; RIBEIRO, Antonio Carlos. 5 Aproximacao. **Recomendações Para o Uso de Corretivos e Fertilizantes em Minas Gerais - 5º Aproximação**, p. 13–20, 1999.

HOU, Jingxiang *et al.* Effect of biochar addition and reduced irrigation regimes on growth, physiology and water use efficiency of cotton plants under salt stress. **Industrial Crops and Products**, v. 198, p. 116702, 1 Aug. 2023.

IBGE. **Brasil | Cidades e Estados | IBGE**. Disponível em: <<https://www.ibge.gov.br/cidades-e-estados>>. Acesso em: 6 jul. 2026.

JARRELL, W. M.; BEVERLY, R. B. The dilution effect in plant nutrition studies. **Advances in Agronomy**, v. 34, n. C, p. 197–224, 1981.

JOSEPH, Stephen *et al.* How biochar works, and when it doesn't: A review of mechanisms controlling soil and plant responses to biochar. **GCB Bioenergy**, v. 13, n. 11, p. 1731–1764, 1 Nov. 2021.

KUNZ, Airton; STEINMETZ, Ricardo Luis Radis; AMARAL, André Cestonaro do. **Fundamentos da digestão anaeróbia, purificação do biogás, uso e tratamento do digestato**. Concórdia: Sbera: Embrapa Suínos e Aves, 2019. v. 53

LI, H. *et al.* Dynamics of phosphorus fractions in the rhizosphere of common bean (*Phaseolus vulgaris* L.) and durum wheat (*Triticum turgidum durum* L.) grown in monocropping and intercropping systems. **Plant and Soil**, v. 312, n. 1–2, p. 139–150, 21 Nov. 2008.

LIU, Xuezhi *et al.* Effects of biochar amendment and reduced irrigation on growth, physiology, water-use efficiency and nutrients uptake of tobacco (*Nicotiana tabacum* L.) on two different

- soil types. **Science of The Total Environment**, v. 770, p. 144769, 20 May 2021.
- LUSTOSA FILHO, José Ferreira *et al.* Aging of biochar-based fertilizers in soil: Effects on phosphorus pools and availability to *Urochloa brizantha* grass. **Science of the Total Environment**, v. 709, p. 136028, 2020.
- MANIMEL WADU, Mihiri C. W. *et al.* Exchangeable Calcium/Magnesium Ratio Affects Phosphorus Behavior in Calcareous Soils. **Soil Science Society of America Journal**, v. 77, n. 6, p. 2004–2013, 1 Nov. 2013.
- MUTIMURA, Mupenzi; GHIMIRE, Sita. Brachiaria Grass for Sustainable Livestock Production in Rwanda under Climate Change. **Handbook of Climate Change Management: Research, Leadership, Transformation**, v. 1, p. 195–211, 1 Jan. 2021.
- NARDIS, Bárbara Olinda *et al.* Phosphorus recovery using magnesium-enriched biochar and its potential use as fertilizer. **Archives of Agronomy and Soil Science**, v. 67, n. 8, p. 1017–1033, 2021.
- NARDIS, Bárbara Olinda *et al.* Production of engineered-biochar under different pyrolysis conditions for phosphorus removal from aqueous solution. **Science of the Total Environment**, v. 816, 2022.
- NASCIMENTO, Heloisa Rocha do *et al.* A new methodological approach for simulating water deficit in soybean genotypes. **Journal of Agronomy and Crop Science**, v. 207, n. 6, p. 946–955, 2 Dec. 2021.
- NASCIMENTO, Larissa Almeida *et al.* Biochar from Swine Manure: An Alternative for Nutrient Recovery and Slow-Release Fertilization. **ACS Omega**, 25 Feb. 2026.
- OLIVEIRA, Paulo Armando V. de *et al.* **Suinocultura de baixa emissão de carbono**. Brasília/DFMinistério da Agricultura, Pecuária e Abastecimento, , 2016.
- OLIVEIRA, Fernanda R. *et al.* Environmental application of biochar: Current status and perspectives. **Bioresource Technology**, v. 246, n. July, p. 110–122, 2017.
- RATHNAYAKE, Dilani *et al.* Biochar from animal manure: A critical assessment on technical feasibility, economic viability, and ecological impact. **GCB Bioenergy**, v. 15, n. 9, p. 1078–1104, 5 Sep. 2023.
- SHAKOOR, Muhammad Bilal; YE, Zhi Long; CHEN, Shaohua. Engineered biochars for recovering phosphate and ammonium from wastewater: A review. **Science of The Total Environment**, v. 779, p. 146240, 20 Jul. 2021.
- SPILLER, Marc *et al.* Environmental and economic sustainability of the nitrogen recovery paradigm: Evidence from a structured literature review. **Resources, Conservation and Recycling**, v. 184, n. March, p. 106406, 2022.
- SUI, Fengfeng *et al.* Pig manure biochar for contaminated soil management: nutrient release, toxic metal immobilization, and Chinese cabbage cultivation. **Ecotoxicology and Environmental Safety**, v. 257, n. June 2022, p. 114928, 2023.
- TEIXEIRA, Paulo César *et al.* **Manual de métodos de análise de solo**. 3. ed. Brasília, DF: Embrapa, 2017.
- WALSH, Michael; SCHENK, Gerhard; SCHMIDT, Susanne. Realising the circular phosphorus economy delivers for sustainable development goals. **npj Sustainable Agriculture**

2023 1:1, v. 1, n. 1, p. 2-, 4 Oct. 2023.

YE, Lili *et al.* Biochar effects on crop yields with and without fertilizer: A meta-analysis of field studies using separate controls. **Soil Use and Management**, v. 36, n. 1, p. 2–18, 2020.

ZHANG, Kangning *et al.* Leaf senescence in forage and turf grass progress and prospects. **Grass Research 2024 1:e004**, v. 4, n. 1, p. 4, 2024.

ZHOU, Lingling *et al.* Recent advances in swine wastewater treatment technologies for resource recovery: A comprehensive review. **Science of The Total Environment**, v. 924, p. 171557, 10 May 2024.

8. GENERAL CONCLUSIONS AND FUTURE PERSPECTIVES

This thesis demonstrated that magnesium-modified swine manure biochars technical as an efficient strategy for sustainable management and resource recovery in agribusiness. In the first stage, it was determined that the physicochemical characteristics of the material are strongly influenced by pyrolysis and activation conditions. Activation with magnesium chloride (MgCl_2) at a 3:1 (w/v) ratio at 800 °C enhances the subsequent removal of nitrogen and phosphorus. Mechanistically, kinetic assays revealed that phosphate retention occurs through heterogeneous chemisorption regulated by the Elovich model, while ammonium follows pseudo-second-order kinetics. Adsorption equilibrium data were best described by the Langmuir model for phosphate, with monolayer adsorption and maximum capacity of 67.56 mg g⁻¹, and by the Freundlich model for ammonium, confirming the high potential of the material as a high-performance adsorbent.

In the second phase, the performance of the selected biochar in the simultaneous recovery of nutrients and immobilization of enrofloxacin (ENR) was evaluated. The multicomponent assays showed 100% phosphate removal and 93% for ammonium, a performance attributed to surface chemical precipitation of stable mineral phases such as struvite. In contrast, the retention of the antibiotic ENR was limited due to direct competition for metal-rich active sites and enrofloxacin speciation under alkaline conditions. However, desorption assays confirmed the safety reuse of biochar, indicated by high release of macronutrients (150% for phosphorus and 40% for nitrogen) simultaneous with a reduced and leaching of the antibiotic (< 7%), thereby preventing environmental contamination.

In the final stage, agronomic experiment confirmed that the enriched biochar effectively acts as a high-efficiency slow-release fertilizer in the cultivation of hybrid *Brachiaria* cv. Sabiá. Although biochar resulted in lower initial shoot biomass production due to the gradual release of nutrients, the development of root biomass and total biomass were comparable to those obtained with conventional mineral fertilizer. Furthermore, soil chemical analysis showed that the incorporation of biochar promoted long-term improvements, increasing organic matter content and maintaining adequate levels of available phosphorus in the soil. From the perspective of plant nutrition and environmental safety, foliar chemical analysis attested to a real increase in phosphorus availability to plants, while restricting the bioavailability and uptake of potentially toxic elements native to the soil, such as copper.

In summary, the integrated results of this thesis establish that magnesium-modified swine manure biochar promotes nutrient recovery, emerging contaminant mitigation, and good agricultural performance. Future studies should evaluate the performance of the material under more realistic conditions, including real swine wastewater or digestate, continuous-flow systems, and longer-term soil and plant experiments. Further research should also investigate the fate of enrofloxacin and other pharmaceuticals in soil–plant systems, including their potential accumulation, transformation, and effects on soil microbial communities and antibiotic resistance. Field-scale trials, together with techno-economic and life-cycle assessments, would be important to determine the practical feasibility and environmental performance of this integrated approach.

APPENDIX A

**Supporting Information for Chapter 1: Biochar From Swine Manure: An
Alternative For Nutrient Recovery**

Table S1. Phosphorus Release Test

Treatmeant	P-PO ₄ ³⁻ [mg L ⁻¹]
BC 800	3.67 (± 0.22)
BC 400	8.26 (±0.06)
BC 800-MgCl ₂ (3:1)	-0.059 (< LQ)

The water extraction test revealed distinct differences in the stability of phosphorus among the evaluated biochars. The unmodified materials released measurable amounts of P into solution, with BC400 showing the highest concentration (8.26 ± 0.06 mg L⁻¹) and BC800 releasing significantly less (3.67 ± 0.22 mg L⁻¹). This decrease with increasing pyrolysis temperature is consistent with the greater mineral stability and reduced solubility of P-bearing phases formed at higher carbonization temperatures¹.

Table S2. Proximate analysis of SM

Parameter	Value (wt.%)
Moisture	5.67
Volatile matter	69.20
Ash	26.50

Table S3. Elemental and mineral composition of SM

Element	Content (wt.%)
C	26.6
O	13.1
N	4.4
P	2.4
K	0.8
Ca	4.0

R. Li *et al.*, “Enhancing phosphate adsorption by Mg/Al layered double hydroxide functionalized biochar with different Mg/Al ratios”, *Sci. Total Environ.*, vol. 559, p. 121–129, jul. 2016, doi: 10.1016/J.SCITOTENV.2016.03.151.