

PROGRAMA DE PÓS-GRADUAÇÃO EM PRODUÇÃO VEGETAL

José Mendes dos Santos Júnior

**Fertilizantes granulados à base de biocarvão com aglutinantes agroindustriais
para melhorar a eficiência de uso do fósforo e a saúde de solos tropicais**

Montes Claros

2026

José Mendes dos Santos Júnior

**Fertilizantes granulados à base de biocarvão com aglutinantes agroindustriais
para melhorar a eficiência de uso do fósforo e a saúde de solos tropicais**

Tese apresentada ao Programa de Pós-Graduação em Produção Vegetal da Universidade Federal de Minas Gerais, como requisito parcial para a obtenção do título de Doutor em Produção Vegetal.

Orientador: Prof. Luiz Arnaldo Fernandes

Montes Claros
Fevereiro de 2026

Santos Júnior, José Mendes dos.

S237f
2026 Fertilizantes granulados à base de biocarvão com aglutinantes agroindustriais para melhorar a eficiência de uso do fósforo e a saúde de solos tropicais [manuscrito] / José Mendes dos Santos Júnior. Montes Claros, 2026.
130 f. : il.

Tese (doutorado) - Área de concentração em Produção Vegetal. Universidade Federal de Minas Gerais / Instituto de Ciências Agrárias.

Orientador(a): Luiz Arnaldo Fernandes.

Banca examinadora: Fernando Colen, Rodinei Facco Pegoraro, Amário Nuno Meireles Duarte, Enilson de Barros Silva, Luiz Arnaldo Fernandes.

Inclui referências: f. 23–26; 42–44; 64–68; 116–120.

1. Fertilidade do solo. 2. Adubos e fertilizantes. 3. Pirólise. I. Fernandes, Luiz Arnaldo. II. Universidade Federal de Minas Gerais. Instituto de Ciências Agrárias. III. Título.

CDU: 631.8

ATA DE DEFESA DE TESE

Aos 25 dias do mês de fevereiro de 2026 às 8:00 horas, sob a Presidência do Professor Luiz Arnaldo Fernandes, D. Sc. (Orientador - UFMG/ICA) e com a participação dos Professores Fernando Colen, D. Sc. (UFMG/ICA), Rodinei Facco Pegoraro, D. Sc. (UFMG/ICA), Amário Nuno Meireles Duarte, D. Sc. (UFTM) e Enilson de Barros Silva, D. Sc. (UFVJM), reuniu-se, por videoconferência, a Banca de tese de **José Mendes dos Santos Júnior**, aluno do Curso de Doutorado em Produção Vegetal. O resultado da defesa de tese intitulada: **"Fertilizantes granulados a base de biocarvão com aglutinantes agroindustriais para melhorar a eficiência de uso do fósforo e a saúde de solos tropicais"**, sendo o aluno considerado **aprovado**. E, para constar, eu, Professor Luiz Arnaldo Fernandes, Presidente da Banca, lavrei a presente ata que depois de lida e aprovada, será assinada por mim e pelos demais membros da Banca examinadora.

OBS.: O aluno somente receberá o título após cumprir as exigências do **ARTIGO 65** do regulamento do Curso de Doutorado em Produção Vegetal, conforme apresentado a seguir:

Art. 65 Para dar andamento ao processo de efetivação do grau obtido, o candidato deverá, após a aprovação de sua Dissertação ou Tese e da realização das modificações propostas pela banca examinadora, se houver, encaminhar à secretaria do Colegiado do Programa, com a anuência do orientador, 1 (um) exemplar impresso e 1 (um) exemplar eletrônico da dissertação ou tese, no prazo de 60 (sessenta) dias.

Montes Claros, 25 de fevereiro de 2026.

Documento assinado digitalmente
 **FERNANDO COLEN**
Data: 26/02/2026 09:48:07-0300
Verifique em <https://validar.iti.gov.br>

Fernando Colen
Membro

Documento assinado digitalmente
 **RODINEI FACCO PEGORARO**
Data: 26/02/2026 08:41:52-0300
Verifique em <https://validar.iti.gov.br>

Rodinei Facco Pegoraro
Membro

Documento assinado digitalmente
 **AMARIO NUNO MEIRELES DUARTE**
Data: 25/02/2026 13:39:59-0300
Verifique em <https://validar.iti.gov.br>

Amário Nuno Meireles Duarte
Membro

Documento assinado digitalmente
 **ENILSON DE BARROS SILVA**
Data: 25/02/2026 16:24:45-0300
Verifique em <https://validar.iti.gov.br>

Enilson de Barros Silva
Membro

Documento assinado digitalmente
 **LUIZ ARNALDO FERNANDES**
Data: 25/02/2026 12:45:54-0300
Verifique em <https://validar.iti.gov.br>

Luiz Arnaldo Fernandes
Orientador

*A Deus, por me sustentar em cada etapa e por
transformar sonhos em caminhos possíveis;
Aos meus pais, José e Cleide Mendes, pelo amor
incondicional e pelo exemplo de perseverança;
À minha esposa, Bruna, pelo companheirismo
inabalável;
Aos meus filhos, Manuela e José Francisco, minha
melhor motivação.*

DEDICO

AGRADECIMENTOS

A Deus, o autor da minha fé e sustentador da minha vida. Nos momentos de incerteza, sua Palavra foi meu refúgio: *“Ainda que a figueira não floresça e não haja frutos nas videiras, ainda que a colheita de azeitonas não dê em nada e os campos fiquem vazios e improdutivos, ainda que os rebanhos morram nos campos e os currais fiquem vazios, mesmo assim me alegrarei no Senhor; exultarei no Deus de minha salvação!”* (Habacuque 3:17-18).

Aos meus pais, José e Cleide Mendes, e à minha irmã, Carolina. Vocês são meu alicerce e meu primeiro exemplo de dedicação. Obrigado por acreditarem em mim e por me ensinarem que a educação e o caráter são bens inestimáveis.

À minha esposa, Bruna, meu porto seguro. Obrigado por caminhar ao meu lado, dividindo os fardos e multiplicando as alegrias. Aos meus filhos, Manuela e José Francisco, presentes divinos que ressignificaram minha jornada e renovam minhas forças.

Aos meus sogros, Francisco e Prisca, e aos meus cunhados, Susana e Abraão. Minha gratidão pelo acolhimento generoso e pelo apoio familiar sempre presente.

Aos meus avós, Manoel, Arlinda, Pedro (*in memoriam*) e Manoelina (*in memoriam*). Seus exemplos de vida e luta permanecem vivos em minha memória e em meu coração.

Aos meus tios, Jair, Ivânia, Maria Zilma, Gerson, Joyce, Josilene, Gilson, João, Ailma, Gilda, Ademir, Anita, Ana, Jorge e Cida. A presença e o auxílio de vocês em diversas etapas da minha vida foram fundamentais para que eu chegasse até aqui.

Aos meus primos, Bruna, Felipe, Jefferson, Jéssica, João Lucas, Jônatas, Larissa, Melquisedeque e Melissa, pela amizade e torcida constante.

Aos meus amigos Vinícius e Julyard, presenças constantes desde sempre. A amizade de vocês é anterior a qualquer título e mais valiosa que todos eles.

Ao Professor Luiz Arnaldo Fernandes, pela orientação. Sua condução sábia, paciência e rigor científico não apenas moldaram este trabalho, mas contribuíram decisivamente para o meu amadurecimento profissional.

Aos membros da banca examinadora, Professores Fernando Colen, Rodinei, Amário e Enilson. Agradeço pela leitura atenta e pelas valiosas considerações que elevaram a qualidade final desta tese.

À Universidade Federal de Minas Gerais (UFMG) e ao Instituto de Ciências Agrárias (ICA), pela excelência no ensino e pela infraestrutura disponibilizada para o desenvolvimento desta pesquisa.

À Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG), à Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) e ao Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), pelo suporte financeiro essencial para a realização deste trabalho.

Aos amigos e colegas de laboratório e pós-graduação, pelo convívio diário, pelas trocas de conhecimento e pelo apoio mútuo nos desafios da vida acadêmica.

A todos que torceram por mim e contribuíram, de alguma forma, para a realização deste sonho.

Não vivam preocupados com coisa alguma; em vez disso, orem a Deus pedindo aquilo de que precisam e agradecendo-lhe por tudo que ele já fez. Então vocês experimentarão a paz de Deus, que excede todo entendimento e que guardará seu coração e sua mente em Cristo Jesus.

Filipenses 4:6-7 (Nova Versão Transformadora)

Fertilizantes granulados à base de biocarvão com aglutinantes agroindustriais para melhorar a eficiência de uso do fósforo e a saúde de solos tropicais

RESUMO

O fósforo (P) é rapidamente fixado em Latossolos intemperizados, de modo que a eficiência de recuperação do nutriente proveniente de fertilizantes solúveis é baixa. O biocarvão tem sido proposto como matriz para fertilizantes de liberação lenta; todavia, sua aplicação na forma de pó impõe limitações operacionais, como emissão de material particulado e perdas por deriva eólica. Assim, a presente tese teve como objetivo desenvolver e avaliar fertilizantes granulados à base de biocarvão (*Biochar-based granular fertilizers* – BBGFs), formulados com finos de carvão de eucalipto (*Eucalyptus urograndis*) e fosfato natural reativo na proporção 3:1 (m/m), empregando três aglutinantes agroindustriais: manipueira (CW), extrato pirolenhoso (PE) e bio-óleo (BO). Três estudos complementares foram conduzidos em Latossolo Vermelho-Amarelo distrófico sob Cerrado. No primeiro, avaliaram-se as propriedades granulares dos BBGFs produzidos com cinco proporções de aglutinante (50, 75, 100, 125 e 150% da massa da mistura biocarvão–fosfato), em delineamento inteiramente casualizado (DIC), esquema fatorial 3 x 5; os grânulos com atributos mais favoráveis (75 a 150%) foram selecionados para um bioensaio com feijão comum (*Phaseolus vulgaris* L., cv. BRSMG Uai), em DIC, fatorial 3 x 4 + 4 (três aglutinantes, quatro proporções e quatro controles: solo sem fertilização, fosfato natural, biocarvão + fosfato natural e biocarvão isolado). No segundo, os BBGFs foram incubados por 10 e 40 dias, em DIC, fatorial 3 x 4 + 4, para avaliação das atividades de β -glicosidase, fosfatase ácida e arilsulfatase, além de atributos químicos do solo. No terceiro, avaliou-se a eficácia agrônômica e o efeito residual dos BBGFs em cinco ciclos consecutivos de *Urochloa brizantha* BRS Paiaguás, em blocos casualizados, fatorial 3 x 4 + 4, incluindo controle de P solúvel (KH_2PO_4). Os grânulos com BO apresentaram maior resistência mecânica e densidade, enquanto os com PE exibiram maior índice de salinidade. Os BBGFs promoveram incrementos na matéria seca de parte aérea e de raízes do feijoeiro em relação ao solo sem fertilização, com destaque para os BBGFs-PE, que proporcionaram aumentos de 123,73% e 755,17%, respectivamente. No segundo estudo, todas as formulações elevaram as atividades enzimáticas acima dos controles, com incrementos superiores a 8%. Os BBGFs-BO a 150% mantiveram a atividade enzimática mais estável ao longo do tempo. Os BBGFs-CW foram os mais eficazes no aumento de P disponível ($24,0 \text{ mg kg}^{-1}$), enquanto BBGFs-BO e BBGFs-PE elevaram o carbono orgânico do solo e a capacidade de troca catiônica em até 430% e 163%, respectivamente. No terceiro estudo, os BBGFs-PE a 125% e 150% alcançaram eficácia agrônômica relativa de 96,8% e 101,3%, respectivamente. Na proporção de 150%, os BBGFs-PE elevaram a absorção total de P em 6,5% acima do KH_2PO_4 . Os BBGFs-CW apresentaram fase inicial de baixa liberação, com recuperação a partir do quarto ciclo. Os BBGFs-BO restringiram a produção de biomassa nas proporções mais altas do aglutinante, porém promoveram o maior Índice de Qualidade do Solo. Os BBGFs-PE nas proporções de 125 e 150% constituem a alternativa mais equilibrada para a substituição de fontes fosfatadas solúveis, por combinar eficácia agrônômica, suprimento sustentado de P e melhoria da qualidade edáfica.

Palavras-chave: Atividade enzimática. Ciclagem de nutrientes. Fertilidade do solo. Fertilizantes de liberação lenta. Pirólise. Qualidade do solo.

Biochar-based granular fertilizers with agro-industrial binders to enhance phosphorus use efficiency and soil health in tropical soils

ABSTRACT

Phosphorus (P) is rapidly fixed in highly weathered Oxisols, resulting in low nutrient recovery efficiency from soluble fertilizers. Biochar has been proposed as a matrix for slow-release fertilizers; however, its application in powder form poses operational limitations, such as particulate matter emission and wind-drift losses. Therefore, the objective of this thesis was to develop and evaluate biochar-based granular fertilizers (BBGFs) produced from eucalyptus charcoal fines (*Eucalyptus urograndis*) and reactive natural phosphate at a 3:1 ratio (w/w), using three agro-industrial binders: cassava wastewater (CW), pyroligneous extract (PE), and bio-oil (BO). Three complementary studies were carried out in a dystrophic Red-Yellow Oxisol under Cerrado vegetation. In the first, the granular properties of BBGFs produced with five binder proportions (50, 75, 100, 125, and 150% of the biochar–phosphate mixture weight) were evaluated in a completely randomized design (CRD), 3 x 5 factorial scheme; the granules with the most favorable attributes (75 to 150%) were selected for a bioassay with common bean (*Phaseolus vulgaris* L., cv. BRSMG Uai) in a CRD, 3 x 4 + 4 factorial scheme (three binders, four proportions, and four controls: unfertilized soil, natural phosphate, biochar + natural phosphate, and biochar alone). In the second, BBGFs were incubated for 10 and 40 days in a CRD, 3 x 4 + 4 factorial scheme, to assess β -glucosidase, acid phosphatase, and arylsulfatase activities, as well as soil chemical properties. In the third, the agronomic effectiveness and residual effect of BBGFs were evaluated over five successive cropping cycles of *Urochloa brizantha* BRS Paiaguás in a randomized block design, 3 x 4 + 4 factorial scheme, including a soluble P control (KH_2PO_4). BO granules exhibited the highest crushing strength and density, whereas PE granules showed the highest salinity index. BBGFs promoted increases in shoot and root dry matter of common bean compared to unfertilized soil, particularly BBGFs-PE, which increased shoot and root biomass by 123.73% and 755.17%, respectively. In the second study, all formulations enhanced enzymatic activities above controls, with increases exceeding 8%. BBGFs-BO at 150% maintained the most stable enzymatic activity over time. BBGFs-CW were the most effective in increasing available P (24.0 mg kg^{-1}), while BBGFs-BO and BBGFs-PE enhanced soil organic carbon and cation exchange capacity by up to 430% and 163%, respectively. In the third study, BBGFs-PE at 125% and 150% achieved relative agronomic effectiveness of 96.8% and 101.3%, respectively. At the 150% proportion, BBGFs-PE increased total P uptake by 6.5% over KH_2PO_4 . BBGFs-CW exhibited an initial low-release phase, with agronomic recovery from the fourth cycle onward. BBGFs-BO restricted biomass production at the highest binder proportions but promoted the highest Soil Quality Index. BBGFs-PE at the 125 and 150% proportions represent the most balanced alternative for replacing soluble phosphate sources, as they combine agronomic effectiveness, sustained P supply, and improved soil quality.

Keywords: Enzymatic activity. Nutrient cycling. Soil fertility. Slow-release fertilizers. Pyrolysis. Soil quality.

SUMÁRIO

1	INTRODUÇÃO.....	12
2	OBJETIVOS	15
2.1	Objetivo Geral.....	15
2.2	Objetivos Específicos.....	15
3	REVISÃO DE LITERATURA	16
3.1	Biocarvão como alternativa sustentável	16
3.2	Matérias-primas e temperatura de pirólise nas propriedades físico-químicas do biocarvão 18	
3.3	Impactos do biocarvão na qualidade biológica do solo	20
3.4	Desafios dos solos tropicais e o biocarvão como estratégia de eficiência	21
3.5	Referências.....	23
4	ARTIGOS.....	27
4.1	Artigo 1 – Granulated organomineral fertilizers from by-products of the agricultural and forestry sector.....	27
	Abstract.....	28
1	INTRODUCTION.....	29
2	MATERIALS AND METHODS.....	29
3	RESULTS.....	34
4	DISCUSSION.....	38
	REFERENCES	42
4.2	Artigo 2 – Biochar-based granular fertilizers with agro-industrial binders enhance enzymatic activity and nutrient cycling in tropical Oxisols.....	45
	Abstract.....	46
1	INTRODUCTION.....	47
2	MATERIALS AND METHODS.....	48
2.1	Biochar Production	48
2.2	Physical and Chemical Characteristics of Biochar and Binders.....	48
2.3	Biochar-Based Fertilizers Production.....	50
2.4	Experimental Design	50
2.5	Soil Enzyme Activity and Chemical Analysis.....	51
2.6	Statistical Analysis.....	52
3	RESULTS.....	52
3.1	Physical and Chemical Analysis.....	52
3.2	β-Glucosidase	53
3.3	Acid Phosphatase	54
3.4	Arylsulfatase.....	55
3.5	Comparative Effects of BBGFs on Soil Enzyme Activities	55
3.6	Principal Component Analysis of Soil Properties and Enzyme Activities over Time	56
4	DISCUSSION.....	59

5	CONCLUSIONS.....	63
	References.....	64
	APÊNDICE A	69
4.3	Artigo 3 – Unlocking residual phosphorus in tropical soils: The role of agro-industrial binders in biochar-based granular fertilizers efficiency and soil health	73
	Abstract.....	74
	INTRODUCTION.....	75
	MATERIALS AND METHODS.....	76
	Production and characterization of biochar-based fertilizers	76
	Greenhouse pot experiment	77
	Soil quality index	79
	Statistical analysis.....	80
	RESULTS.....	80
	Morphological analysis by scanning electron microscopy (SEM)	80
	Soil chemical analysis	83
	Soil Quality Index (SQI _{FERTBIO}) and soil functional indicators	85
	Paiaguás grass biomass production and relative agronomic effectiveness.....	87
	Nutrient uptake.....	92
	Phosphorus use efficiency	99
	DISCUSSION.....	102
	Morphological characterization of biochar-based granular fertilizers (BBGFs).....	102
	Soil properties	103
	Biochar-Based Granular Fertilizers (BBGFs) on soil health indicators (SQI _{FERTBIO}).....	106
	Plant growth and agronomic efficiency of fertilizers	109
	Phosphorus dynamics: Uptake and Use Efficiency by Paiaguás grass	113
	Calcium, Magnesium and Potassium uptake	114
	CONCLUSIONS.....	115
	REFERENCES	116
	APÊNDICE B	121
5	CONSIDERAÇÕES FINAIS.....	129

1 INTRODUÇÃO

A crescente demanda global por alimentos impõe pressão contínua sobre os sistemas agrícolas, particularmente nos trópicos, onde a intensificação produtiva esbarra em limitações edáficas severas (BASAK et al., 2022; LIU; LAL, 2015). Entre os nutrientes essenciais, o fósforo (P) constitui o fator mais restritivo à produção vegetal em solos intemperizados, como os Latossolos, que predominam nas regiões agrícolas do Brasil. Nesses ambientes, a predominância de oxi-hidróxidos de ferro e alumínio na fração argila, aliada à elevada acidez, promove a fixação específica do P por meio de reações de adsorção e precipitação que convertem rapidamente as formas lábeis aplicadas via fertilizantes em formas indisponíveis às plantas (MARSCHNER; RENGEL, 2023; NOVAIS; SMYTH, 1999). Em consequência, a eficiência de recuperação do P proveniente de fertilizantes solúveis dificilmente ultrapassa 20% no primeiro ciclo de cultivo (SOLANKI et al., 2015), o que obriga os agricultores a aplicar doses que excedem a exportação pelas culturas e resulta no acúmulo progressivo de reservas de P de difícil mobilização (KHAN et al., 2025; NOVAIS; SMYTH, 1999).

Para compensar essa baixa eficiência, o manejo convencional recorre à aplicação de fertilizantes minerais de alta solubilidade, prática que, embora necessária, é intrinsecamente suscetível a perdas no sistema solo-planta e onera significativamente os custos de produção (CHEN et al., 2018; LAM et al., 2022; NOVAIS; SMYTH, 1999). Diante desse panorama, torna-se imperativo o desenvolvimento de tecnologias de fertilização capazes de sincronizar a liberação de nutrientes com a demanda das culturas, aumentar a eficiência de uso do P e, simultaneamente, promover a melhoria da qualidade do solo em condições tropicais (CARNEIRO et al., 2021; HAN et al., 2025; SANTOS JÚNIOR et al., 2024).

O biocarvão, material sólido rico em carbono obtido pela conversão termoquímica de biomassa em ambiente com oxigênio limitado, tem sido amplamente investigado como condicionador de solo e potencial veículo para a formulação de fertilizantes de eficiência aprimorada (GHODAKE et al., 2021; LEHMANN; JOSEPH, 2009; LOPES et al., 2021; LUO et al., 2025; SANTOS JÚNIOR et al., 2024). A estrutura porosa, a elevada área superficial e a presença de grupos funcionais reativos conferem ao biocarvão capacidade de aumentar a capacidade de troca catiônica, reter água e nutrientes e neutralizar a acidez de solos tropicais (JOSEPH et al., 2021; SANTOS JÚNIOR et al., 2024; TOMCZYK; SOKOŁOWSKA; BOGUTA, 2020). Ademais, o carbono aromático presente na matriz do biocarvão é altamente recalcitrante, o que posiciona esse material como estratégia promissora para o sequestro de carbono e a mitigação de emissões de gases de efeito estufa (BASAK et al., 2022; JOSEPH et al., 2021; LEHMANN; JOSEPH, 2009; SONG et al., 2024).

A utilização do biocarvão como matriz para fertilizantes (*Biochar-based fertilizers* – BBFs) representa uma evolução conceitual que redefine a finalidade do material para além do condicionamento edáfico. Nessa abordagem, o biocarvão atua como reservatório estrutural que protege fisicamente as partículas de fosfato em sua rede porosa, retardando o contato direto com os sítios de sorção do solo e propiciando liberação gradual e sincronizada com a demanda vegetal (CARNEIRO et al., 2021; HAN et al., 2025; HOU et al., 2024; POGORZELSKI et al., 2020). Estudos conduzidos com BBFs demonstraram que esses materiais alteram a dinâmica do P, por meio do aumento das frações lábeis e moderadamente lábeis no solo ao longo do tempo, com incrementos de produtividade e eficiência de uso superiores aos obtidos com fontes solúveis convencionais (CARNEIRO et al., 2021; LUSTOSA FILHO et al., 2017; LUSTOSA FILHO et al., 2020; SILVA et al., 2024).

Entretanto, a viabilidade agronômica e operacional do biocarvão enfrenta entraves que restringem sua adoção em larga escala. A demanda por doses elevadas para a obtenção de ganhos produtivos expressivos impõe desafios logísticos (JEFFERY et al., 2017; FRIMPONG et al., 2025). Ademais, o manejo do material na forma de pó resulta na emissão de partículas finas durante o manuseio e o preparo do solo, o que representa riscos à saúde respiratória dos trabalhadores rurais. A baixa densidade das partículas favorece, ainda, perdas por deriva eólica em aplicações a lanço, o que prejudica a uniformidade de distribuição e a eficiência da fertilização (LI; BAIR; PARIKH, 2018).

Com isso, a granulação do biocarvão com fontes de nutrientes configura-se como uma estratégia tecnológica para mitigar os entraves operacionais do material e elevar a eficiência da fertilização (LOPES et al., 2021; SANTOS JÚNIOR et al., 2024). Nesse cenário, o emprego de aglutinantes agroindustriais na síntese de fertilizantes granulados à base de biocarvão (*Biochar-based granular fertilizers* – BBGFs) representa uma abordagem pertinente. Tal processo integra a valorização de coprodutos das cadeias agrícola e florestal à obtenção de grânulos com atributos físico-químicos moduláveis (SANTOS JÚNIOR et al., 2025a). A manipueira (CW), proveniente do processamento da mandioca, o extrato pirolenhoso (PE) e o bio-óleo (BO), subprodutos da produção de carvão vegetal, constituem-se como ligantes potenciais para a síntese de BBGFs, de modo a conferir estabilidade e qualidade aos grânulos (SANTOS JÚNIOR et al., 2025a; CHENG et al., 2022).

Para além das propriedades físico-químicas dos grânulos, é fundamental compreender como os BBGFs interagem com o sistema solo ao longo do tempo. Uma vez que os BBGFs podem modular a atividade da comunidade microbiana (LOPES et al., 2021; MELO et al., 2022; YUAN et al., 2022), a avaliação da resposta biológica do solo torna-se etapa indispensável para validar a funcionalidade desses fertilizantes. A atividade enzimática do solo, mediada por enzimas como β -glicosidase, fosfatase ácida e arilsulfatase, constitui indicador sensível das transformações na ciclagem de carbono, fósforo e enxofre, respectivamente, e reflete a capacidade funcional da comunidade microbiana (MENDES et al., 2019; MENDES et al., 2021; LOPES et al., 2021). Estudos conduzidos com biocarvão demonstraram que sua incorporação ao solo pode estimular a atividade enzimática e a biomassa microbiana em doses moderadas (aproximadamente 20 t ha⁻¹), porém promover efeito inibitório em doses elevadas (> 30 t ha⁻¹), devido à adsorção de enzimas e substratos ou à presença de compostos tóxicos (GODLEWSKA; OK; OLESZCZUK, 2021; LOPES et al., 2021).

Apesar dos avanços no desenvolvimento de BBFs, lacunas importantes permanecem no que concerne à avaliação integrada de BBGFs formulados com aglutinantes agroindustriais. Em particular, são escassos os estudos que abordem simultaneamente as propriedades físico-mecânicas dos grânulos, seus efeitos sobre a biologia do solo e sua eficácia agronômica em cultivos sucessivos sob condições tropicais. Diante dessas lacunas, a presente tese foi organizada em três estudos complementares, precedidos por uma revisão de literatura que fundamenta os conceitos relativos à produção e às propriedades do biocarvão, seus impactos na qualidade biológica do solo e os desafios da fertilização fosfatada em solos tropicais. No primeiro estudo, produziram-se e caracterizaram-se BBGFs formulados com biocarvão de eucalipto, fosfato natural reativo e os aglutinantes CW, PE e BO, e avaliou-se seu efeito no crescimento inicial de feijoeiro comum. A hipótese formulada foi de que o tipo de aglutinante altera a qualidade físico-química dos grânulos, incluindo a capacidade de troca iônica e a biodisponibilidade de nutrientes, com reflexos na produção de matéria seca da parte aérea e de raízes de *Phaseolus vulgaris* L. No segundo

estudo, avaliou-se o impacto dos BBGFs sobre a atividade enzimática (β -glicosidase, fosfatase ácida e arilsulfatase) e os atributos químicos do solo em dois períodos de incubação em Latossolo. Hipotetizou-se que a incorporação de CW, PE e BO aos BBGFs altera a atividade enzimática e as propriedades químicas do solo, uma vez que PE e BO, por potencialmente conterem compostos tóxicos derivados da pirólise, poderiam exercer efeito inibitório sobre a microbiota, enquanto CW, de natureza predominantemente lábil, estaria sujeita à rápida mineralização. No terceiro estudo, determinou-se a eficácia agronômica e o efeito residual dos BBGFs na produção de biomassa e absorção de P em cinco ciclos consecutivos de *Urochloa brizantha* cv. BRS Paiaguás, e propôs-se um Índice de Qualidade do Solo (SQI) que integra fertilidade química e atividade enzimática. A hipótese foi de que os BBGFs formulados com aglutinantes agroindustriais proporcionam suprimento sustentado de P superior ao de fontes solúveis a longo prazo, com consequente melhoria da eficiência de uso do P e da qualidade edáfica em Latossolo tropical. Essa abordagem sequencial, do desenvolvimento tecnológico à validação agronômica, confere à pesquisa uma perspectiva abrangente e aplicada ao manejo sustentável da fertilidade de solos tropicais. As principais conclusões e perspectivas são apresentadas nas Considerações Finais.

2 OBJETIVOS

2.1 Objetivo Geral

– Desenvolver e avaliar fertilizantes granulados à base de biocarvão (BBGFs), formulados com finos de carvão de eucalipto e fosfato natural reativo empregando manipueira (CW), extrato pirolenhoso (PE) e bio-óleo (BO) como aglutinantes, para melhorar a eficiência de uso do fósforo e a qualidade do solo em condições tropicais.

2.2 Objetivos Específicos

- Caracterizar as propriedades granulares e físico-químicas dos BBGFs e avaliar seu efeito sobre o crescimento inicial de plantas de feijão comum (*Phaseolus vulgaris* L.) em casa de vegetação.
- Avaliar o impacto dos BBGFs sobre as atividades enzimáticas (β -glicosidase, fosfatase ácida e arilsulfatase) e os atributos químicos do solo em dois períodos de incubação em Latossolo.
- Determinar a eficácia agrônômica, a eficiência de uso do fósforo e o efeito residual dos BBGFs em cinco ciclos consecutivos de cultivo de *Urochloa brizantha* BRS Paiaguás, bem como propor um Índice de Qualidade do Solo integrando atributos de fertilidade e atividade enzimática.

3 REVISÃO DE LITERATURA

3.1 Biocarvão como alternativa sustentável

O biocarvão é definido como um material sólido rico em carbono, produzido pela conversão termoquímica de biomassa em ambiente com oxigênio limitado ou ausente (LEHMANN; JOSEPH, 2009; WANG; WANG, 2019; GHODAKE et al., 2021). Embora o biocarvão seja caracterizado por sua estabilidade química, o grau de recalcitrância não é uniforme; ele é diretamente dependente das condições de processamento, sobretudo da temperatura de pirólise. Temperaturas mais elevadas (acima de 400–500 °C) favorecem a condensação de anéis aromáticos e a redução das razões molares H:C e O:C, conferindo ao material maior resistência à degradação biológica e química no solo (LEHMANN; JOSEPH, 2009; LUSTOSA FILHO et al., 2025).

O desenvolvimento tecnológico do biocarvão fundamenta-se nos estudos sobre a gênese das Terras Pretas de Índio (TPI) da Bacia Amazônica. Contudo, é fundamental distinguir que a fertilidade sustentada desses antrossolos não resulta isoladamente da presença do carbono pirogênico. Evidências pedológicas e arqueológicas demonstram que a TPI se originou, em grande parte, de zonas de descarte de resíduos (*middens*) e práticas agrícolas domésticas, resultando na acumulação simultânea de carvão, cinzas, ossos de animais e excrementos (SCHMIDT et al., 2014; GLASER; BIRK, 2012). Esse processo gerou um ambiente edáfico no qual o biocarvão atua como uma matriz estável que retém os nutrientes aportados pelos resíduos orgânicos, uma funcionalidade que o biocarvão moderno busca adaptar-se através do desenvolvimento de fertilizantes organominerais (LEHMANN; JOSEPH, 2009; MELO et al., 2022; SANTOS JÚNIOR et al., 2024).

A distribuição dos produtos da pirólise é governada pela cinética térmica e pela termodinâmica do reator. Na pirólise lenta, a tecnologia predominante para a produção de biocarvão, operam-se taxas de aquecimento brandas (0,1–1,0 °C/s) e tempos de residência de sólidos estendidos, que podem variar de minutos a dias (AL-RUMAIHI et al., 2022; OSMAN et al., 2023). Essas condições de exposição prolongada maximizam as reações de desidratação e a repolimerização de compostos aromáticos, resultando em rendimentos elevados de uma matriz sólida estável e rica em carbono (AL-RUMAIHI et al., 2022; GHODAKE et al., 2021; YOGALAKSHMI et al., 2022). Em contraste, a pirólise rápida emprega taxas de aquecimento de 10–200 °C/s e tempos de residência de vapor extremamente curtos (0,5–10 s) para mitigar o craqueamento secundário e maximizar a fração líquida (bio-óleo) (LI et al., 2023). Já a pirólise *flash*, caracterizada por taxas de aquecimento superiores a 1000 °C/s e tempos de residência inferiores a 1 s, fragmenta abruptamente a biomassa para maximizar a produção imediata de voláteis (AL-RUMAIHI et al., 2022). Por fim, a fração gasosa (gás de síntese), composta por CO, CO₂, H₂ e hidrocarbonetos, origina-se predominantemente de mecanismos de fragmentação de ligações covalentes em temperaturas elevadas (OSMAN et al., 2023).

A composição lignocelulósica da biomassa precursora determina a estequiometria e a qualidade dos produtos da devolatilização (LI et al., 2023; LEHMANN; JOSEPH, 2009). A degradação térmica obedece a uma sequência de estabilidade química distinta: a hemicelulose, o polímero mais instável, decompõe-se predominantemente entre 200 e 315 °C, liberando voláteis leves, CO₂ e ácidos orgânicos (YOGALAKSHMI et al., 2022; GHODAKE et al., 2021). A celulose degrada-se numa faixa intermediária e estreita (300–390 °C) através de mecanismos de despolimerização e clivagem glicosídica, sendo a principal responsável pela formação de levoglucosana e pelo rendimento de bio-óleo (OSMAN et al., 2023; VUPPALADADIYAM

et al., 2023). Em contraste, a lignina, devido à sua estrutura polimérica aromática e tridimensional, exibe a maior resistência térmica, degradando-se lentamente ao longo de uma ampla faixa (160–900 °C) e consolidando-se como a fonte primária do esqueleto de carbono fixo e da matriz recalcitrante do biocarvão (VUPPALADADIYAM et al., 2023; LI et al., 2023).

É válido destacar que a formação da estrutura recalcitrante em biocarvões derivados de biomassas não lignocelulósicas, tais como lodos de esgoto, dejetos animais e resíduos alimentares, distingue-se fundamentalmente das matrizes vegetais. Enquanto a estabilidade em biocarvões de madeira é regida pela polimerização da lignina (LEHMANN; JOSEPH, 2009; SEOW et al., 2022), nessas matrizes alternativas, a recalcitrância química advém da degradação térmica de uma estrutura complexa, rica em proteínas, lipídeos e minerais (HU; CHEN, 2025; LI; JIANG, 2017). Essa composição favorece reações de desaminação e Maillard, resultando na incorporação de heteroátomos (como nitrogênio e enxofre) à rede carbônica e na formação de estruturas heterocíclicas estáveis (LI; JIANG, 2017; WANG et al., 2024).

Simultaneamente, a estabilidade física desses materiais é catalisada e assegurada pela elevada fração inorgânica (cinzas). Os metais presentes na biomassa atuam como catalisadores que aceleram a aromatização da matriz orgânica, enquanto cátions metálicos e fosfatos fundem-se para formar fases cristalinas (como a apatita) e complexos organominerais que conferem proteção física à matriz carbônica contra a oxidação e imobilizam nutrientes (HU; CHEN, 2025; LUSTOSA FILHO et al., 2025). Dessa forma, o biocarvão proveniente dessas fontes consolida-se como uma matriz mineral funcionalizada, por meio da qual a recalcitrância é garantida pela interação sinérgica entre a fase mineral abundante e as estruturas heterocíclicas formadas (CAO et al., 2024; LU et al., 2013).

Contudo, o controle rigoroso dos parâmetros de pirólise é vital para a segurança ambiental. Condições operacionais severas, especificamente temperaturas superiores a 600 °C combinadas com longos tempos de residência dos vapores, favorecem a ocorrência de reações secundárias indesejadas (SIA; KOOH; LIM, 2025). Nesse cenário, compostos voláteis que deveriam ser liberados acabam sofrendo processos de condensação e polimerização sobre a superfície do material, o que resulta na síntese e deposição de contaminantes orgânicos persistentes, como os Hidrocarbonetos Policíclicos Aromáticos (HPAs) (LI et al., 2023; SIA; KOOH; LIM, 2025). Diante disso, estudos ecotoxicológicos indicam que o monitoramento analítico e o uso de doses agronômicas prudentes são estratégias essenciais para mitigar riscos à biota edáfica, garantindo que o biocarvão cumpra sua função de condicionador de solo sem introduzir toxicidade (COSTA et al., 2024; JOSEPH et al., 2021; SIA; KOOH; LIM, 2025). O biocarvão difere, portanto, do carvão vegetal comum justamente por ser desenhado especificamente para aplicações no solo, visando a maximização de benefícios agronômicos com riscos ambientais controlados (LEHMANN; JOSEPH, 2009).

Além dos benefícios agronômicos, o biocarvão atua como uma ferramenta estratégica de manejo de carbono e mitigação climática. O seu potencial de sequestro não se restringe à estabilidade intrínseca do carbono pirogênico; a sua aplicação promove a estabilização do carbono orgânico do solo (COS) nativo através de mecanismos de proteção física (formação de macroagregados) e do aumento da eficiência de uso do carbono pelas comunidades microbianas (SONG et al., 2024; JOSEPH et al., 2021).

Adicionalmente, o biocarvão contribui para a mitigação das emissões de óxido nitroso (N₂O). Embora o processo de pirólise volatilize parte do nitrogênio da biomassa (DOMINGUES et al., 2020; SANTOS JÚNIOR et al., 2024), o material resultante atua no solo como um mediador de elétrons e

corretivo de acidez, facilitando a redução completa do N_2O a nitrogênio molecular (N_2) durante a desnitrificação microbiana, evitando assim a emissão do gás de efeito estufa (JOSEPH et al., 2021; BASAK et al., 2022). Esse mecanismo, aliado à capacidade do biocarvão de atuar como matriz para a retenção de nutrientes, resulta em menor perda de nitrogênio para o ambiente e maior eficiência agrônômica (MELO et al., 2022).

Portanto, a consolidação do biocarvão na agricultura requer uma evolução nas estratégias de manejo. O foco não deve se restringir à aplicação volumosa do material puro, mas sim priorizar o seu uso como matriz tecnológica para o desenvolvimento de Fertilizantes à Base de Biocarvão (BBFs – *Biochar-based fertilizers*) (CARNEIRO et al., 2021; LUO et al., 2025; POGORZELSKI et al., 2020; SANTOS JÚNIOR et al., 2024; SANTOS JÚNIOR et al., 2025a). Essa abordagem sincroniza a liberação de nutrientes com a demanda das culturas e aumenta a eficiência de uso de nitrogênio e fósforo, elementos críticos em solos tropicais intemperizados (CARNEIRO et al., 2021; GUO et al., 2025; SANTOS JÚNIOR et al., 2024). Consequentemente, tornam-se viáveis incrementos de produtividade com doses agrônômicas reduzidas (frequentemente próximas a 1,5 t/ha ou inferiores) (AN et al., 2022; MELO et al., 2022). Tal estratégia concilia a viabilidade econômica com a sustentabilidade ambiental e permite a substituição parcial de fertilizantes minerais solúveis (LUO et al., 2025; LUSTOSA FILHO et al., 2025).

3.2 Matérias-primas e temperatura de pirólise nas propriedades físico-químicas do biocarvão

A produção de biocarvão no Brasil fundamenta-se em uma expressiva disponibilidade de biomassa residual. O setor agrícola gera anualmente cerca de 850 milhões de toneladas de resíduos culturais, enquanto a pecuária contribui com, aproximadamente, 1,2 bilhão de toneladas de dejetos ao ano (PROCHNOW et al., 2024). Essa abundância, contudo, não se traduz em uniformidade do produto carbonáceo. A composição da biomassa precursora dita a trajetória do carbono e dos constituintes inorgânicos durante a pirólise (OTONI et al., 2024).

Em biomassas vegetais, a perda de componentes voláteis resulta na concentração de carbono fixo, gerando materiais com alto teor de carbono e baixo teor de cinzas, conforme observado na Tabela 1 para o bagaço de cana-de-açúcar (DOMINGUES et al., 2020; LEHMANN; JOSEPH, 2009).

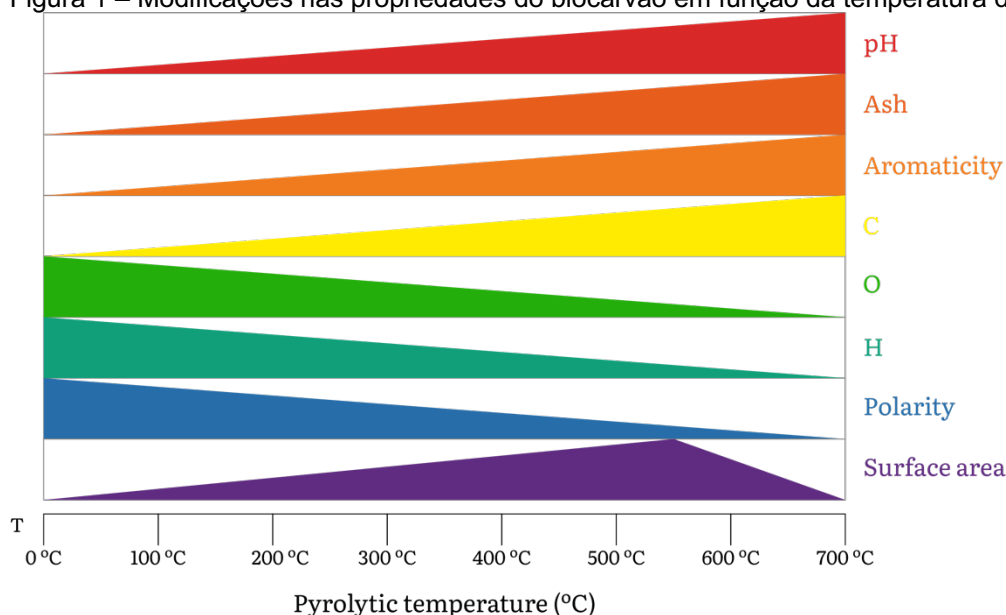
Tabela 1 – Caracterização de biocarvões derivados de diferentes matérias-primas, produzidos em temperaturas comumente utilizadas para a aplicação de material pirolisado no solo.

Biocarvão	Temperatura °C	Cinzas %	C	N	P	K	Ca	Mg	Referências
g kg ⁻¹									
Cama de aves	350	51,2	261,0	28,8	37,5	31,6	143,0	17,3	OTONI et al. (2024)
Palha de milho	350	6,2	634,0	15,2	6,5	5,0	0,3	1,0	
Esterco suíno	450	50,3	382,7	30,0	48,8	36,7	70,2	58,4	SARFARAZ et al. (2020)
Bagaço de cana-de-açúcar	350	1,9	747,0	-	-	-	-	-	DOMINGUES et al. (2020)
	450	2,1	816,0	-	-	-	-	-	
	750	2,2	905,0	-	-	-	-	-	
Esterco bovino	450	36,2	167,9	6,4	32,6	5,4	19,3	23,2	SANTOS JÚNIOR et al. (2024)
Lodo de esgoto	450	24,0	271,0	16,1	33,8	5,4	45,4	4,1	ZELAYA et al. (2019)

Em contraste, biocarvões derivados de esterco animal e lodos de esgoto apresentam uma dinâmica distinta, governada pela concentração relativa de cinzas. Nesses materiais, a fração mineral não é volatilizada e se acumula na matriz sólida, reduzindo proporcionalmente o teor final de carbono (SARFARAZ et al., 2020; ZELAYA et al., 2019). Dados analíticos demonstram que biocarvões de resíduos animais podem apresentar teores de cinzas entre, aproximadamente, 30% e 50% (Tabela 1), limitando o teor de carbono a faixas inferiores a 400 g kg^{-1} , mas conferindo ao material elevado caráter alcalino e potencial fertilizante (DOMINGUES et al., 2020; OTONI et al., 2024; SANTOS JÚNIOR et al., 2024; SARFARAZ et al., 2020).

Do ponto de vista termodinâmico, a conversão da biomassa obedece a uma evolução de fases moleculares descrita por Keiluweit et al. (2010) e sintetizada na Figura 1. Em temperaturas moderadas ($300\text{--}450^\circ\text{C}$), ocorre a despolimerização da celulose e hemicelulose, gerando uma fase de transição que preserva uma maior densidade de grupos funcionais oxigenados e a polaridade superficial (Figura 1). A reatividade química nesse estágio é otimizada pela presença de sítios de troca iônica e complexação, fundamentais para a retenção de nutrientes e contaminantes catiônicos via adsorção eletrostática (EL-NAGGAR et al., 2022).

Figura 1 – Modificações nas propriedades do biocarvão em função da temperatura de pirólise (T).



Fonte: Adaptado de GHODAKE et al., 2021.

Com a elevação da temperatura ($>600^\circ\text{C}$), consolida-se a estrutura turbostática, caracterizada pela policondensação de anéis aromáticos e eliminação de grupos funcionais (desidroxilação e descarboxilação) (KEILUWEIT et al., 2010; LEHMANN; JOSEPH, 2009). Esse rearranjo aumenta a aromaticidade e a estabilidade (Figura 1), mas reduz a capacidade de troca catiônica (CTC) (DOMINGUES et al., 2020; TOMCZYK; SOKOŁOWSKA; BOGUTA, 2020).

A área superficial específica tende a aumentar com a temperatura devido à expulsão de voláteis, mas pode sofrer declínio em temperaturas excessivas ou em biomassas ricas em cinzas devido ao colapso de poros e sinterização mineral, limitando a adsorção física em certos regimes térmicos (JOSEPH et al., 2021; LEHMANN; JOSEPH, 2009; TOMCZYK; SOKOŁOWSKA; BOGUTA, 2020). Nesse cenário de alta

temperatura, a imobilização de contaminantes deixa de ser governada pela quimissorção superficial e passa a depender de mecanismos de oclusão física e precipitação (EL-NAGGAR et al., 2022).

A alcalinidade do biocarvão também segue uma tendência de aumento com a temperatura (Figura 1). É fundamental notar que esse comportamento não resulta apenas da perda de grupos funcionais ácidos, mas precipuamente da hidrólise de cátions básicos (carbonatos, óxidos e hidróxidos) formados pela concentração de metais alcalinos na fração de cinzas (DOMINGUES et al., 2020; LEHMANN; JOSEPH, 2009; OTONI et al., 2024).

Portanto, a seleção da matéria-prima e da temperatura de pirólise define a aptidão tecnológica do material. Biocarvões de resíduos animais processados em temperaturas moderadas priorizam a reatividade química e o fornecimento de nutrientes, sendo indicados para o manejo da fertilidade do solo (DOMINGUES et al., 2020; OTONI et al., 2024). Em contrapartida, biocarvões lignocelulósicos produzidos em alta temperatura desenvolvem caráter hidrofóbico e elevada aromaticidade, características que favorecem a estabilidade do carbono (DOMINGUES et al., 2020; SARFAZ et al., 2020; SONG et al., 2024) e a retenção de contaminantes orgânicos, como herbicidas e hidrocarbonetos (JOSEPH et al., 2021; TOMCZYK; SOKOŁOWSKA; BOGUTA, 2020).

3.3 Impactos do biocarvão na qualidade biológica do solo

Os microrganismos presentes no solo são vitais para os processos bioquímicos, pois atuam na manutenção da fertilidade do solo e na saúde do ecossistema. Nessa perspectiva, solos de alta qualidade caracterizam-se não apenas pela produtividade, mas pela atividade biológica, eficiência no uso de nutrientes e capacidade de sequestro de carbono (MENDES et al., 2019). Ademais, os microrganismos atuam como bioindicadores precoces de alterações edáficas decorrentes das práticas de manejo adotadas (SANTOS JÚNIOR et al., 2025b).

A incorporação de biocarvão introduz um micro-habitat poroso que altera a dinâmica das comunidades microbianas. Em temperaturas de pirólise elevadas (>500 °C), o material desenvolve uma estrutura aromática que confere estabilidade física aos macroporos e microporos, o que impede seu colapso no solo. Essa estrutura facilita a circulação de água e oxigênio, além de criar refúgios contra predadores e reduzir a competição por recursos, fatores que favorecem a colonização biológica (LEHMANN; JOSEPH, 2009; GHODAKE et al., 2021).

Essa alteração física reflete-se na abundância de grupos bacterianos específicos. Em solos tropicais intemperizados, a aplicação de biocarvão de madeira (400 °C) associado a composto orgânico estimulou a proliferação de gêneros benéficos, tais como *Azospirillum* (fixadores de nitrogênio) e *Conexibacter* (redutores de nitrato e envolvidos na ciclagem de carbono), além de *Bacillus* e *Clostridium*, importantes para a solubilização de fosfato e redução de sulfato (JIEN et al., 2021).

Entretanto, a resposta biológica não é invariavelmente positiva e depende da toxicidade potencial e da dose aplicada. Azeem et al. (2021) reportaram que uma dose elevada (10% p/p) de biocarvão de ossos produzido em temperatura moderada (500 °C) resultou na redução da comunidade de *Proteobacteria*. Embora este filo seja composto majoritariamente por microrganismos copiotróficos, que geralmente proliferam em resposta ao aumento de carbono lábil (PAN et al., 2025), o seu declínio neste caso específico indica um efeito de toxicidade química. A pirólise incompleta da matriz orgânica dos ossos a 500 °C

preservou compostos orgânicos voláteis e óleos residuais que, na alta dose aplicada, criaram condições inibitórias para estes grupos bacterianos, superando o benefício da disponibilidade de nutrientes.

A atividade enzimática, indicador funcional da qualidade do solo, responde a essa dinâmica de dose e tempo. O aumento da atividade de β -glucosidase e urease ocorre até um limite de aplicação (30 Mg ha^{-1}), e decai em doses superiores devido à provável oclusão ou adsorção física das enzimas nos microporos do biocarvão (LOPES et al., 2021). Adicionalmente, essa resposta é temporal: fertilizantes granulados à base de biocarvão promoveram picos de atividade de β -glucosidase, fosfatase ácida e arilsulfatase nos primeiros 10 dias de incubação, seguidos de redução aos 40 dias (SANTOS JÚNIOR et al., 2025b).

Esse comportamento ilustra a transição do efeito *priming*. Inicialmente, ocorre um *priming* positivo (estímulo à mineralização) impulsionado pelo co-metabolismo do carbono lábil presente no biocarvão. Com o tempo e o esgotamento dessa fração lábil, predomina-se o efeito *priming* negativo, no qual a recalcitrância do biocarvão e a formação de complexos organominerais protegem a matéria orgânica nativa da decomposição e favorecem o sequestro de carbono a longo prazo (SANTOS JÚNIOR et al., 2025b; LEHMANN; JOSEPH, 2009).

Em síntese, a resposta biológica ao biocarvão é não-linear e dependente do balanço entre a provisão de habitat físico, a disponibilidade de substratos energéticos (carbono lábil e nutrientes) e a introdução de compostos químicos voláteis (JOSEPH et al., 2021; SANTOS JÚNIOR et al., 2025b). Enquanto doses agronômicas moderadas ($\leq 30 \text{ t ha}^{-1}$) maximizam a atividade enzimática ao fornecerem abrigo e recursos metabólicos (LOPES et al., 2021), aplicações massivas ou materiais com carbonização incompleta induzem toxicidade severa a microrganismos (AZEEM et al., 2021). Portanto, o manejo eficiente requer o ajuste da dose para modular a transição temporal entre o estímulo metabólico inicial e a estabilização conservativa do carbono no solo (BASAK et al., 2022; SONG et al., 2024).

3.4 Desafios dos solos tropicais e o biocarvão como estratégia de eficiência

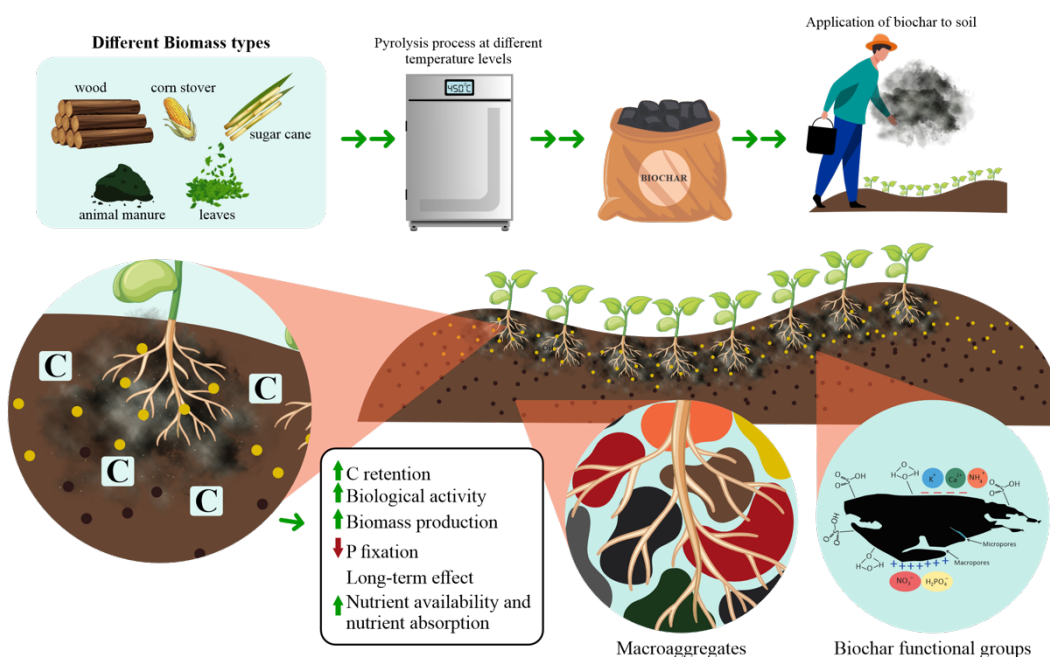
A agricultura em regiões tropicais enfrenta limitações edáficas intrínsecas decorrentes do intenso intemperismo. Solos como os Latossolos caracterizam-se, majoritariamente, pela baixa fertilidade natural, elevada acidez, toxidez por alumínio (Al^{3+}) e, predominantemente, pela alta capacidade de fixação de fósforo (P) em óxidos de ferro e alumínio (NOVAIS; SMYTH, 1999). Tais características resultam em baixa eficiência no uso de nutrientes, de modo que se estima que grande parte do N, P e K aplicados via fertilizantes convencionais sofre imobilização, lixiviação ou volatilização, o que restringe o potencial produtivo das culturas, bem como a produção de alimentos nessas regiões (BASAK et al., 2022; LIU; LAL, 2015).

Para mitigar essas perdas, o manejo convencional recorre à correção da acidez (calagem e gessagem) e à aplicação de fertilizantes minerais contendo macro e micronutrientes (BRIGNOLI; BATISTA, 2025; NOVAIS; SMYTH, 1999). No entanto, a elevada solubilidade e a rápida liberação intrínsecas à maioria dessas fontes convencionais as tornam altamente suscetíveis a perdas no sistema solo-planta, o que resulta em baixa eficiência de uso dos nutrientes. Essa dinâmica impõe a necessidade de aplicações compensatórias em doses elevadas, prática que não apenas onera os custos de produção, mas também exacerba os riscos de impacto ambiental (CHEN et al., 2018; LAM et al., 2022).

Nesse contexto, metanálises indicam que o biocarvão atua como um condicionador eficaz, com os maiores incrementos em produtividade observados justamente em solos ácidos e intemperizados,

impulsionados pelo efeito de calagem e pelo aumento da capacidade de retenção de água e nutrientes (JEFFERY et al., 2017; JOSEPH et al., 2021; SCHMIDT et al., 2021). A estrutura porosa e a recalcitrância do material promovem a retenção de íons, de modo a reduzir a lixiviação em perfis drenáveis (BASAK et al., 2022; GUO et al., 2025). A integração desses mecanismos e o seu impacto potencial na produtividade e na dinâmica de nutrientes e carbono no solo são representados na Figura 2.

Figura 2 – Representação esquemática das interações promovidas pelo biocarvão em solos intemperizados.



Fonte: Elaborado pelo autor, 2025.

Contudo, a viabilidade agrônômica do uso de biocarvão puro esbarra em gargalos logísticos. Estudos experimentais e metanálises indicam que incrementos significativos na produtividade muitas vezes requerem doses de aproximadamente 10 a 40 t ha⁻¹, o que torna a operação inviável em larga escala (FRIMPONG et al., 2025; JEFFERY et al., 2017; MELO et al., 2022; SCHMIDT et al., 2021). Biocarvões de madeira, como os de eucalipto, tendem a apresentar baixa CTC inicial se comparados a materiais ricos em cinzas, o que demanda tempo para oxidação e funcionalização no solo ou doses elevadas para surtir efeitos pertinentes (DOMINGUES et al., 2020; OTONI et al., 2024).

Adicionalmente, a aplicação de biocarvão na forma de pó (partículas finas) impõe riscos operacionais. A baixa densidade do material favorece a perda por deriva durante a aplicação superficial e gera emissões de material particulado que representam riscos à saúde (LI; BAIR; PARIKH, 2018). Dessa forma, a evolução do biocarvão de um condicionador de solo dependente de altas doses para uma tecnologia de fertilização eficiente fundamenta-se na estratégia de formulação via granulação (POGORZELSKI et al., 2020; SANTOS JÚNIOR et al., 2024).

Essa evolução tecnológica consolida-se nos BBFs. Nesta abordagem, o biocarvão atua como uma matriz estável para nutrientes minerais. Estudos promissores demonstram a eficácia dos BBFs como transportadores de nutrientes com características de liberação lenta, e provam que estes materiais alteram positivamente a dinâmica do P por meio do aumento das frações lábeis e moderadamente lábeis no solo

ao longo do tempo (CARNEIRO et al., 2021; LUSTOSA FILHO et al., 2020; SILVA et al., 2024). Esse comportamento indica um mecanismo de proteção contra a fixação específica em óxidos e uma disponibilização sincronizada com a demanda da cultura. Portanto, a tecnologia permite alcançar maior eficiência agrônômica com doses reduzidas, de modo a superar as limitações logísticas do uso de biocarvão puro e a ineficiência das fontes solúveis convencionais (LIU; LAL, 2015; MELO et al., 2022; SANTOS JÚNIOR et al., 2024).

3.5 Referências

AL-RUMAIHI, A. et al. A review of pyrolysis technologies and feedstock: a blending approach for plastic and biomass towards optimum biochar yield. **Renewable and Sustainable Energy Reviews**, v. 167, n. 112715, 2022.

AN, N. et al. Biochar application with reduced chemical fertilizers improves soil pore structure and rice productivity. **Chemosphere**, v. 298, n. 134304, 2022.

AZEEM, M. et al. Effects of sheep bone biochar on soil quality, maize growth, and fractionation and phytoavailability of Cd and Zn in a mining-contaminated soil. **Chemosphere**, v. 282, n. 131016, 2021.

BASAK, B. B. et al. Revamping highly weathered soils in the tropics with biochar application: what we know and what is needed. **Science of The Total Environment**, v. 822, n. 153461, 2022.

BRIGNOLI, F. M.; BATISTA, M. A. Lime and gypsum in Brazilian grain production: a bibliometric review of three decades of research. **International Journal of Agronomy**, v. 2025, n. 3582798, 2025.

CAO, J. et al. Sludge-based biochar preparation: pyrolysis and co-pyrolysis methods, improvements, and environmental applications. **Fuel**, v. 373, n. 132265, 2024.

CARNEIRO, J. S. da S. et al. Long-term effect of biochar-based fertilizers application in tropical soil: agronomic efficiency and phosphorus availability. **Science of The Total Environment**, v. 760, n. 143955, 2021.

CHEN, J. et al. Environmentally friendly fertilizers: a review of materials used and their effects on the environment. **Science of The Total Environment**, v. 613–614, p. 829–839, 2018.

CHENG, J. et al. Synthesis of an environmentally friendly binding material using pyrolysis byproducts and modified starch binder for slow-release fertilizers. **Science of The Total Environment**, v. 819, n. 153146, 2022.

COSTA, V. B. da et al. How much biochar is safe? Exploring potential ecotoxicological consequences for soil invertebrates and plants. **Applied Soil Ecology**, v. 202, n. 105552, 2024.

DOMINGUES, R. R. et al. Enhancing cation exchange capacity of weathered soils using biochar: feedstock, pyrolysis conditions and addition rate. **Agronomy**, v. 10, n. 824, 2020.

EL-NAGGAR, A. et al. Modified and pristine biochars for remediation of chromium contamination in soil and aquatic systems. **Chemosphere**, v. 303, n. 134942, 2022.

FRIMPONG, K. A. et al. Effect of biochar application rates on soil properties and growth of *Amaranthus caudatus*. **Discover Agriculture**, v. 3, n. 21, 2025.

GHODAKE, G. S. et al. Review on biomass feedstocks, pyrolysis mechanism and physicochemical properties of biochar: state-of-the-art framework to speed up vision of circular bioeconomy. **Journal of Cleaner Production**, v. 297, n. 126645, 2021.

GLASER, B.; BIRK, J. J. State of the scientific knowledge on properties and genesis of Anthropogenic Dark Earths in Central Amazonia (terra preta de Índio). **Geochimica et Cosmochimica Acta**, v. 82, p. 39–51, 2012.

- GODLEWSKA, P.; OK, Y. S.; OLESZCZUK, P. The dark side of black gold: ecotoxicological aspects of biochar and biochar-amended soils. **Journal of Hazardous Materials**, v. 403, n. 123833, 2021.
- GUO, R. et al. Biochar-based urea enhances nitrogen use efficiency and mitigates nitrogen leaching in greenhouse vegetable production. **Environmental Technology & Innovation**, v. 38, n. 104104, 2025.
- HAN, J. et al. Phosphate sorption mechanisms in biochar: insights from depth profiling of porous structure across pH and pyrolysis conditions. **Bioresource Technology**, v. 418, n. 131953, 2025.
- HOU, J. et al. The effect of combined application of biochar and phosphate fertilizers on phosphorus transformation in saline-alkali soil and its microbiological mechanism. **Science of The Total Environment**, v. 951, n. 175610, 2024.
- HU, Y.; CHEN, Z. Thermochemical conversion of sewage sludge: progress in pyrolysis and gasification. **Water**, v. 17, n. 12, 2025.
- JEFFERY, S. et al. Biochar boosts tropical but not temperate crop yields. **Environmental Research Letters**, v. 12, n. 053001, 2017.
- JIEN, S.-H. et al. Effects of field scale in situ biochar incorporation on soil environment in a tropical highly weathered soil. **Environmental Pollution**, v. 272, n. 116009, 2021.
- JOSEPH, S. 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, p. 1731–1764, 2021.
- KEILUWEIT, M. et al. Dynamic molecular structure of plant biomass-derived black carbon (biochar). **Environmental Science & Technology**, v. 44, n. 4, p. 1247–1253, 2010.
- KHAN, M. N. et al. Impact of modified biochar on phosphorus fractionation and biochemical properties for different soils. **Environmental Science Europe**, v. 37, n. 80, 2025.
- LAM, S. K. et al. Next-generation enhanced-efficiency fertilizers for sustained food security. **Nature Food**, v. 3, p. 575–580, 2022.
- LEHMANN, J.; JOSEPH, S. (Eds.). **Biochar for environmental management: science and technology**. London: Earthscan, 2009. 438 p.
- LI, C.; BAIR, D. A.; PARIKH, S. J. Estimating potential dust emissions from biochar amended soils under simulated tillage. **Science of The Total Environment**, v. 625, p. 1093–1101, 2018.
- LI, D.-C.; JIANG, H. The thermochemical conversion of non-lignocellulosic biomass to form biochar: a review on characterizations and mechanism elucidation. **Bioresource Technology**, v. 246, p. 57–68, 2017.
- LI, Y. et al. Review of biochar production via crop residue pyrolysis: development and perspectives. **Bioresource Technology**, v. 369, n. 128423, 2023.
- LIU, R.; LAL, R. Potentials of engineered nanoparticles as fertilizers for increasing agronomic productions. **Science of The Total Environment**, v. 514, p. 131–139, 2015.
- LOPES, É. M. G. et al. Biochar increases enzyme activity and total microbial quality of soil grown with sugarcane. **Environmental Technology & Innovation**, v. 21, n. 101270, 2021.
- LU, H. et al. Characterization of sewage sludge-derived biochars from different feedstocks and pyrolysis temperatures. **Journal of Analytical and Applied Pyrolysis**, v. 102, p. 137–143, 2013.
- LUO, P. et al. Biochar-based fertilizers: advancements, applications, and future directions in sustainable agriculture – a review. **Agronomy**, v. 15, n. 1104, 2025.
- LUSTOSA FILHO, J. F. et al. Co-pyrolysis of poultry litter and phosphate and magnesium generates alternative slow-release fertilizer suitable for tropical soils. **ACS Sustainable Chemistry & Engineering**, v. 5, n. 10, 2017.

- LUSTOSA FILHO, J. F. 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, n. 136028, 2020.
- LUSTOSA FILHO, J. F. et al. Changes in phosphorus due to pyrolysis and in the soil-plant system amended with sewage sludge biochar compared to conventional P fertilizers: a global meta-analysis. **Chemosphere**, v. 371, n. 144055, 2025.
- MARSCHNER, P.; RENGEL, Z. Nutrient availability in soils. In: RENGEL, Z. et al. (eds.). **Marschner's Mineral Nutrition of Higher Plants**. 4. ed. London: Academic Press, 2023. p. 499–522.
- MELO, L. C. A. et al. Biochar-based fertilizer effects on crop productivity: a meta-analysis. **Plant and Soil**, v. 472, p. 45–58, 2022.
- MENDES, I. C. et al. Critical limits for microbial indicators in tropical Oxisols at post-harvest: the FERTBIO soil sample concept. **Applied Soil Ecology**, v. 139, p. 85–93, 2019.
- MENDES, I. C. et al. Soil quality and grain yield: a win-win combination in clayey tropical oxisols. **Geoderma**, v. 388, n. 114880, 2021.
- NOVAIS, R. F.; SMYTH, T. J. **Fósforo em solo e planta em condições tropicais**. Viçosa: UFV, 1999. 399 p.
- OSMAN, A. I. et al. Materials, fuels, upgrading, economy, and life cycle assessment of the pyrolysis of algal and lignocellulosic biomass: a review. **Environmental Chemistry Letters**, v. 21, n. 3, p. 1419–1476, 2023.
- OTONI, J. P. et al. Potential for agronomic and environmental use of biochars derived from different organic waste. **Journal of Cleaner Production**, v. 449, n. 141826, 2024.
- PAN, X. et al. Effects of organic fertilizer replacement on the microbial community structure in the rhizosphere soil of soybeans in albic soil. **Scientific Reports**, v. 15, n. 12271, 2025.
- POGORZELSKI, D. et al. Biochar as composite of phosphate fertilizer: characterization and agronomic effectiveness. **Science of The Total Environment**, v. 743, n. 140604, 2020.
- PROCHNOW, F. D. et al. Biochar: From Laboratory to Industry Scale – An Overview of Scientific and Industrial Advances, Opportunities in the Brazilian Context, and Contributions to Sustainable Development. **Processes**, v. 12, n. 1006, 2024.
- SANTOS JÚNIOR, J. M. dos et al. Biochar pellets as soil conditioner on the growth of *Urochloa brizantha* BRS Paiguás. **Revista Ciência Agronômica**, v. 55, n. e20238690, 2024.
- SANTOS JÚNIOR, J. M. dos et al. Granulated organomineral fertilizers from by-products of the agricultural and forestry sector. **Scientia Agricola**, v. 82, n. e20240132, 2025a.
- SANTOS JÚNIOR, J. M. dos et al. Biochar-based granular fertilizers with agro-industrial binders enhance enzymatic activity and nutrient cycling in tropical Oxisols. **Agronomy**, v. 15, n. 9, 2025b.
- SARFARAZ, Q. et al. Characterization and carbon mineralization of biochars produced from different animal manures and plant residues. **Scientific Reports**, v. 10, n. 955, 2020.
- SCHMIDT, H.-P. et al. Biochar in agriculture: a systematic review of 26 global meta-analyses. **GCB Bioenergy**, v. 13, p. 1708-1730, 2021.
- SCHMIDT, M. J. et al. Dark earths and the human built landscape in Amazonia: a widespread pattern of anthrosol formation. **Journal of Archaeological Science**, v. 42, p. 152–165, 2014.
- SEOW, Y. X. et al. A review on biochar production from different biomass wastes by recent carbonization technologies and its sustainable applications. **Journal of Environmental Chemical Engineering**, v. 10, n. 107017, 2022.

SIA, C. J.; KOOH, M. R. R.; LIM, L. H. Polycyclic aromatic hydrocarbons in biochar: influence of thermochemical parameters and analytical considerations. **Journal of Analytical and Applied Pyrolysis**, v. 192, n. 107296, 2025.

SILVA, R. W. da et al. Organophosphate fertilizers based on biochars and phosphorus availability in the soil. **ACS Agricultural Science & Technology**, v. 4, n. 10, 2024.

SOLANKI, P. et al. Nano-fertilizers and their smart delivery system. In: RAI, M. et al. (eds.). **Nanotechnologies in Food and Agriculture**. Cham: Springer International Publishing, 2015. p. 81–101.

SONG, K. et al. Biochar improves soil organic carbon sequestration potential in the topsoil and subsoil of a paddy field. **Current Research in Environmental Sustainability**, v. 8, n. 100267, 2024.

TOMCZYK, A.; SOKOŁOWSKA, Z.; BOGUTA, P. Biochar physicochemical properties: pyrolysis temperature and feedstock kind effects. **Reviews in Environmental Science and Bio/Technology**, v. 19, p. 191–215, 2020.

VUPPALADADIYAM, A. K. et al. A critical review on biomass pyrolysis: reaction mechanisms, process modeling and potential challenges. **Journal of the Energy Institute**, v. 108, n. 101236, 2023.

WANG, J.; WANG, S. Preparation, modification and environmental application of biochar: a review. **Journal of Cleaner Production**, v. 227, p. 1002–1022, 2019.

WANG, Y. et al. Effect of different production methods on physicochemical properties and adsorption capacities of biochar from sewage sludge and kitchen waste: Mechanism and correlation analysis. **Journal of Hazardous Materials**, v. 461, n. 132690, 2024.

YOGALAKSHMI, K. N. et al. Lignocellulosic biomass-based pyrolysis: a comprehensive review. **Chemosphere**, v. 286, n. 131824, 2022.

YUAN, Y. et al. Co-application of biochar and pyroligneous acid improved peanut production and nutritional quality in a coastal soil. **Environmental Technology & Innovation**, v. 28, n. 102886, 2022.

ZELAYA, K. P. S. et al. Biochar in sugar beet production and nutrition. **Ciência Rural**, v. 49, n. 5, 2019.

4 ARTIGOS

4.1 Artigo 1 – Granulated organomineral fertilizers from by-products of the agricultural and forestry sector

Este artigo foi elaborado e publicado conforme as normas da revista **Scientia Agricola**.

SANTOS JÚNIOR, José Mendes dos *et al.* Granulated organomineral fertilizers from by-products of the agricultural and forestry sector. **Sci. agric.**, v. 82, e20240132, 2025. DOI: <https://doi.org/10.1590/1678-992X-2024-013>.

Granulated organomineral fertilizers from by-products of the agricultural and forestry sector

Abstract

The present study evaluated the granular properties of organomineral fertilizers produced from charcoal fines (biochar) and natural phosphate with three distinct binders: cassava wastewater (CW), pyroligneous extract (PE), and bio-oil (BO). The objective was to ascertain the potential of these fertilizers to increase common bean production. To form the granules, a 3:1 ratio of biochar to natural phosphate was employed, along with five binder doses (50, 75, 100, 125, and 150 % of the biochar-phosphate mixture weight). The granules were evaluated based on their crushing strength, water absorption ratio (WAR), granule density, impact resistance index (IRI), salinity index (SI), and pH. The most optimal granules were selected for the experiment with the common bean, using a completely randomized design in a $3 \times 4 + 4$ factorial scheme with three replications. The treatments comprised three binders (CW, PE, and BO), four binder doses (75, 100, 125, and 150 %), and four controls: unfertilized soil (NS), natural phosphate (NP), biochar mixed with natural phosphate (B + NP), and biochar (B). Compared to the CW or PE granules, the BO granules exhibited superior crushing resistance, density, and IRI, accompanied by a reduced WAR. The PE granules exhibited a higher SI and a lower pH. The application of CW, PE, or BO granules resulted in a significant increase in shoot dry matter (SDM), with values of 98.31, 123.73, and 47.46 %, respectively, compared to the NS. Similarly, root dry matter (RDM) notably increased, with values of 331.03, 755.17 and 141.38 %, respectively. The physicochemical properties of organomineral fertilizers are influenced by the type of binder used, affecting common bean production. Further research is needed to ascertain the long-term effects of these slow-release fertilizers.

Keywords: biochar; bio-oil; cassava wastewater; pyroligneous extract; waste recovery.

1 INTRODUCTION

One of humanity's most significant challenges currently is the search for effective strategies to mitigate atmospheric greenhouse gas emissions. In response to this challenge, the concept of a circular economy has emerged as a prominent approach in the field of sustainable waste management, offering a potential pathway to reduce environmental impacts (Casau et al., 2022).

Pyrolysis is a thermochemical depolymerization process of organic compounds in an environment with a low concentration or no oxygen (Li et al., 2022). This process forms charcoal, known as biochar (B), for agronomic purposes. B is a porous material rich in recalcitrant carbon (Yang et al., 2022).

The production of charcoal at carbonization plants inevitably generates considerable quantities of waste, mainly attributable to handling the charcoal itself. These residues, designated as charcoal fines (B), are tiny fragments resulting from abrasion and mechanical shock, constituting approximately 20 % of the total charcoal produced. They are a significant source of economic loss and environmental liability (Ronix et al., 2021). Brazil is the world's largest producer of charcoal, with an output exceeding 7.5 million tons in 2022 (FAO, 2022). This indicates potential losses through charcoal fines to reach over 1.5 million tons.

The economic viability of using B in agriculture remains a controversial topic, largely due to the considerable quantities that must be applied, the losses of material during handling, transportation, and application, and the inhalation risks faced by farmers (Mohammadi, 2021). One potential avenue for utilizing B agricultural settings is the production of granular organomineral fertilizers. The quality and stability of the granules are crucial properties, particularly in relation to binders (Riva et al., 2019). Nevertheless, some of these binders are costly and may increase production cost (Peng et al., 2021). One potential solution is the use of alternative binders, such as pyroligneous extract (PE) and bio-oil (BO), by-products of charcoal production, and cassava wastewater (CW), a waste product from the production of cassava starch.

The hypothesis proposed is that the physicochemical quality of the granules produced from organomineral fertilizers is altered by the type of binder used, including their ionic exchange capacity and nutrient bioavailability. This, in turn, is expected to increase shoot dry matter (SDM) and root dry matter (RDM) production in the common bean (*Phaseolus vulgaris* L. BRSMG Uai). The objective of this study was to assess the granular properties of organomineral fertilizers produced from B and natural phosphate (NP) with three binders (CW, PE, and BO), and their capacity to enhance common bean production.

2 MATERIALS AND METHODS

The experiment was conducted in two stages. During the initial stage, granular organomineral fertilizers were produced and a physical-chemical characterization was performed. Subsequently, the granules exhibiting the most favorable characteristics were selected for incubation in soil and for the cultivation of bean plants (Figure 1).

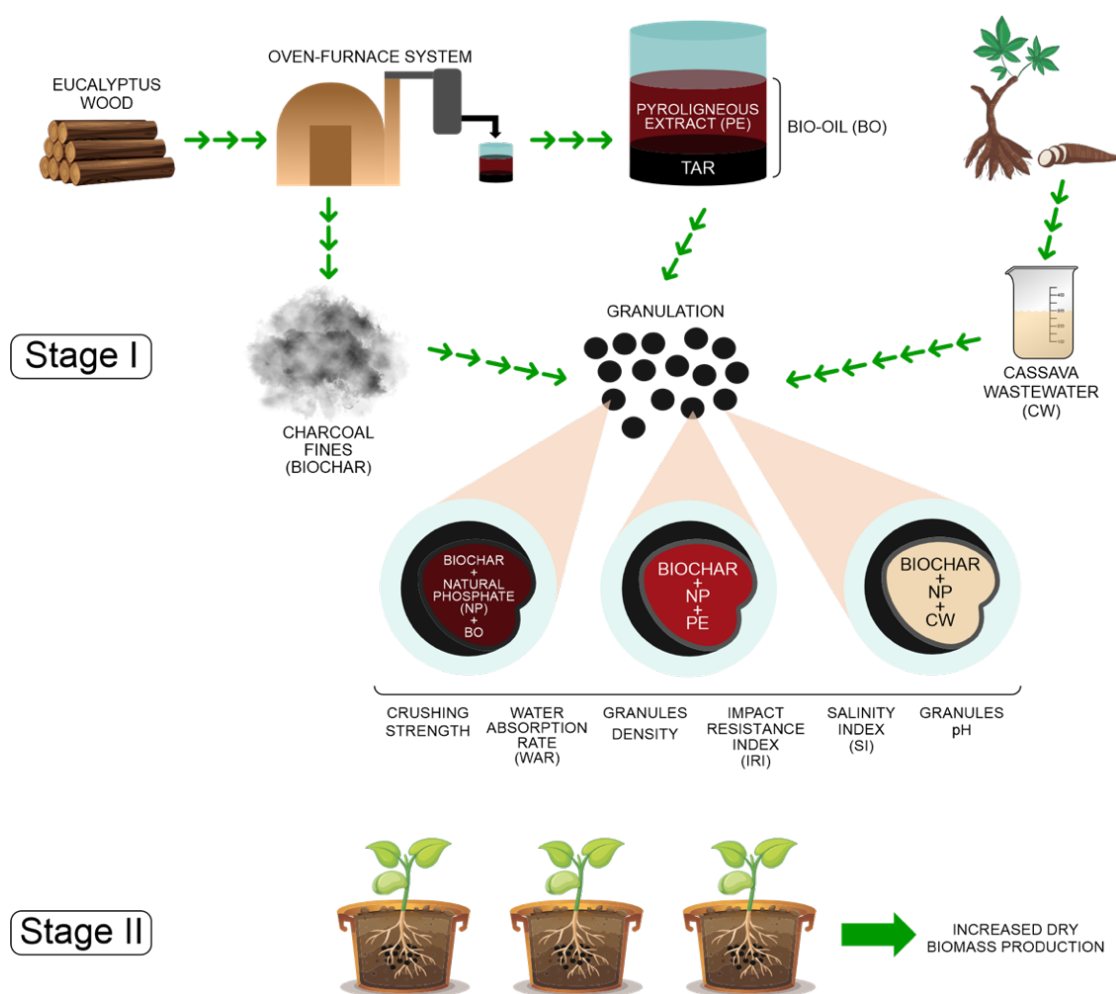


Figure 1 – Schematic representation of the experiment. BO = bio-oil; PE = pyroligneous extract; CW = cassava wastewater; NP = natural phosphate; WAR = water absorption rate; IRI = impact resistance index; SI = salinity index.

The B was obtained from the oven-furnace system of the Instituto de Ciências Agrárias of the Universidade Federal de Minas Gerais, located in the Minas Gerais state, Brazil (16°41'2.03" S, 43°50'19.28" W, altitude 646 m). The production of charcoal was achieved through the slow pyrolysis of wood derived from the *Eucalyptus urograndis* (*Eucalyptus urophylla* S.T. Blake × *Eucalyptus grandis* W. Hill ex Maiden clonal hybrid I144) species at 450 °C. The internal temperature of the ovens was monitored at 30-min intervals during the heating and drying stages and 8-h intervals during the cooling stage using an infrared sensor (Schettini et al., 2022).

The B was subjected to mechanical grinding and sieving using a 0.25 mm mesh to standardize the particles' size and characterize their chemical and physical properties (Table 1). All analyses were conducted in quadruplicate. The pH and electrical conductivity (EC) were determined using a 1:20 ratio of B to deionized water after stirring for 1.5 h at 12.57 rad s⁻¹ to ensure equilibrium between the solution and the B surfaces (Rajkovich et al., 2012). Bulk density was determined by filling a 10 mL graduated cylinder with the B, which was then shaken for 1 min, and subsequently weighed (Santos et al., 2019). The moisture, volatile material, ash and fixed carbon were determined by the methodology outlined in the American Society for Testing and Materials (ASTM) standard D1762-84 (ASTM, 2021). The organic carbon and nutrient content were determined in alignment with the approach described by Tedesco et al. (1995).

Table 1 – Basic properties of the eucalyptus wood charcoal fines (biochar).

Property	Results	Property	Results
pH	8.96 (0.01)	P (g kg ⁻¹)	3.29 (0.03)
EC (μS cm ⁻¹)	786.33 (5.94)	K (g kg ⁻¹)	1.08 (0.05)
Density (kg dm ⁻³)	0.61 (0.01)	Ca (g kg ⁻¹)	50.66 (4.33)
Ash (%)	50.66 (1.06)	Mg (g kg ⁻¹)	4.26 (0.24)
VC (%)	23.67 (4.60)	Na (g kg ⁻¹)	0.86 (0.03)
Moisture (%)	4.91 (1.18)	S (g kg ⁻¹)	3.57 (0.30)
FC (%)	20.76 (2.48)	Fe (g kg ⁻¹)	17.52 (0.45)
OC (g kg ⁻¹)	507.50 (2.3)	Zn (mg kg ⁻¹)	27.21 (0.09)
Total N (g kg ⁻¹)	1.99 (0.05)	Mn (mg kg ⁻¹)	479.49 (12.74)
C/N	255.03 (5.91)	Cu (mg kg ⁻¹)	17.88 (0.27)

Values in parentheses show the 95 % confidence intervals. EC = electrical conductivity; VC = volatile compounds; FC = fixed carbon; OC = organic carbon.

The CW, PE, and BO binders were employed in the initial process stage to produce the granules. The CW binder is a liquid residue resulting from the processing of cassava roots to produce starch. The PE and BO binders were derived from the production of charcoal using wood from *E. urograndis* in an oven-furnace system through the condensation of pyrolysis vapors. After six-month of standing, the layers were decanted and separated.

The granules were produced in a plate-type granulator. A 3:1 ratio of B to reactive NP (obtained from phosphorites containing 27 % total P₂O₅ and 8.1 % soluble P₂O₅ in 2 % citric acid) was employed to form the granules. The respective binders were uniformly sprayed onto the B and phosphate mixture and homogenized for approximately 40 min at 32.98 rad s⁻¹.

The quantity of each binder was determined based on the weight of a 3:1 mixture of B and NP, corresponding to 50, 75, 100, 125, and 150 % of the weight of the mixture. Therefore, a dose corresponding to 50 % was prepared using 500 g of the mixture (comprising 375 g of B + 125 g of NP) and 250 mL of binder. For the doses corresponding to 75, 100, 125, and 150 % of the mixture (375 g of B + 125 g of NP), a respective volume of 375, 500, 625, and 750 mL of binder was utilized. The granules were subsequently subjected to drying in an oven maintained at a temperature of 65 ± 5 °C for approximately 72 h to attain constant weight (Santos et al., 2019). The granules were cooled to room temperature and stored in plastic containers.

The binders were characterized by their EC, pH, and total solids content (Table 2). Each analysis was conducted in triplicate. The EC and pH were directly measured in the CW and PE samples (liquid samples). For BO (liquid-pasty samples), a ratio of 1:5 was employed, whereby the BO was diluted in deionized water and the resulting aqueous extract was subjected to analysis (Tedesco et al., 1995). The total solids were determined in accordance with the ASTM method E1756-08 (ASTM, 2020). This entailed the placement of 50 mL of sample in porcelain crucibles within a water bath maintained at 65 °C for 16 h, followed by heating in an oven for a further 24 h at 103 °C. Thereafter, the crucibles were transferred to desiccators for cooling, and the weight of the solids was determined.

Table 2 – Basic properties of the binders applied to the granules with charcoal fines (biochar).

Binder	pH	EC	TS
	-	---- $\mu\text{S cm}^{-1}$ ----	---- g L^{-1} ----
BO	2.76 (0.18)	1386.67 (37.34)	115.20 (4.09)
PE	3.31 (0.08)	9963.33 (26.67)	71.93 (1.19)
CW	4.34 (0.13)	567.67 (4.16)	230.80 (26.20)

Values in parentheses show the 95 % confidence intervals. EC = electrical conductivity; TS = total solids; BO = bio-oil; PE = pyrolygneous extract; CW = cassava wastewater.

The experimental design was completely randomized in a 3×5 factorial scheme, with five replications. The treatments comprised three binders (CW, PE, and BO) in five doses, corresponding to 50, 75, 100, 125, and 150 % of the weight of a 3:1 mixture of B and NP. The granules were characterized in terms of the following technological properties: crushing strength (consistency), water absorption ratio (WAR), granule density, impact resistance index (IRI), salinity index (SI), and pH. To determine the crushing strength, the granules were separated by size into fractions of 1, 2, and 4 mm.

The granules were subjected to a compression resistance test to determine their crushing strength, employing a methodology adapted from that described by Nunes et al. (2022). This was done with the objective of measuring the force required to fragment the granules. In order to conduct the test, the granules were separated into three distinct size categories: 1, 2, and 4 mm. A total of five granules were randomly selected from each size category for the resistance test, which employed the use of a portable digital penetrometer. The granules were positioned on a regular, flat surface and subjected to mechanical force, quantified in newtons (N), until they reached a state of fracture.

The WAR of the granules was determined using a method adapted from Santos et al. (2020). In a 20 mL bottle containing purified water, 1 g of granules was added. After 24 h at room temperature, the mixture was filtered, and the moisture content of the granules was determined. The granules were then dried in an oven until they reached a constant weight, after which the dry matter was determined. The WAR was calculated using Eq. (1):

$$\text{WAR (\%)} = \frac{\text{Weight of dry granules}}{\text{Weight of wet granules}} \times 100 \quad (1)$$

The density of the granules was determined using a method adapted from Santos et al. (2019). First, a 10 mL graduated cylinder was filled with the respective granule samples after they were oven-dried to a constant weight. Then, the granules were weighed, and their density was calculated using Eq. (2):

$$\text{Granule density (g cm}^{-3}\text{)} = \frac{\text{Weight of dry granules}}{\text{Volume of the dry sample}} \quad (2)$$

The IRI of the granules was determined using a method adapted from Richards (1990). The granules were dropped from a height of 2 m onto a hard surface, and the number of fragments that resulted from the impact was recorded. The granules were then subjected to repeated impacts and releases until entirely fragmented. This procedure was repeated five times until all the granules had shattered. The IRI was then estimated using Eq. (3):

$$\text{IRI (\%)} = \frac{N_d}{N_p} \times 100 \quad (3)$$

where N_d is the number of times the sample was dropped from a height of 2 m and N_p is the number of fragments generated by the impacts.

The SI and pH of the granules were determined in accordance with the recommendations established by MAPA (2017). The SI represents the osmotic pressure exerted by a given material compared to sodium nitrate, with an estimated value derived from the EC. To determine the SI, 1 g of finely ground granules was solubilized and homogenized in 100 mL of deionized water. Following a 30-min period, the EC of the supernatant was determined using a conductivity meter. The procedure was then repeated using a 10 g L^{-1} solution of sodium nitrate. The SI was subsequently calculated from the relationship between the EC of the sample solution (ECS) and the EC of the nitrate solution (ECNaNO_3), in accordance with Eq. (4):

$$\text{SI (\%)} = \frac{\text{ECS}}{\text{ECNaNO}_3} \times 100 \quad (4)$$

To determine the pH value, 10 g of finely ground granules were added to 50 mL of a 0.01 mol L^{-1} calcium chloride solution. The mixture was agitated for 30 min, stirring at 10-min intervals. The pH of the solution was then determined using a pH meter.

In the second stage of the study, the treatments comprised granular organomineral fertilizers synthesized with doses of 75, 100, 125, and 150 % of the CW, PE, and BO binders. The additional treatments were natural or unfertilized soil (NS), natural phosphate (NP), a mixture of biochar and natural phosphate (B+NP), and biochar (B). The experimental design was a completely randomized $3 \times 4 + 4$ factorial scheme (three types of binder in four different doses for producing the granules and four additional treatments), with three replications, resulting in 48 experimental plots.

The quantity of granular organomineral fertilizer applied to the soil was calculated based on the dry matter produced by the mixture utilized to prepare the granules at the corresponding binder dose (B, NP, and binders) to achieve the level of P fertilization recommended by Malavolta (1980), namely 200 mg dm^{-3} . This calculation was made with the understanding that the composition of NP is 27 % P_2O_5 .

Additional treatments with B and NP, whether alone or in combination, were applied in a conventional (non-granular) form. For the combined application of B and NP, a B to NP ratio of 3:1 was utilized, which is the same ratio employed in the production of granular fertilizers.

The soil utilized in the experiment was collected from the 0 to 20 cm layer of an Oxisol from a native region of the Cerrado and subjected to sieving through a 2 mm mesh. The chemical properties of the soil were determined in accordance with the methodology proposed by Teixeira et al. (2017): pH (H_2O) = 5.80; P (resin method) = 1.30 mg dm^{-3} ; available P (Mehlich 1) = 0.95 mg dm^{-3} ; K = 13.71 mg dm^{-3} ; S = 1.87 mg dm^{-3} ; Ca = $0.31 \text{ cmol}_c \text{ dm}^{-3}$; Mg = $0.05 \text{ cmol}_c \text{ dm}^{-3}$; Al = $0.05 \text{ cmol}_c \text{ dm}^{-3}$; base saturation (V %) = 38 %; cation exchange capacity at pH 7.00 = $1.19 \text{ cmol}_c \text{ dm}^{-3}$, and soil organic carbon = 2.00 g kg^{-1} .

The soil and treatments were homogenized and placed in 500 cm^3 pots. Four seeds of the common bean were then sown per pot. Ten days after sowing, at the vegetative stage V1, the plants were thinned out to leave one plant per pot, which was then allowed to develop for 50 days, corresponding to the end of stage V4 and the start of flowering.

Four distinct top dressings were applied at the specific growth stage of the bean plants: at 23 (early V3), 28 (mid V3), 36 (late V3), and 41 (mid V4) days after sowing, utilizing a concentration of 50 mg dm^{-3} of 20-00-20 NPK fertilizer. Soil acidity was corrected with calcium and magnesium carbonate (Ca:Mg ratio

of 4:1) in each treatment to increase the soil V % to 70 %. The soil moisture was maintained at a level close to field capacity throughout the experimental period.

In the initial phase of the experiment, the data were evaluated for normality of variances using the Shapiro-Wilk test and subjected to analysis of variance (ANOVA) using the F-test. When a significant difference was identified, the binders were compared using Tukey's test ($p < 0.05$), with regression analysis employed for the doses. The data were transformed into arcsine ($\sqrt{x}$) to analyse crushing strength. The Kruskal-Wallis non-parametric test was utilized for IRI, and multiple comparisons were conducted using the Dunn's test ($p < 0.05$).

At the conclusion of the second phase of the experiment (phenological stage V4), the SDM, the concentration of macro- and micronutrient, the accumulated amount, and the RDM were quantified. The data were subjected to ANOVA, and when significant, regression analysis was conducted for the variables under study as a function of the binder dose. Regardless of dose, the mean values for each binder were compared using the Tukey's test ($p < 0.05$). The additional treatments were compared with the other treatments using the Dunnett's test ($p < 0.05$). The R software, version 4.2.2, was utilized.

3 RESULTS

The crushing strength increased linearly with the amounts of binder present in the mixture of B + NP used to produce the organomineral fertilizer (Figure 2A), irrespective of the specific type of binder or granule size employed.

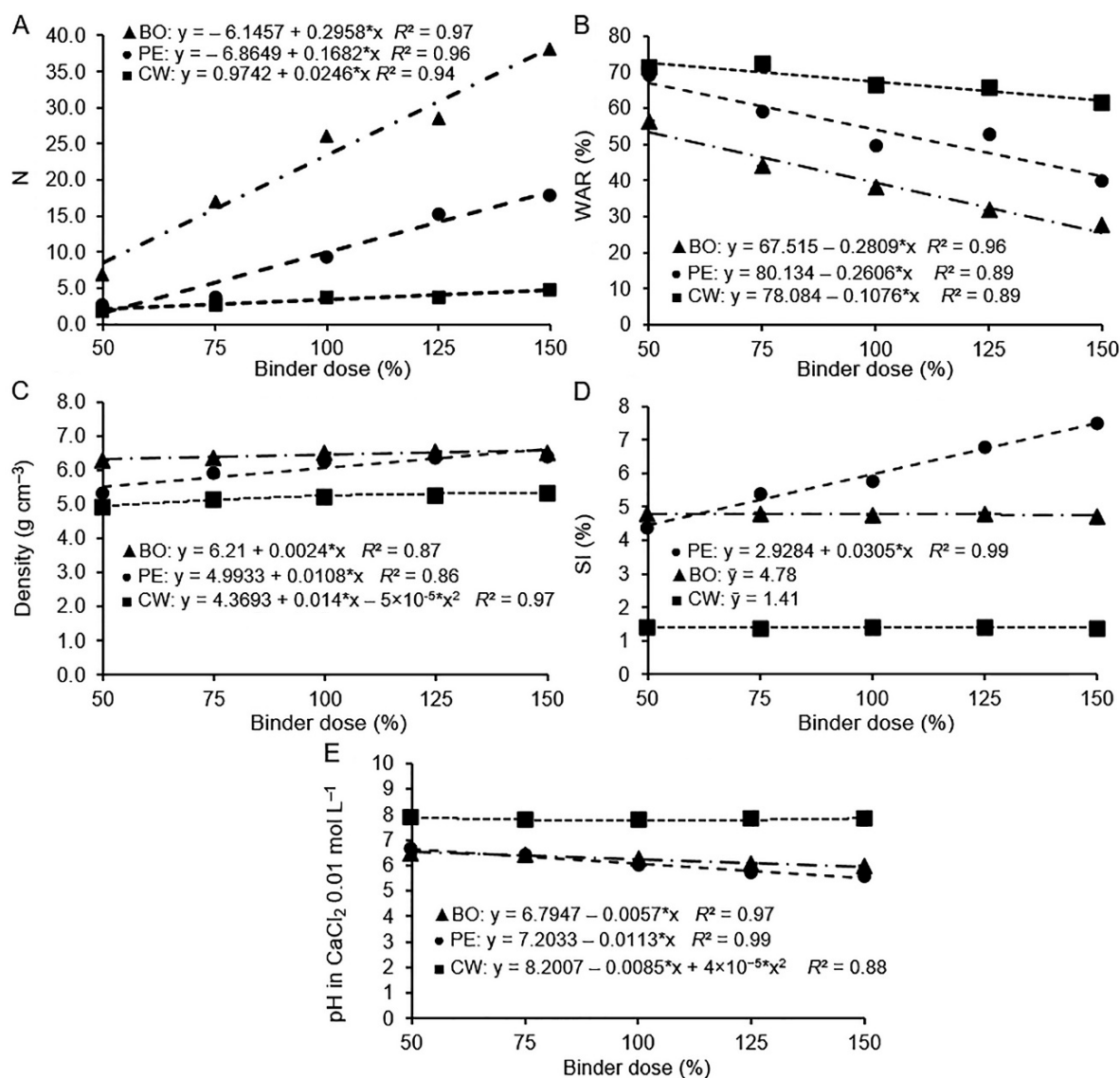


Figure 2 – Physicochemical properties demonstrated by the granules with charcoal fines (biochar) as a function of different doses of cassava wastewater (CW), pyroligneous extract (PE) and bio-oil (BO). *significant at 5 %. WAR = water absorption rate; SI = salinity index; pH (CaCl₂) = hydrogen potential in 0.01 mol L⁻¹ CaCl₂.

The larger the size of the granules in each of the binders (CW, PE, and BO), the greater the resistance to breakage. This is evidenced by the greater crushing strength required to fragment the granules (Table 3). For particles of sizes 1, 2, or 4 mm, the force required to fracture the BO granules was 6.0, 6.7, and 7.2 times greater, respectively, than that needed to fracture the CW granules (Table 3). With regard to the binders, the granules with BO exhibited the greatest resistance to breakage, while those with CW demonstrated the least (Figure 2A).

Table 3 – Crushing force applied to the granules with charcoal fines (biochar) of different sizes and with different doses of cassava wastewater (CW), pyroligneous extract (PE) and bio-oil (BO).

Binder	Particle Size (mm)		
	1	2	4
	----- N -----		
BO	10.704 (6.0) A	20.167 (6.7) A	39.679 (7.2) A
PE	5.530 (3.1) B	8.729 (2.9) B	15.431 (2.8) B
CW	1.784 (1.0) C	3.010 (1.0) C	5.511 (1.0) C
Mean	6.006 c	10.635 b	20.207 a

Mean values followed by the same uppercase letters in a column and lowercase letters in a row do not differ by the Tukey's test ($p > 0.05$) within the respective particle size. Values in parentheses represent the crushing resistance relative to CW. N = newton.

The WAR of the granules decreased linearly with the increase of the binder dose (Figure 2B). At the lowest dose (50 % binder), no distinction was observed between the CW and PE binders, which exhibited WAR values of 71.37 and 69.21 %, respectively (Figure 2B). As the binder dose increased, the WAR values for the PE granules were consistently lower than those for the CW granules (Figure 2B). Conversely, at all doses, the WAR values for granules with BO were lower than those with CW or PE (Figure 2B). Regardless of the binder dose, the WAR values for granules with BO, PE, or CW, were 39.43, 54.08, and 67.32 %, respectively (Table 4).

Table 4 – Physical and chemical characteristics of the granules with charcoal fines (biochar) and different binders.

Binder	WAR	Density	IRI	SI	pH (CaCl ₂)
	----- % -----	---- g cm ⁻³ ----	----- % -----	----- % -----	-
BO	39.43 C	6.45 A	409.52 A	4.78 B	6.23 B
PE	54.08 B	6.07 B	241.53 B	5.97 A	6.08 B
CW	67.32 A	5.19 C	32.86 C	1.41 C	7.81 A

Mean values followed by the same uppercase letters in a column do not differ by the Tukey's test ($p > 0.05$). WAR = water absorption rate; IRI = impact resistance index; SI = salinity index; pH (CaCl₂) = hydrogen potential in 0.01 mol L⁻¹ CaCl₂; BO = bio-oil; PE = pyroligneous extract; CW = cassava wastewater.

The type of binder and respective doses influenced granule density (Figure 2C), which increased linearly for granules with PE and BO. For CW, the maximum density (5.35 g cm⁻³) was obtained at a dose of 140 % (Figure 2C). In general, regardless of the dose, granules with BO exhibited a higher density than those with PE or CW (Table 4), with the granules with CW displaying the lowest values for density (Table 4).

The highest IRI values were observed in granules with BO (409.52 %), which differed from those with CW and PE, regardless of the binder dose (Table 4). Similarly, granules with PE (241.53 %) exhibited higher IRI values than those with CW (32.86 %) (Table 4).

No differences were observed for SI between the doses of BO and CW (Figure 2D). Conversely, a linear increase in SI was noted with an increasing dose of PE (Figure 2D). The highest mean values were obtained with PE, followed by BO and CW (Table 4).

The pH values of the granules with CW, adjusted to a quadratic model, are shown as a function of the binder dose in Figure 2E. The pH of granules with PE or BO decreased linearly with the respective dose (Figure 2E). In contrast, the highest pH was obtained with CW, regardless of the dose, as demonstrated in Table 4. Furthermore, there was no discernible difference in the average pH of granules with PE or BO (Table 4).

The application of B, whether individually or in combination with NP, irrespective of granulation, resulted in a notable increase in the SDM and RDM of the bean plants when compared to the NS. The increases were as follows: B + NP = 72.88 and 182.76 %; B = 72.88 and 148.28 %; CW = 98.31 and 331.03 %; PE = 123.73 and 755.17 %; and BO = 47.46 and 141.38 %, respectively (Table 5).

Table 5 – Shoot dry matter (SDM), root dry matter (RDM) and the amount of nutrients accumulated in the SDM of common bean plants at the phenological stage V4.

Variable	Treatment						
	NS	NP	B+NP	B	CW	PE	BO
SDM (g per pot)	0.20 d	0.23 cd	0.34 bc	0.34 bc	0.39 ab	0.44 a	0.29 c
RDM (g per pot)	0.29 e	0.54 d	0.82 c	0.72 c	1.25 b	2.48 a	0.70 c
N (g kg ⁻¹)	10.66 d	12.29 cd	18.43 bc	18.43 bc	21.37 ab	23.72 a	15.63 c
P (g kg ⁻¹)	0.25 d	0.28 cd	0.43 bc	0.43 bc	0.49 ab	0.55 a	0.36 c
K (g kg ⁻¹)	6.92 d	7.98 cd	11.97 bc	11.97 bc	13.87 ab	15.40 a	10.15 c
Ca (g kg ⁻¹)	3.80 d	4.38 cd	6.57 bc	6.57 bc	7.61 ab	8.45 a	5.57 c
Mg (g kg ⁻¹)	1.17 d	1.34 cd	2.02 bc	2.02 bc	2.34 ab	2.59 a	1.71 bc
S (g kg ⁻¹)	1.55 d	1.78 cd	2.67 bc	2.67 bc	3.10 ab	3.44 a	2.27 c
B (mg kg ⁻¹)	8.65 d	9.97 cd	14.96 bc	14.96 bc	17.34 ab	19.25 a	12.69 c
Zn (mg kg ⁻¹)	2.75 d	3.17 cd	4.76 bc	4.76 bc	5.52 ab	6.13 a	4.04 c
Fe (mg kg ⁻¹)	35.40 d	40.80 cd	61.20 bc	61.20 bc	70.95 ab	78.75 a	51.90 c
Mn (mg kg ⁻¹)	12.78 cd	14.73 cd	22.10 bc	22.10 bc	25.62 ab	28.44 a	18.74 c
Cu (mg kg ⁻¹)	0.65 cd	0.75 cd	1.13 bc	1.13 bc	1.31 ab	1.45 a	0.96 c

Mean values followed by the same lowercase letters in a row do not differ from each other by the Tukey's test ($p > 0.05$). NS = unfertilized soil; NP = natural phosphate; B + NP = biochar mixed with natural phosphate; B = biochar; CW = cassava wastewater; PE = pyroligneous extract; BO = bio-oil.

The application of granular fertilizer containing CW did not result in significant differences in SDM compared to the conventional application of B, whether used alone or in combination with NP, while PE resulted in significantly higher SDM values (Table 5). Conversely, bean plants treated with granular organomineral fertilizer containing CW or PE exhibited a marked increase in RDM, reaching 78.57 and 254.29 %, respectively, compared to the treatment containing BO, regardless of the binder dose (Table 5).

The binder dose did not affect SDM production in soils fertilized with granular organomineral fertilizer (Figure 3A). In contrast, for RDM, the treatments containing PE or BO granules exhibited a linear reduction, while those containing CW granules demonstrated a linear increase (Figure 3B).

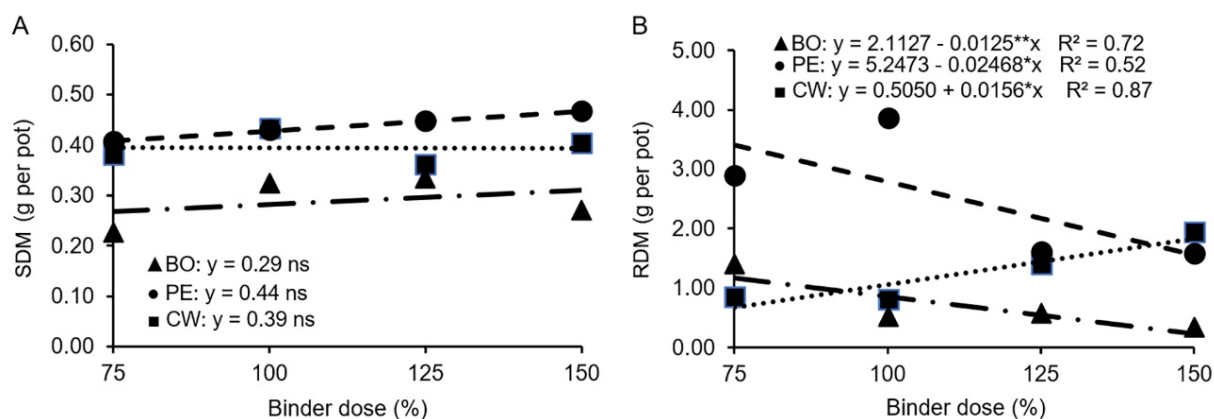


Figure 3 – Regression equations adjusted for the dry matter of shoots (SDM) and roots (RDM) of bean plants observed at phenological stage V4, following the application of granular organomineral fertilizer with different binder doses. * and **significant at 5 and 1 %, respectively. BO = bio-oil; PE = pyrolygneous extract; CW = cassava wastewater.

The data revealed a no statistically significant difference among the treatments concerning the macro- and micronutrient content of the bean plants. The results indicated that the average nutrient concentrations were as follows: N = 54.21 g kg⁻¹; P = 1.25 g kg⁻¹; K = 35.20 g kg⁻¹; Ca = 19.31 g kg⁻¹; Mg = 5.93 g kg⁻¹; S = 7.86 g kg⁻¹; B = 44.00 mg kg⁻¹; Zn = 14.00 mg kg⁻¹; Fe = 180.00 mg kg⁻¹; Mn = 65.00 mg kg⁻¹, and Cu = 3.32 mg kg⁻¹. However, regarding to the quantity of nutrients accumulated in the SDM of the bean plants, the highest values were observed in the treatment with PE, while the lowest values were evident in NS and NP (Table 5).

4 DISCUSSION

The linear increase in crushing strength with the different binder doses can be attributed to the proportional increase in the solid fraction that remains following the evaporation of water from the binders. It is possible that the solid fraction of the binders may have occupied the pores of the Bs and NP particles through polymerization (Riva et al., 2019). In this context, the binding mechanisms between the B and the different binders may have played a role in stabilizing the granules. These mechanisms are influenced by the various polar functional groups, including hydroxyl (OH), carboxyl (COOH), and/or carbonyl (CO) groups, present in the structure of Bs and binders. This hypothesis posits that these functional groups can facilitate an electrostatic attraction between particles, such as Van der Waals forces and hydrogen (Anukam et al., 2021).

In this study, a high crushing strength was required to fragment the granules containing the BO binder, which may be related to the presence of various aromatic and heterocyclic compounds of high molecular weight originating from the polymerization and condensation reactions of low-molecular-weight components (Frainetti and Klinghoffer, 2023). These compounds are derived from the thermal decomposition of lignin, hemicellulose, and cellulose from the biomass (eucalyptus wood), which renders the BO highly viscous and adhesive (Zhang et al., 2020).

The greater resistance to breakage exhibited by the granules with PE, in comparison to those with CW, can be attributed to the viscosity and composition of the binder. Despite this inferiority in relation to BO, the PE binder can contain chemical compounds, including aldehydes, phenols, pyrolytic lignin, and aromatic and aliphatic groups, which promote robust interactions between the solid particles (Asafu-Adjaye et al., 2022).

The high compressive crushing strength of the granules, irrespective of the binder utilized, may also be associated with the degree of cohesion between the binder, the B particles, and the NP particles. The binder plays a significant role in the mechanical strength and durability of the granules, influencing their consistency. It facilitates the formation of solid bridges between the particles (Peng et al., 2021). Moreover, the drying temperature of the granules (65 ± 5 °C for 72 h) may have facilitated thermal interactions between the solid fraction of the binder and the other components of the organomineral fertilizer after the evaporation and volatilization of the liquid and volatile fractions of the binders (Butler et al., 2023).

In terms of size, the larger granules demonstrated greater resistance to crushing, potentially due to the distributed force required to break the granules across a larger surface area. These findings align with those obtained by Nunes et al. (2022), who observed similar results with granules ranging in diameter from 3.35 to 4 mm, composed of B, organic polymers, and MgO, necessitating a breaking force of approximately 88.26 N.

The WAR decreased as the binder dose increased. This phenomenon can be attributed to the porous structures of the B being filled by the solid fraction of the binders, thereby reducing the available spaces for water absorption. Furthermore, at higher doses, binders have the potential to form a more cohesive matrix around the B particles, which helps to further reduce the water absorption capacity of the granules (Sarker et al., 2023).

The discrepancy the WAR values of the three binders can be attributed to both their hydrophobicity and their capacity to fill the porous spaces of the B structure, particularly the mesopores and micropores measuring less than 100 μm in size. The presence of hydrophobic compounds, including aliphatic and aromatic hydrocarbons, in the PE and particularly the BO binders may be associated with the moderate temperatures (< 500 °C) utilized to produce the B, as proposed by Gondim et al. (2018).

The same hypothesis previously used to explain the crushing strength of the granules can also be employed to elucidate the underlying mechanisms of the WAR. The higher water absorption of granules with PE compared to those with BO can be attributed to the presence of hydrophilic components and oxygenated functional groups (Cheng et al., 2022). Similarly, the elevated level of water absorption exhibited by the granules with CW in comparison to those with PE and BO can be attributed to the presence of starch. Due to its hydrophilic nature, even with prior gelatinization of the polysaccharide, less resistant and brittle granules may be formed because of the swelling caused by water absorption and breaking intermolecular bonds (Butler et al., 2023).

Concerning density, the lower values observed in granules with the CW binder may be attributed to the weak bonds between the particles, which influence on the cohesion forces between them and compaction, as previously discussed. The hydrophilic nature of starch may affect the density, as the irreversible swelling of the granules may result from the changes in this polysaccharide when the intermolecular hydrogen bonds are broken. The drying temperature of the granules may have prevented or hindered gelatinization and, subsequently, on cooling, recrystallization of the amylose and amylopectin chains, the main constituents of starch (Channab et al., 2023).

The density of granules density is correlated with their crushing strength. Therefore, the hypothesis posits that the incorporation of BO and PE into the constituents of the granules facilitates their penetration into the B pores, thereby creating a homogeneous and compact structure. Furthermore, the presence of these elements strengthens the bonds between the particles, establishing solid bridges that enhance the

granules' mechanical properties (Sarker et al., 2023). However, compared to PE, BO contains compounds of high molecular weight that are insoluble in water and demonstrate high resistance to volatilization, contributing to an increase in granule density (Lachos-Perez et al., 2023).

In this regard, both BO and PE serve as binders, facilitating the formation of denser granules that are more homogeneous in shape and size and exhibit greater resistance to breakage during transport and storage (Sarker et al., 2023). These attributes contribute to a reduction in the rate of water diffusion within the granule, resulting in a fertilizer with a slower release of nutrients (Cheng et al., 2022). With regard to the application of the granules, a more uniform distribution is achieved when they are placed directly in the planting furrow, thereby reducing the loss due to wind drift when they are broadcast.

The linear increase in the dose of PE suggests a proportional addition of water-soluble salts by the binder, as evidenced by the elevated EC levels (Table 2). The PE may contain more than 200 water-soluble chemical compounds, predominantly derived from the pyrolysis of cellulose and hemicellulose. These can potentially influence the EC, SI, and pH of the granules. Conversely, water-insoluble compounds in BO may account for the comparatively lower SI of granules with this binder (Lachos-Perez et al., 2023).

Using fertilizers with a high SI can have detrimental effects on plants, particularly when applied in large quantities and near the plant roots. In this regard, the high capacity of Bs to adsorb ions, which is attributed to the presence of surface electric charges resulting from the ionization of functional groups, can serve to reduce the SI of binders, such as PE (Nunes et al., 2022).

The elevated pH values observed in granules with CW can be attributed to the reduced buffering capacity and less acidic nature of the binder (Table 2), which can be attributed to the presence of basic compounds such as $\text{Ca}(\text{OH})_2$ (Cheng et al., 2022). Moreover, the alkaline pH of these granules, irrespective of the dose, is influenced by interaction with NP, which is also alkaline in nature. This hypothesis is supported by the findings of Mikolaitienė and Šlinkšienė (2022), who observed a pH close to neutral in fertilizers based on urea, microalgae, and potato starch.

As the binder dose decreased, granules with BO and PE showed a linear reduction in pH. This behavior is associated with the higher acidity of the binders (Table 2), which, due to the complexation of porous structures and basic cationic groups, exceeds the alkalinity of the B (Shetty and Prakash, 2020).

The acidity of the BO and PE components is attributable to both the raw material and the pyrolysis process. During pyrolysis, the cellulose, hemicellulose, and lignin present in wood undergo degradation, resulting in the production of a range of organic acids, including acetic acid, butanoic acid, formic acid, and propanoic acid, among others (Cheng et al., 2022; Zhang et al., 2020).

The present research demonstrated that the application of B, whether alone or in combination with NP, significantly influenced the production of SDM and RDM in bean plants, regardless of the granulation of organomineral fertilizers. This improvement in productivity can be attributed to the increased availability of nutrients for the plants and the liming effect of B with a high ash content (Table 1). This effect is particularly important in acidic tropical soils, as it reduces P fixation, increasing its availability for crops (Santos Júnior et al., 2024).

Furthermore, B exhibits a high reactive potential due to the surface charges. These charges predominantly originate from functional heterocyclic oxygen groups, including the carboxylate, phenolate, and oxonic groups. This attribute enables the B to compete with P for adsorption sites on minerals in

weathered soils. Consequently, there is a reduction in nutrient precipitation reactions with Al and Fe oxides (Nunes et al., 2022).

The notable contribution of granular organomineral fertilizer to the production of SDM and RDM in bean plants can be attributed to the CW, PE, and BO binders, which enrich the soil with a variety of bioactive compounds and nutrients. The binders facilitate the release of a range of compounds, including aldehydes, ketones, alcohols, organic acids, esters, and essential minerals. This process stimulates root development and microbial activity in the soil. The granular form of these fertilizers allows for a controlled and continuous release of nutrients, thereby enhancing availability and the efficiency with which the plants absorb them (Cheng et al., 2022).

As previously discussed, the combination of B with the CW, PE, and BO binders results in the formation of surface functional groups, particularly oxygenated groups (OH, COOH, and CO), which are responsible for enhancing the polarity of the organomineral fertilizer and facilitating the adsorption of nutrient ions through various binding mechanisms, including as surface complexation, ion exchange, coprecipitation, electrostatic attraction, and physicochemical adsorption (El-Naggar et al., 2022).

The diminished dry matter production of plants cultivated in soils treated with granular fertilizers comprising BO, in comparison to those treated with granules containing PE and CW, can be attributed to the compact structure of the BO granules. This density creates a barrier that limits the diffusion of water from the soil and the dissolution of mineral elements from the granules, resulting in a slower release of nutrients and, consequently, a reduction in the initial crop yield (Cheng et al., 2022). The hydrophobic nature of the granular BO fertilizer also contributes to this effect (Zhang et al., 2020).

In contrast, the granules comprising the CW and PE binders contain a considerable quantity of water-soluble compounds, which can exert a more rapid influence on the physicochemical properties of the soil. This has the effect of improving the soil pH, water retention capacity, nutrient availability, and soil microbial community. Furthermore, the greater WAR of these binders may have increased water absorption in the rhizosphere, promoting the dissolution and availability of nutrients. This process contributes to better root development, mineralization, diffusion and nutrient assimilation, especially P from NP, increasing crop productivity (Santos et al., 2020).

The linear reduction in RDM as a function of the dose of the BO and PE binders can be explained by the proportional reduction in the water absorption capacity of the granules due to their reduced porous structure, resulting in less nutrient dissolution. In contrast, granular fertilizers containing CW had the opposite effect since starch, due to its hydrophilic properties, favors gelatinization and, consequently, better water absorption in the rhizosphere.

The effects of concentration and dilution (Jarrell and Beverly, 1981), associated with lower and higher dry matter production, respectively, may have contributed to the lack of any significant difference between treatments regarding the nutrient content of the bean shoots. The brief cultivation period may have constrained nutrients' bioavailability due to the organomineral fertilizers' slow-release nature, which retains nutrients within their structure. This may have initially favored the bio-stimulant effect of the binders. The greater amount of nutrients accumulated by the plants in the PE treatment is associated with the increase in dry matter production obtained with this treatment (Table 5).

Therefore, the technological properties of the organic fertilizer granules containing B and NP were modified by the diverse binders. The granules with BO exhibited the highest values for crushing strength,

density, and IRI; CW demonstrated the highest values for WAR and pH, while PE exhibited the highest values for SI. The granular fertilizers, regardless of the binder utilized, were observed to increase SDM and RDM production in the bean plants. However, the results suggest that the biostimulant effect of the binders was more pronounced during the short cultivation period due to the slow-release nature of the fertilizer. Consequently, further research with longer cultivation periods is necessary to investigate more thoroughly the soil-plant-environment interactions with organomineral fertilizers containing distinct binders.

ACKNOWLEDGMENTS

The authors would like to thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the scientific productivity fellowship granted to the last author. This research was funded by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq/Brazil), the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES/Brazil) and the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG/Brazil).

AUTHORS' CONTRIBUTIONS

Conceptualization: Santos Júnior JM, Fernandes LA. Investigation: Santos Júnior JM, Fernandes LA, Colen F. Formal analyses: Santos Júnior JM, Fernandes LA, Colen F. Methodology: Santos Júnior JM, Fernandes LA, Colen F. Original draft: Santos Júnior JM, Fernandes LA, Colen F, Frazão LA, Pegoraro RF.

CONFLICT OF INTEREST STATEMENT

The authors declare there to be no conflicts of interest.

DATA AVAILABILITY STATEMENT

The data supporting the findings of this study are available in the paper. Should any raw data files be needed in another format they are available from the corresponding author upon request.

DECLARATION OF USE OF AI TECHNOLOGIES

No generative artificial intelligence (AI) was used in this study.

REFERENCES

- American Society for Testing and Materials – International [ASTM]. 2020. Standard Test Method for Determination of Total Solids in Biomass. ASTM, West Conshohocken, PA, USA. <http://dx.doi.org/10.1520/E1756-08R20>
- American Society for Testing and Materials – International [ASTM]. 2021. Standard Test Method for Chemical Analysis of Wood Charcoal. ASTM, West Conshohocken, PA, USA. <http://dx.doi.org/10.1520/D1762-84R21>
- Anukam A, Berghel J, Henrikson G, Frodeson S, Ståhl M. 2021. A review of the mechanism of bonding in densified biomass pellets. *Renewable and Sustainable Energy Reviews* 148: 111249. <https://doi.org/10.1016/j.rser.2021.111249>
- Asafu-Adjaye OA, Street J, Bansode A, Auad ML, Peresin MS, Adhikari S, et al. 2022. Fast pyrolysis bio-oil-based epoxy as an adhesive in oriented strand board production. *Polymers* 14: 1244. <https://doi.org/10.3390/polym14061244>

- Butler JW, Skrivan W, Lotfi S. 2023. Identification of optimal binders for torrefied biomass pellets. *Energies* 16: 3390. <https://doi.org/10.3390/en16083390>
- Casau M, Dias MF, Matias JCO, Nunes LJR. 2022. Residual biomass: a comprehensive review on the importance, uses and potential in a circular bioeconomy approach. *Resources* 11: 35. <https://doi.org/10.3390/resources11040035>
- Channab BE, Idrissi AE, Zahouily M, Essamlali Y, White JC. 2023. Starch-based controlled release fertilizers: a review. *International Journal of Biological Macromolecules* 238: 124075. <https://doi.org/10.1016/j.ijbiomac.2023.124075>
- Cheng J, Liao Z, Hu SC, Geng ZC, Zhu MQ, Xu WZ. 2022. Synthesis of an environmentally friendly binding material using pyrolysis byproducts and modified starch binder for slow-release fertilizers. *Science of the Total Environment* 819: 153146. <http://dx.doi.org/10.1016/j.scitotenv.2022.153146>
- El-Naggar A, Mosa A, Ahmed N, Niazi NK, Yousaf B, Sarkar B, et al. 2022. Modified and pristine biochars for remediation of chromium contamination in soil and aquatic systems. *Chemosphere* 303: 134942. <https://doi.org/10.1016/j.chemosphere.2022.134942>
- Food and Agriculture Organization [FAO]. 2022. Forestry Production and Trade: FAOSTAT. FAO, Rome, Italy. Available at: <https://www.fao.org/faostat/en/#data/FO> [Accessed May 02, 2024]
- Frainetti AJ, Klinghoffer NB. 2023. Recent experimental advances on the utilization of biochar as a tar reforming catalyst: a review. *International Journal of Hydrogen Energy* 48: 8022- 8044. <https://doi.org/10.1016/j.ijhydene.2022.11.127>
- Gondim RS, Munis CR, Lima CEP, Santos CLA. 2018. Explaining the water-holding capacity of biochar by scanning electron microscope images. *Revista Caatinga* 31: 972-979. <https://doi.org/10.1590/1983-21252018v31n420rc>
- Jarrell WM, Beverly RB. 1981. The dilution effect in plant nutrition studies. *Advances in Agronomy* 34: 197-224. [https://doi.org/10.1016/S0065-2113\(08\)60887-1](https://doi.org/10.1016/S0065-2113(08)60887-1)
- Lachos-Perez D, Vieira-Martins JC, Missau J, Anshu K, Siakpebru OK, Thengane SK, et al. 2023. Review on biomass pyrolysis with a focus on bio-oil upgrading techniques. *Analytica* 4: 182- 205. <https://doi.org/10.3390/analytica4020015>
- Li H, Xu J, Nyambura SM, Wang J, Li C, Zhu X, et al. 2022. Food waste pyrolysis by traditional heating and microwave heating: a review. *Fuel* 324: 124574. <https://doi.org/10.1016/j.fuel.2022.124574>
- Malavolta E. 1980. *Elementos de Nutrição Mineral de Plantas*. Editora Agrônoma Ceres, São Paulo, SP, Brazil (in Portuguese).
- Mikolaitienė A, Šlinkšienė R. 2022. Effect of various binders on the properties of microalgae-enriched urea granules. *Plants* 11: 3362. <https://doi.org/10.3390/plants11233362>
- Ministério da Agricultura, Pecuária e Abastecimento [MAPA]. 2017. *Manual de Métodos Analíticos Oficiais para Fertilizantes e Corretivos*. MAPA, Brasília, DF, Brazil (in Portuguese).
- Mohammadi A. 2021. Overview of the benefits and challenges associated with pelletizing biochar. *Processes* 9: 1591. <https://doi.org/10.3390/pr9091591>
- Nunes APP, Santos CF, Guelfi D. 2022. Interfaces between biodegradable organic matrices coating and MAP fertilizer for improve use efficiency. *Science of the Total Environment* 804: 149896. <https://doi.org/10.1016/j.scitotenv.2021.149896>
- Peng J, Zhang L, Meulien ES, Bi XT, Lim JC, Chen W. 2021. Waste plastics as an effective binder for biochar palletization. *Energy & Fuels* 35: 13840-13846. <https://doi.org/10.1021/acs.energyfuels.1c01884>
- Rajkovich S, Enders A, Hanley K, Hyland C, Zimmerman AR, Lehmann J. 2012. Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil. *Biology and Fertility of Soils* 48: 271-284. <https://doi.org/10.1007/s00374-011-0624-7>

- Richards SR. 1990. Physical testing of fuel briquettes. *Fuel Processing Technology* 25: 89-100. [https://doi.org/10.1016/0378-3820\(90\)90098-D](https://doi.org/10.1016/0378-3820(90)90098-D)
- Riva L, Nielsen HK, Skreiberg Ø, Wang L, Bartocci P, Barbanera M, et al. 2019. Analysis of optimal temperature, pressure and binder quantity for the production of biocarbon pellet to be used as a substitute for coke. *Applied Energy* 256: 113933. <https://doi.org/10.1016/j.apenergy.2019.113933>
- Ronix A, Cazetta AL, Ximenez GR, Spessato L, Silva MC, Fonseca JM, et al. 2021. Biochar from the mixture of poultry litter and charcoal fines as soil conditioner: optimization of preparation conditions via response surface methodology. *Bioresource Technology Reports* 15: 100800. <https://doi.org/10.1016/j.biteb.2021.100800>
- Santos SR, Lustosa Filho JF, Vergütz L, Melo LCA. 2019. Biochar association with phosphate fertilizer and its influence on phosphorus use efficiency by maize. *Agricultural Sciences* 43: e025718. <http://dx.doi.org/10.1590/1413-7054201943025718>
- Santos CF, Aragão OOS, Silva DRG, Jesus EC, Chagas WFT, Correia PS, et al. 2020. Environmentally friendly urea produced from the association of N-(n-butyl) thiophosphoric triamide with biodegradable polymer coating obtained from a soybean processing byproduct. *Journal of Cleaner Production* 276: 123014. <https://doi.org/10.1016/j.jclepro.2020.123014>
- Santos Júnior JM, Colen F, Pegoraro RF, Heinrichs R, Frazão LA, Sampaio RA, et al. 2024. Biochar pellets as soil conditioner on the growth of *Urochloa brizantha* BRS Paiaguás. *Revista Ciência Agronômica* 55: e20238690. <https://doi.org/10.5935/1806-6690.20240044>
- Sarker TR, Borugadda VB, Meda V, Dalai AK. 2023. Optimization of palletization process conditions and binder concentration for production of fuel pellets from oat hull and quality evaluation. *Biomass and Bioenergy* 174: 106825. <https://doi.org/10.1016/j.biombioe.2023.106825>
- Schettini BLS, Jacovine LAG, Torres CMME, Carneiro ACO, Villanova PH, Rocha SJSS, et al. 2022. Furnace-kiln system: how does the use of new technologies in charcoal production affect the carbon balance? *Industrial Crops and Products* 187: 115330. <https://doi.org/10.1016/j.indcrop.2022.115330>
- Shetty R, Prakash NB. 2020. Effect of different biochars on acid soil and growth parameters of rice plants under aluminium toxicity. *Scientific Reports* 10: 12249. <https://doi.org/10.1038/s41598-020-69262-x>
- Tedesco JM, Gianello C, Bissani CA, Bohnen H, Volkweiss SJ. 1995. Análises de Solo, Plantas e outros Materiais. UFRGS-Faculdade de Agronomia, Porto Alegre, RS, Brazil (in Portuguese).
- Teixeira PC, Donagemma GK, Fontana A, Teixeira WG. 2017. Manual de Métodos de Análise de Solo. Embrapa Solos, Rio de Janeiro, RJ, Brazil (in Portuguese).
- Yang Y, Sun K, Han L, Chen Y, Liu J, Xing B. 2022. Biochar stability and impact on soil organic carbon mineralization depend on biochar processing, aging and soil clay content. *Soil Biology and Biochemistry* 169: 108657. <https://doi.org/10.1016/j.soilbio.2022.108657>
- Zhang C, Zhang L, Gao J, Zhang S, Liu Q, Duan P, et al. 2020. Evolution of the functional groups/structures of biochar and heteroatoms during the pyrolysis of seaweed. *Algal Research* 48: 101900. <https://doi.org/10.1016/j.algal.2020.101900>

4.2 Artigo 2 – Biochar-based granular fertilizers with agro-industrial binders enhance enzymatic activity and nutrient cycling in tropical Oxisols

Este artigo foi elaborado e publicado conforme as normas da revista **Agronomy**.

SANTOS JÚNIOR, José Mendes dos *et al.* Biochar-Based Granular Fertilizers with Agro-Industrial Binders Enhance Enzymatic Activity and Nutrient Cycling in Tropical Oxisols. **Agronomy**, v. 15, n. 9, 2025. DOI: <https://doi.org/10.3390/agronomy15092230>.

Biochar-based granular fertilizers with agro-industrial binders enhance enzymatic activity and nutrient cycling in tropical Oxisols

Abstract

The low fertility of tropical Oxisols challenges sustainable agriculture. While biochar-based granular fertilizers (BBGFs) offer a solution, the influence of different organic binders is unclear. This study investigated how BBGFs formulated with bio-oil (BO), pyroligneous extract (PE), and cassava wastewater (CW) impact soil enzyme activities and nutrient dynamics over time. Eucalyptus biochar (B) and natural phosphate (NP) were granulated with three binders at four doses. These treatments, plus controls (unfertilized soil, NP, B with NP, and B alone), were incubated in an Oxisol, assessing soil samples after 10 and 40 days of incubation. All BBGFs significantly enhanced β -glucosidase, acid phosphatase, and arylsulfatase activities over controls, with increases exceeding 8%. While the BBGFs-BO formulation sustained the highest enzymatic activity, BBGFs-PE at 125% maximized acid phosphatase at 10 days, with a subsequent decline, and inhibited arylsulfatase at the 150% dose. BBGFs-CW was most effective for increasing P availability (up to 24.0 mg kg⁻¹). BBGFs-BO and BBGFs-PE also enhanced soil organic carbon and cation exchange capacity by up to 430% and 163%, respectively. The BBGFs-BO at 150% dose is the most effective and stable formulation to enhance nutrient cycling and soil health, offering a viable pathway to convert agricultural residues into high-value fertilizers.

Keywords: β -glucosidase; acid phosphatase; arylsulfatase; nutrient cycling; agricultural residues; biological indicators

1 INTRODUCTION

Sustainable soil management is crucial to meeting modern agricultural demands, particularly in the context of climate change and growing pressure for more efficient practices [1]. Tropical soils, such as Oxisols, are highly weathered and characterized by low natural fertility due to high acidity and low nutrient and organic matter contents [2,3]. Intensive agriculture in tropical soils favors the mineralization of organic matter and, consequently, increased acidity, aluminum toxicity, and nutrient leaching. The reduction in organic matter also affects soil particle aggregation, aggregate stability, and water retention and storage capacity [4]. Furthermore, the predominance of Fe and Al oxyhydroxides and kaolinite in the clay fraction, combined with high acidity, favors phosphorus fixation reactions, significantly reducing phosphorus availability and the efficiency of phosphate fertilizers [5].

Improving soil organic matter through carbon-rich amendments represents a critical strategy to counteract these limitations and restore fertility in highly weathered tropical soils [6]. In this context, biochar emerges as a particularly promising amendment due to its ability to enhance key soil properties, boost agricultural productivity, and provide environmental benefits, including mitigation of greenhouse gas emissions and reduced carbon footprint [7].

Biochar is a solid carbonaceous product obtained through the pyrolysis of organic materials under low or no oxygen conditions, exhibiting significant properties such as high carbon stability, porosity, and specific surface area [4]. These characteristics improve soil chemical, physical, and biological conditions, including increased cation exchange capacity (CEC), carbon sequestration, elevation of pH in acidic and highly weathered soils, enhanced nutrient cycling, and reduced nutrient leaching losses [6,8,9]. Furthermore, biochar application has been associated with increased soil microbial activity, a key indicator for assessing soil ecosystem health [10,11].

Biochar offers several benefits for soil properties and for the remediation of soils and waters contaminated by potentially toxic elements, as heavy metals [12] and organic pollutants, especially emerging pollutants such as perfluoroalkyl and polyfluoroalkyl substances (PFASs), which pose serious risks to the ecosystem and human health [13]. However, there is a risk that biochar itself may add pollutants to the soil, resulting from the raw material and the pyrolysis process, with negative effects on the environment, plants, animals, microorganisms, and even human health [14]. Given this scenario, it is important to monitor the potential impacts of biochar-based fertilizers using indicators sensitive to environmental pollution, such as soil enzyme activity.

Soil enzymatic activity, mediated by microbial extracellular enzymes such as β -glucosidase, phosphatases, and arylsulfatase, plays a pivotal role in organic matter decomposition and nutrient cycling, catalyzing oxidative and hydrolytic reactions [15]. These processes are directly influenced by soil management practices and input applications, making them widely used as indicators to evaluate the impacts of fertilization strategies and land use [16,17].

β -Glucosidase catalyzes the hydrolysis of maltose and cellobiose, yielding glucose. Phosphatases facilitate phosphorus mineralization by hydrolyzing esters and anhydrides of phosphoric acid, while arylsulfatase hydrolyzes organic sulfate esters in the soil, contributing to the release of bioavailable sulfur forms [18,19]. In Brazil, the enzymes β -glucosidase and arylsulfatase are used by farmers to evaluate agricultural soil quality, as they are related, directly or indirectly, to the productive potential and sustainability of land use [16,17].

The production of biochar-based granular fertilizers (BBGFs) using alternative binders such as bio-oil (BO), pyroligneous extract (PE) — byproducts of charcoal production — and cassava wastewater (CW), a residue from cassava starch production, represents a promising approach for tropical soils [20]. CW is a residue produced in large volumes in the cassava starch agroindustry, rich in nutrients and with great polluting potential if disposed of inappropriately. In addition to increasing fertilizer granule stability to improve application quality, alternative binders have the potential to reduce production costs, promote controlled nutrient release, and improve plant nutrient use efficiency [20,21,22]. This strategy increases soil nutrient bioavailability and contributes to the sustainability of agricultural systems.

Although the impact of biochar on soil microbiota is not yet fully understood, its physicochemical properties are known to vary depending on feedstock materials and pyrolysis conditions [9]. These properties directly influence microorganisms, which are sensitive to environmental changes and serve as indicators of soil quality [17]. Thus, investigating how biochar, particularly in BBGFs formulations, affects microbial activity is essential for optimizing its application in sustainable soil fertility management.

We hypothesize that incorporating alternative binders, such as CW, PE, and BO, into BBGFs alters soil enzymatic activity and chemical properties. Although these binders provide carbon and nutrients, PE and BO may contain toxic pyrolysis-derived compounds that harm soil microorganisms, while CW may undergo rapid mineralization. To evaluate the toxicity of PE and BO, soil enzymes were evaluated in comparison to CW, which is supposedly non-toxic and favors soil microbial activity. Soil enzymes are widely used as indicators of soil health due to their strong correlation with soil quality, and are significantly influenced by different agricultural practices, such as organic amendments [10,23]. Thus, the objective of this study was to evaluate alternative binders to produce BBGFs and their respective effects on soil chemical properties and enzymatic activity, as indicators of soil health over time.

2 MATERIALS AND METHODS

2.1 Biochar Production

Biochar was produced through slow pyrolysis of *Eucalyptus urograndis* wood in a kiln-furnace system (Figure S1A) located at the Institute of Agricultural Sciences, Federal University of Minas Gerais, Montes Claros, MG, Brazil, whose geographical coordinates are 16°41'2.03" S, 43°50'19.28" W, altitude 646 m. The biochar consisted of fines generated during the pyrolysis process, conducted at 450 °C with a heating rate of 0.1 °C min⁻¹ and a residence time of six days (Figure S1B). Furnace temperatures were monitored using an infrared sensor every 30 min during the heating and drying stages and every 8 h during the cooling stage [24].

2.2 Physical and Chemical Characteristics of Biochar and Binders

After mechanical grinding, the biochar was sieved through a 0.25 mm mesh to standardize particle size. The chemical and physical properties of the biochar were characterized, as shown in Table 1, with methodological details described by [20]. Briefly, pH and electrical conductivity (EC) were determined in a biochar:deionized water solution (1:20, w/v) after shaking for 1.5 h on an orbital shaker. Bulk density was calculated by filling a 10 mL graduated cylinder with biochar, compacting it by shaking for 1 min, and weighing the sample. Moisture, volatile matter, ash, and fixed carbon (FC) contents were determined by heating in a muffle furnace according to the protocol in ASTM D1762-84 [25]. Total carbon and nitrogen

contents were analyzed using the wet oxidation method with potassium dichromate followed by titration with ferrous sulfate and the Kjeldahl method, respectively [26]. Oxygen and hydrogen contents were estimated based on correlations established by [27]. Samples were subjected to acid digestion with a 3:1 (v/v) nitric-perchloric acid solution in a digestion block for nutrient determination. Phosphorus was quantified using the phosphomolybdovanadate method, potassium, and sodium by flame photometry (B 462, Micronal S.A., Osasco, SP, Brazil), sulfur by the turbidimetric method with barium chloride, and other nutrients by atomic absorption spectrometry (Varian AAS 240 FS, Agilent Technologies, Palo Alto, CA, USA).

Table 1. Proximate, ultimate analysis and physicochemical characteristics of biochar obtained from eucalyptus wood fines generated as byproducts after pyrolysis.

Feature	Results
pH	8.9 (0.0)
EC ($\mu\text{S cm}^{-1}$)	786.3 (5.9)
Density (kg dm^{-3})	0.6 (0.0)
Ash (%)	50.6 (1.0)
VC (%)	23.6 (4.6)
Moisture (%)	4.9 (1.1)
FC (%)	20.7 (2.4)
C (%)	50.7 (2.3)
H (%)	1.9 (0.3)
O (%)	7.8 (2.2)
Total N (g kg^{-1})	1.9 (0.1)
C/N	255.0 (5.9)
P (g kg^{-1})	3.3 (0.0)
K (g kg^{-1})	1.1 (0.0)
Ca (g kg^{-1})	50.6 (4.3)
Mg (g kg^{-1})	4.2 (0.2)
S (g kg^{-1})	3.5 (0.3)
Na (g kg^{-1})	0.8 (0.0)
Fe (g kg^{-1})	17.5 (0.4)
Zn (mg kg^{-1})	27.2 (0.1)
Mn (mg kg^{-1})	479.4 (12.7)
Cu (mg kg^{-1})	17.8 (0.2)

Values in parentheses show the 95% confidence intervals ($n = 4$). EC = electrical conductivity; VC = volatile compounds; FC = fixed carbon.

The three binders used in this study (CW, PE and BO) were obtained from different agro-industrial processes. The CW is a liquid residue acquired from local agro-industries in Montes Claros, MG, Brazil, generated during the processing of cassava roots for starch production.

The PE and BO binders were obtained as byproducts from the same slow pyrolysis process in the kiln-furnace system used for biochar production. The vapors released during wood pyrolysis were channeled, cooled, and condensed into a raw liquid. This liquid was then stored and left undisturbed for a six-month period, allowing for spontaneous gravitational separation of its phases. After decantation, two distinct fractions were separated: the dense, viscous, water-insoluble phase (pyrolysis tar) that settled at the bottom was collected as BO, while the overlying aqueous phase was collected as PE.

The binders were characterized for pH, EC, and total solids (Table 2). The pH and EC were measured directly in liquid samples of CW and PE. For BO samples (liquid-pasty consistency), a 1:5 (BO:distilled water, v/v) ratio was used, with measurements performed on the aqueous extract [26]. Total solids were determined according to the protocol in ASTM E1756-08 [28], involving heating 50 mL of the sample in

porcelain crucibles in a water bath at 65 °C for 16 h, followed by drying in an oven at 103 °C for 24 h. After drying, the crucibles were cooled in desiccators to determine the mass of solids.

Table 2. Basic properties of binders used to produce biochar-based granular fertilizers.

Binder	pH	EC	TS
	-	$\mu\text{S cm}^{-1}$	g L^{-1}
BO	2.7 (0.1)	1386.6 (37.3)	115.2 (4.0)
PE	3.3 (0.0)	9963.3 (26.6)	71.9 (1.2)
CW	4.3 (0.1)	567.6 (4.1)	230.8 (26.2)

Values in parentheses show the 95% confidence intervals ($n = 3$). EC = electrical conductivity; TS = total solids; BO = bio-oil; PE = pyroligneous extract; CW = cassava wastewater.

Fourier-transform infrared (FTIR) spectroscopy was employed to identify the main functional groups present in the biochar and binders. Spectra were recorded using a Cary 640 FTIR spectrometer (Agilent Technologies Inc., Santa Clara, CA, USA), operating in the 4000–500 cm^{-1} range, with a resolution of 2 cm^{-1} and 64 scans per sample. The potassium bromide (KBr)-pressed pellet technique was applied, in which 1 mg of dried sample was mixed with 100 mg of spectroscopic-grade KBr (Merck and Co., Rahway, NJ, USA) and compressed into a pellet for analysis.

2.3 Biochar-Based Fertilizers Production

Biochar-based granular fertilizers (BBGFs) were produced using a disk granulator, employing a 3:1 (w/w) ratio of biochar to reactive natural phosphate (NP) sourced from phosphorites containing 27% total P_2O_5 and 8.1% P_2O_5 soluble in 2% citric acid. Binders were applied by spraying onto the biochar-NP mixture, followed by a homogenization process lasting approximately 40 min at 32.98 rad s^{-1} .

The binder quantity was determined as a percentage of the physical mixture (biochar + NP) weight, at proportions of 75, 100, 125, and 150%. For the 75% dose, 1 kg of the mixture (750 g biochar + 250 g NP) was combined with 750 mL of binder, with increments of 250 mL for each 25% increase. After granulation, the BBGFs were dried in an oven at 65 ± 5 °C for approximately 72 h until constant weight. The granules were cooled to room temperature and stored in plastic containers.

2.4 Experimental Design

Two experiments were conducted to evaluate the activities of β -glucosidase, acid phosphatase, and arylsulfatase enzymes, as well as the chemical properties of soil fertilized with BBGFs. Experiment 1 involved a 10-day incubation period of the fertilizers in the soil, while Experiment 2 extended to 40 days (Figure 1).

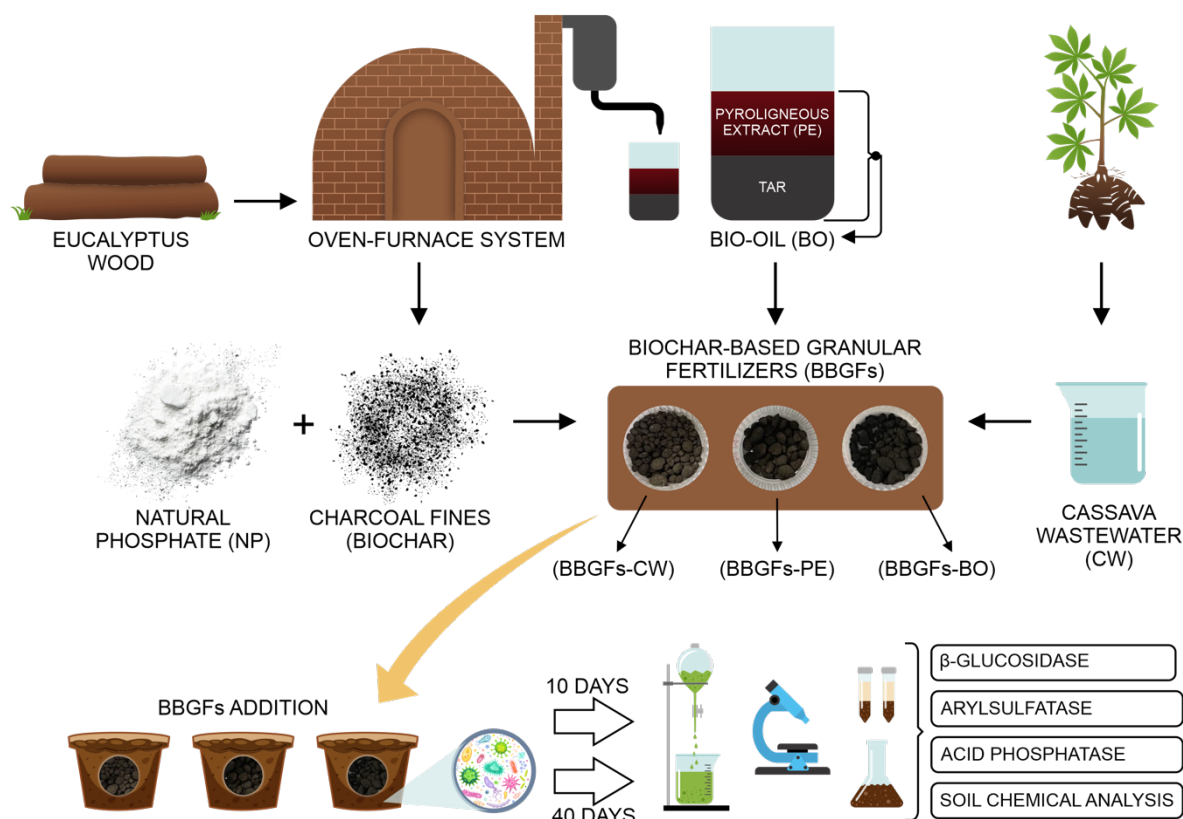


Figure 1. Experimental methodology for testing biochar-based granular fertilizers (BBGFs) in a tropical Oxisol.

Both experiments were conducted in a completely randomized design, with treatments arranged in a $4 \times 3 + 4$ factorial scheme with three replications, totaling 48 experimental units. The treatments comprised four binder proportions for granule production (75, 100, 125, and 150%), three binder types (CW, PE, and BO), and four additional treatments: natural soil or unfertilized soil (NS), reactive natural phosphate (NP), biochar and natural phosphate (B + NP), and biochar alone (B).

2.5 Soil Enzyme Activity and Chemical Analysis

In both experiments, pots were filled with 100 cm³ of a dystrophic Oxisol (Red Yellow Latosol, according to the Brazilian Soil Classification System) collected from the 0–20 cm layer under Cerrado biome (largest savanna region in South America). Soil samples were air-dried and sieved through 2.0 mm. The soil exhibited low fertility, with available P and K⁺ contents of 0.9 and 13.7 mg dm⁻³ (Mehlich-1 method), respectively, pH 5.2 (water), and exchangeable Ca²⁺ and Mg²⁺ concentrations of 0.3 and 0.1 cmol_c kg⁻¹ (1 M KCl extraction), respectively. Soil organic carbon (SOC) was 0.1 dag kg⁻¹, measured via loss on ignition according to [29].

Soil acidity was corrected with a mixture of calcium carbonate and magnesium carbonate in a molar ratio of 3:1 (Ca:Mg) to increase soil base saturation to 70%. The soil of each experimental plot was incubated with the carbonate mixture for 30 days, maintaining soil moisture levels close to field capacity. After this period, the different BBGFs were mixed and homogenized with the soil of each experimental unit (pots containing 100 cm³ of soil).

The amount of BBGFs applied to the soil was determined based on the dry mass produced from the granule preparation mixture, considering the respective binder doses for BBGFs-CW, BBGFs-PE, and

BBGFs-BO, to supply 200 mg dm⁻³ of phosphorus to the soil [30]. This calculation accounted for the composition of the natural phosphate, containing 27% P₂O₅.

The additional treatments containing B and NP, applied individually or in combination, were incorporated into the soil conventionally (non-granulated). For the combined application, a 3:1 (B:NP, w/w) ratio was used, consistent with that adopted for BBGFs production.

At the end of Experiment 1 (10 days) and Experiment 2 (40 days), 30 g soil samples were collected from each experimental unit for enzymatic analyses. Samples were sieved through a 1 mm mesh to remove roots and plant debris, stored in plastic bags, and kept at 4 °C until analysis, which occurred within approximately one week of collection [10,15]. In both experiments, soil samples from each treatment were chemically characterized for pH in water, P-Meh (Mehlich-1 P), P-Res (P-Resin), SOC, K⁺, Ca²⁺, Mg²⁺, S, Fe²⁺, and Zn²⁺, following the methodologies of [31]. The CEC was calculated from the results obtained.

The activities of β -glucosidase, acid phosphatase, and arylsulfatase were assessed in triplicate, including a control, according to the method described by [19]. This method involves incubating soil samples for 1 h at 37 °C in buffered solutions containing the substrates p-nitrophenyl- β -D-glucoside, p-nitrophenyl disodium phosphate, and p-nitrophenyl sulfate, respectively. Due to the short incubation period, toluene was omitted from the analyses [16]. After incubation, the amount of p-nitrophenol (PNP) released from the enzymatic reaction was determined, expressed as mg PNP kg⁻¹ dry soil h⁻¹, using UV-visible spectrophotometry.

2.6 Statistical Analysis

The Shapiro–Wilk test was used to verify data normality. Data were subjected to analysis of variance (ANOVA) using the F-test ($p < 0.05$). In cases of significance among binder doses, regression analysis was performed. The best models were selected based on the significance of model parameters and the highest coefficient of determination (R^2). Additional treatments were compared with other treatments, regardless of doses, using Dunnett's test ($p < 0.05$). Additionally, soil chemical and enzymatic variables were subjected to Principal Component Analysis (PCA) and Pearson's correlation matrix. Statistical analyses were conducted using R software, version 4.2.2.

3 RESULTS

3.1 Physical and Chemical Analysis

The main physico-chemical properties of the eucalyptus biochar are presented in Table 1. The biochar exhibited an alkaline pH in water (8.9) and a high ash content of 50.6%. The ultimate analysis showed a total carbon content of 50.7% and a high C/N ratio of 255. Among the mineral elements, Ca was the most abundant at 50.6 g kg⁻¹, followed by Fe at 17.5 g kg⁻¹ and Mg at 4.2 g kg⁻¹.

The FTIR spectra identified the main functional groups present in the biochar and binders (Figure 2). A broad O-H stretching band, characteristic of hydroxyl groups, was observed in all materials between 3450 and 3300 cm⁻¹. Aliphatic C-H stretching was also evident around 3000–2900 cm⁻¹. The binders, particularly PE and BO, were distinguished by a strong C=O stretching peak in the 1750–1600 cm⁻¹ region, associated with ketone and carbonyl groups from the thermal decomposition of cellulose and lignin. The BO spectrum also showed more pronounced peaks in the C-O stretching and aromatic C-H bending region (1100–700 cm⁻¹), confirming a more complex and aromatic structure.

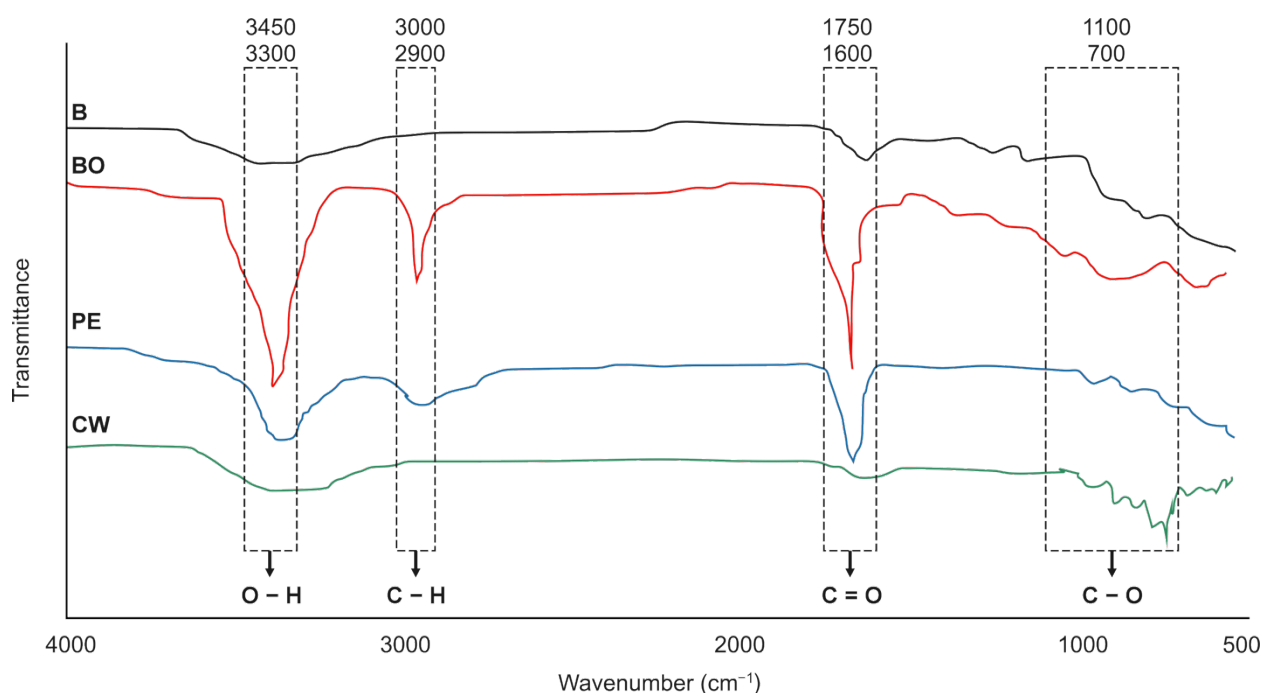


Figure 2. Fourier-transform infrared (FTIR) spectra of biochar (B), cassava wastewater (CW), pyroligneous extract (PE), and bio-oil (BO). The peak assignments are noted above their respective peaks.

3.2 β -Glucosidase

The activity of β -glucosidase in soil amended with BBGFs increased linearly with binder doses after 10 and 40 days of incubation (Figure 3A,B). At 10 days, the highest activities were observed at the 150% dose, with values of 65.38, 105.16, and 134.13 mg PNP kg⁻¹ soil h⁻¹ for BBGFs-CW, BBGFs-PE, and BBGFs-BO, respectively (Figure 3A). After 40 days, the activity decreased across all treatments, but BBGFs-BO at 150% maintained the highest value (134.58 mg PNP kg⁻¹ soil h⁻¹), while BBGFs-CW and BBGFs-PE showed lower activities (47.64 and 58.87 mg PNP kg⁻¹ soil h⁻¹, respectively) (Figure 3B).

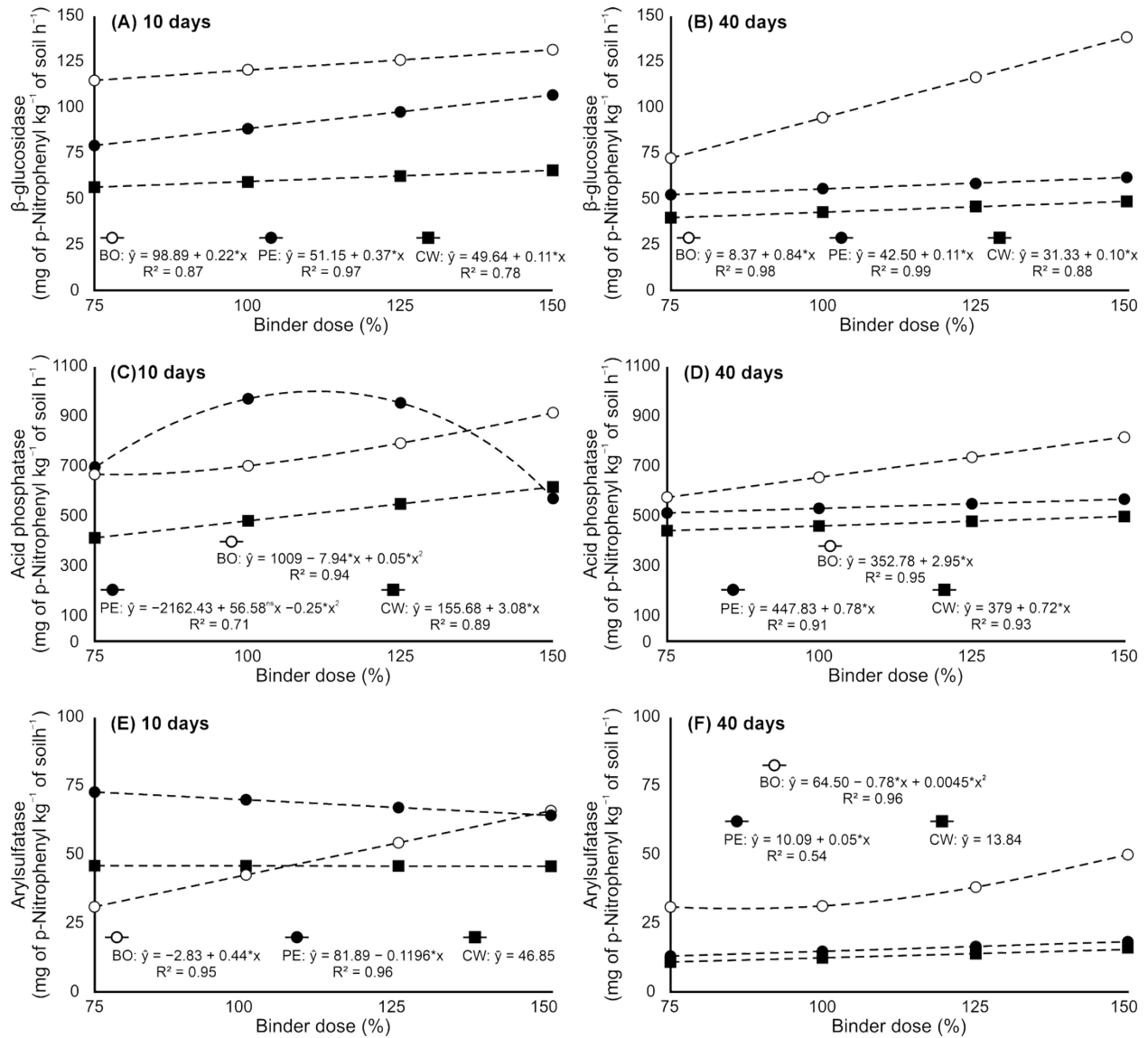


Figure 3. Soil enzyme activity in response to increasing doses of different binders in biochar-based granular fertilizers (BBGFs). The experiment was conducted in a tropical Oxisol, with measurements taken after 10 and 40 days of incubation. The panels show the activity of: (A) β -glucosidase at 10 days; (B) β -glucosidase at 40 days; (C) acid phosphatase at 10 days; (D) acid phosphatase at 40 days; (E) arylsulfatase at 10 days; (F) arylsulfatase at 40 days. * significant by *t*-test (*p*-value < 0.05).

3.3 Acid Phosphatase

Acid phosphatase activity varied depending on the binder type and dose (Figure 3C,D). Enzymatic activity increased linearly with application dose of BBGFs-CW after 10 days of soil incubation, reaching 645.52 mg PNP kg⁻¹ soil h⁻¹ at 150% (Figure 3C). In contrast, BBGFs-PE and BBGFs-BO amendments produced quadratic dose–response curves in soil enzyme activity, with a peak activity of 1082.22 mg PNP kg⁻¹ soil h⁻¹ at 125% for BBGFs-PE, followed by a decrease to 569.84 mg PNP kg⁻¹ soil h⁻¹ at 150%, while the highest values for treatments with BBGFs-BO were observed at the 150% dose (914.62 mg PNP kg⁻¹ soil h⁻¹) (Figure 3C). After 40 days of incubation, soil enzyme activity increased linearly with binder dose for all BBGFs formulations, with BO-amended soils at 150% showing the highest activity (811.54 mg PNP kg⁻¹ soil h⁻¹), followed by BBGFs-PE- (558.62 mg PNP kg⁻¹ soil h⁻¹) and BBGFs-CW-treated soils (490.20 mg PNP kg⁻¹ soil h⁻¹) (Figure 3D).

3.4 Arylsulfatase

After 10 days of incubation, soils fertilized with BBGFs-CW maintained stable arylsulfatase activity ($46.85 \text{ mg PNP kg}^{-1} \text{ soil h}^{-1}$) regardless of application dose (Figure 3E). In contrast, increasing doses of BBGFs-PE significantly reduced arylsulfatase activity in soils from $72.55 \text{ mg PNP kg}^{-1} \text{ soil h}^{-1}$ (75% dose) to $64.17 \text{ mg PNP kg}^{-1} \text{ soil h}^{-1}$ (150% dose) (Figure 3E). After 40 days, soils with BBGFs-BO exhibited a quadratic response, peaking at $50.27 \text{ mg PNP kg}^{-1} \text{ soil h}^{-1}$ at 150%, and soils with BBGFs-PE demonstrated a linear increase in the levels of arylsulfatase activity, reaching peak values at the 150% dose ($18.53 \text{ mg PNP kg}^{-1} \text{ soil h}^{-1}$), while treatments with BBGFs-CW showed no significant dose effect, with mean levels of $13.84 \text{ mg PNP kg}^{-1} \text{ soil h}^{-1}$ (Figure 3F).

3.5 Comparative Effects of BBGFs on Soil Enzyme Activities

All BBGFs significantly enhanced soil enzyme activities for β -glucosidase, acid phosphatase and arylsulfatase, compared to the control treatments, with higher values observed at 10 days than at 40 days across all treatments and enzymes (Figure 4A–C). The mean β -glucosidase activity across binder doses was significantly higher in soils with BBGFs-BO (123.47 and $102.64 \text{ mg PNP kg}^{-1} \text{ soil h}^{-1}$ at 10 and 40 days, respectively) compared to BBGFs-PE (92.43 and $54.70 \text{ mg PNP kg}^{-1} \text{ soil h}^{-1}$) and BBGFs-CW (61.99 and $42.98 \text{ mg PNP kg}^{-1} \text{ soil h}^{-1}$) (Figure 4A). For acid phosphatase, the highest values were observed in soils fertilized with BBGFs-PE (793.36 and $535.78 \text{ mg PNP kg}^{-1} \text{ soil h}^{-1}$ at 10 and 40 days, respectively) and BBGFs-BO (764.50 and $685.08 \text{ mg PNP kg}^{-1} \text{ soil h}^{-1}$) compared to BBGFs-CW (502.61 and $459.66 \text{ mg PNP kg}^{-1} \text{ soil h}^{-1}$) (Figure 4B). Arylsulfatase activity was highest in BBGFs-PE treated soils at 10 days ($68.43 \text{ mg PNP kg}^{-1} \text{ soil h}^{-1}$), while BBGFs-BO achieved greater activity at 40 days ($37.75 \text{ mg PNP kg}^{-1} \text{ soil h}^{-1}$) (Figure 4C).

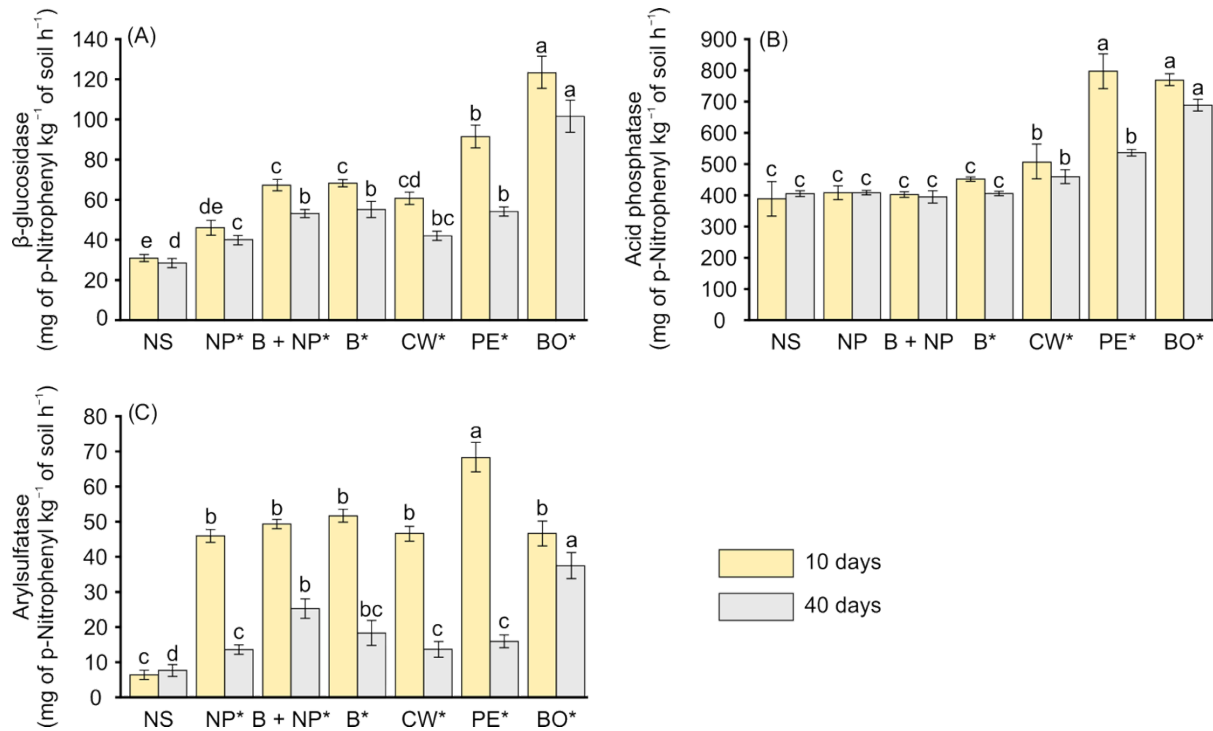


Figure 4. Mean enzymatic activity in a tropical Oxisol treated with biochar-based granular fertilizers (BBGFs) using different binders and controls (unfertilized soil, NS; natural phosphate, NP; biochar, B; biochar + natural phosphate, B + NP) after 10 and 40 days of incubation. The panels show the activity of: (A) β -glucosidase; (B) acid phosphatase; (C) arylsulfatase. Different letters on bars of the same color indicate significant differences among treatments (Tukey's test, $p < 0.05$). An asterisk (*) indicates significant difference between incubation periods (10 and 40 days) for the same treatment (F -test, $p < 0.05$).

3.6 Principal Component Analysis of Soil Properties and Enzyme Activities over Time

PCA was performed to establish relationships between different BBGFs, soil chemical properties, and soil enzymatic activity, considering incubation periods of 10 and 40 days. Regarding soil chemical properties, the first two principal components (PC1 and PC2) accounted for approximately 70% of the total variation after 10 days of incubation (Figure 5A), while at 40 days, these components explained 65.50% of the variability (Figure 5B). Concerning soil enzymatic activity, it was observed that, in both incubation periods, the first two principal components explained more than 78% of the total variation (Figure 5C,D).

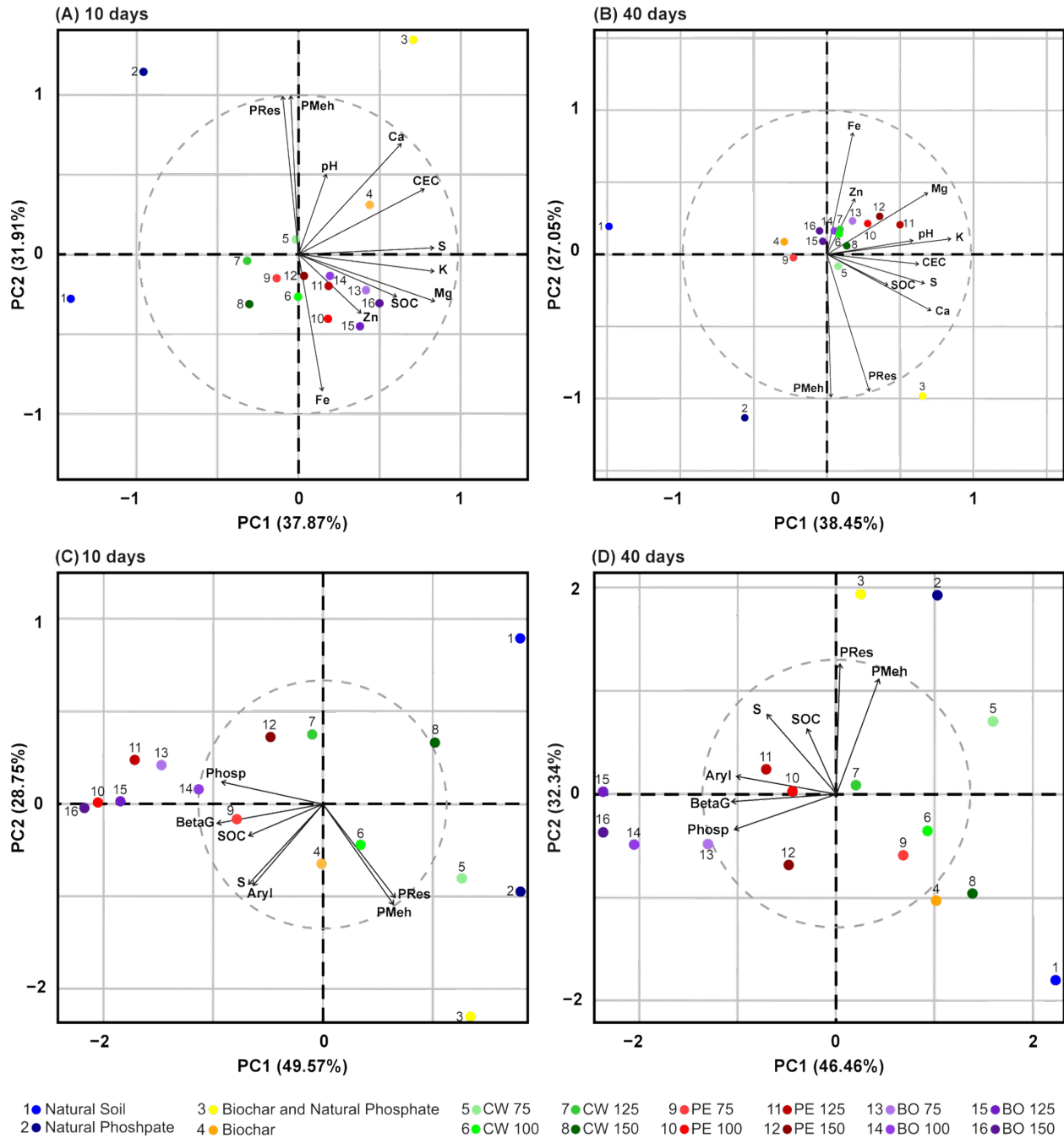


Figure 5. Principal component analysis (PCA) of the effects of different fertilizer treatments on soil properties in a tropical Oxisol. The analysis includes biochar-based granular fertilizers (BBGFs) with cassava wastewater (CW), pyroligneous extract (PE), or bio-oil (BO) binders, and control treatments (unfertilized soil, NS; natural phosphate, NP; biochar, B; biochar + natural phosphate, B + NP). The panels display the effects on: (A) soil nutrient dynamics at 10 days; (B) soil nutrient dynamics at 40 days; (C) enzyme activity at 10 days; (D) enzyme activity at 40 days.

At 10 days of incubation, PCA revealed that soils treated with BBGFs-PE at doses of 100, 125, and 150% and BBGFs-BO at doses of 75 to 150% showed an association with SOC, Mg, Fe, Zn, S and K (Figure 5A). Treatments with BBGFs-CW at a dose of 75% exhibited an association with P-Meh and P-Res. Soils receiving additional treatments with biochar, either alone or combined with NP, were associated with Ca, P-Meh, P-Res, CEC, and pH (Figure 5A). Furthermore, significant positive correlations were found among the studied soil chemical properties at 10 days of incubation: P-Meh and P-Res ($r = 0.89$); CEC and

S ($r = 0.84$); K and S ($r = 0.65$); K and Ca ($r = 0.61$); K and Mg ($r = 0.72$); Ca and CEC ($r = 0.73$); S and Mg ($r = 0.69$); and SOC and Mg ($r = 0.55$) (Figure 6A).

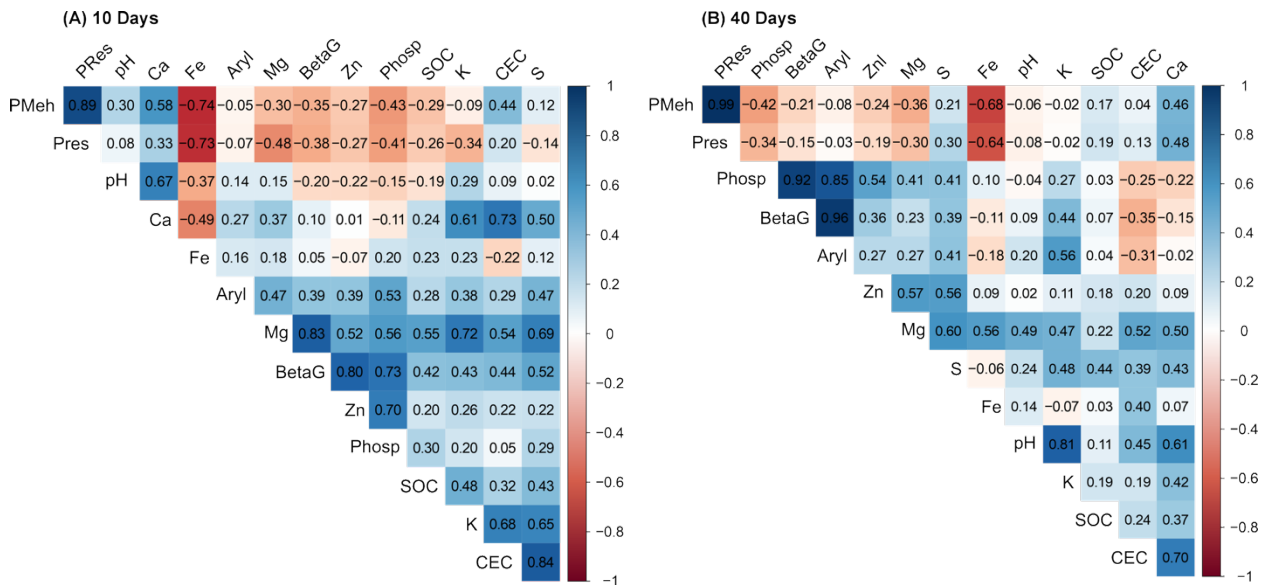


Figure 6. Pearson correlation matrix of the relationships between soil chemical properties and enzymatic activities in a tropical Oxisol after the application of different biochar-based granular fertilizers (BBGFs). Positive correlations are shown in blue and negative correlations in red, with color intensity being proportional to the correlation coefficient (r). The panels display the correlations at: **(A)** 10 days of incubation; and **(B)** 40 days of incubation.

At 40 days of incubation, PCA showed that soils treated with BBGFs containing PE at doses of 100, 125, and 150%, BO at doses of 75 and 100%, and CW at doses of 100, 125, and 150% were associated with K, Mg, Zn, Fe, pH, and CEC (Figure 5B). Additionally, soils incorporated with BBGFs-CW at a 75% dose exhibited an association with SOC, P-Res, P-Meh, Ca, S, and CEC (Figure 5B). Most soils with BBGFs displayed a negative correlation with P-Meh and P-Res, in contrast to soils treated with NP, applied either alone or combined with biochar, and those amended with BBGFs-CW at the 75% dose (Figure 5A,B). The Pearson correlation analysis of soil chemical properties at 40 days revealed the following significant positive associations: P-Meh and P-Res ($r = 0.99$); Ca and pH ($r = 0.61$); K and pH ($r = 0.81$); CEC and Ca ($r = 0.70$); Mg and Zn ($r = 0.57$); Mg and Ca ($r = 0.50$); Mg and CEC ($r = 0.52$); Mg and S ($r = 0.60$); and S and Zn ($r = 0.56$) (Figure 6B).

According to the biplot, overall, at 10 and 40 days of incubation, soils treated with BBGFs containing PE and BO showed a stronger association with the activity of the enzymes β -glucosidase, acid phosphatase and arylsulfatase, except for soils amended with BBGFs-PE at a 75% dose, which exhibited a negative correlation with these enzymes at 40 days (Figure 5C,D). The analysis of the Pearson's correlation matrix showed a positive correlation between acid phosphatase and β -glucosidase ($r \geq 0.73$), arylsulfatase ($r \geq 0.53$), and Zn ($r \geq 0.54$). In contrast, a negative correlation was found between Fe and both P-Meh and P-Res ($r \leq -0.64$), and between acid phosphatase activity and P-Meh ($r \leq -0.42$), across both incubation periods (Figure 6A,B).

4 DISCUSSION

The linear increase in β -glucosidase activity with increasing doses of BBGFs-CW, BBGFs-PE, and BBGFs-BO in granulated fertilizers, observed at both incubation periods, suggests that these materials release a wide variety of organic compounds, including phenolic compounds, aldehydes, ketones, alcohols, organic acids, and readily accessible substrates such as carbohydrates and proteins. These compounds likely stimulate soil microbial activity, enhancing enzyme production [32,33,34,35].

The wide variety of organic compounds is supported by the FTIR spectra of the biochar and binders, which exhibit characteristic functional groups related to such compounds. The spectra exhibit typical O-H stretching bands in the range of 3450–3300 cm^{-1} (Figure 2), attributed to hydroxyl groups present in phenols, alcohols, carboxylic acids, or adsorbed water molecules [3,36]. The vibrational region between 3000 and 2900 cm^{-1} (Figure 2) corresponds to C-H stretching, indicative of aliphatic compounds, and the region between 1750 and 1600 cm^{-1} is associated with ketone groups (C=O) and aromatic structures [37].

These findings align with the observations of [10], who reported elevated β -glucosidase activity in soils amended with eucalyptus-derived biochar, a response attributed to labile carbon inputs. Furthermore, cellulose-rich biochars (e.g., wood-derived biochars) enhance soil enzymatic activity through microbial hydrolysis of cellulose into glucose, releasing labile carbon that feeds microbial metabolism [18].

The superior performance of BBGFs-BO, particularly at 150% application, can be attributed to its high content of recalcitrant carbon compounds, such as aromatic hydrocarbons and heterocyclic structures, which serve as a sustained substrate for β -glucosidase activity [38,39]. This is further supported by the more pronounced vibrational peaks observed for the BO binder around 1600 cm^{-1} and 900–700 cm^{-1} (Figure 2), which are consistent with C=C stretching of aromatic components [36] and out-of-plane C-H bending vibrations in aromatic rings [40], respectively.

BBGFs-PE similarly enhances enzymatic activity through labile carbon release, though mediated by different organic compounds, particularly its carboxaldehydes, hydroxyl groups and organic acids (Figure 2). These water-soluble components rapidly modify critical soil properties including pH, water retention capacity and nutrient availability [33,41,42].

Three possible hypotheses may help explain how granular BBGFs formulations mitigate the potential toxicity of polyaromatic compounds in BO and PE binders: (1) Physical encapsulation: the biochar matrix can physically trap toxic compounds, slowing their release into the soil and preventing microbial inhibition [32]; (2) Chemical adsorption: oxygen-containing functional groups on the biochar surfaces can effectively immobilize harmful compounds through adsorption [43,44]; and (3) Microbial adaptation: over time, soil microbial communities can adapt and gradually degrade recalcitrant aromatics, reducing their concentration and impact in the soil environment [45,46]. These combined mechanisms enhance the efficacy of BO and PE as binders while minimizing their associated environmental risks.

The variable response of acid phosphatase to binder doses reflects complex interactions between phosphorus availability, soil chemistry, and binder properties. The quadratic response of BBGFs-PE at 10 days, peaking at 125% and declining at 150%, is likely driven by two concurrent factors: (1) the high EC of raw PE, measured at 9963.3 $\mu\text{S cm}^{-1}$ (Table 2), which forces microorganisms to divert energy from enzymatic synthesis to osmoregulation [47], and (2) adsorption of polar substrates to biochar and PE's negatively charged functional groups, reducing substrate availability [48]. This salt stress effect is particularly evident for acid phosphatase and arylsulfatase [49]. Notably, PE-amended granules still

demonstrate lower salinity impacts than conventional fertilizers [50], as biochar's charged surfaces adsorb saline ions, partially mitigating osmotic stress [51].

In contrast, the increase in BO and CW binder doses in the BBGFs applied to the soil corresponded with elevated acid phosphatase activity, which suggests these binders create a favorable microenvironment through their lower salinity (Table 2) and ability to maintain moderately acidic to near neutral pH (5.4–6.3; Table S1).

The decrease in arylsulfatase enzyme activity in soil by BBGFs-PE with increasing doses may be associated with the salinity-induced osmotic stress on sulfate-reducing microbes, competitive adsorption of enzyme substrates and products by functional groups, and hydrophobic sequestration, where PE's nonpolar domains trap reaction components in poorly accessible microenvironments, limiting their diffusion and contact [48,52]. These effects are amplified by pH deviations from the enzymatic optimum, particularly when values exceed 6.2 (Table S1), disrupting both microbial enzyme production and catalytic efficiency [19,35]. The similar inhibition of acid phosphatase confirms that amendment chemistry and pH jointly impair anion-hydrolyzing enzymes in soils.

The significant increase in soil arylsulfatase activity following BBGFs-BO addition at 10 and 40 days likely results from the gradual microbial breakdown of complex sulfur-containing compounds, particularly heterocyclic structures [39]. In BBGFs-BO at 150% binder dose, for instance, soil S content reached 4.7 mg kg⁻¹ at 10 days, followed by a decline to 3.3 mg kg⁻¹ at 40 days (Table S2), indicating early mineralization of labile S forms and possible limited degradation of recalcitrant compounds over time.

In contrast, BBGFs-CW maintained stable activity at 10 days but showed reduced values by 40 days, consistent with lower arylsulfatase expression under sulfur availability in the binder (<1.0%; Table S3) [22]. Arylsulfatase serves as both a crucial biocatalyst in the soil sulfur cycle and a sensitive indicator of microbial metabolic activity. This enzyme catalyzes the mineralization of organic sulfur compounds by cleaving sulfate esters, thereby releasing plant-available sulfate (SO₄²⁻). The released sulfate supports soil fertility by enabling the synthesis of sulfur-containing amino acids, coenzymes, and functional proteins [53].

The higher enzymatic activity in soils at 10 days compared to 40 days across all BBGFs indicates a positive priming effect from readily degradable carbon, which diminishes as labile substrates are depleted [54]. Furthermore, the increased β -glucosidase activity likely stimulated other soil enzymes, since this enzyme catalyzes the release of low-molecular-weight sugars that serve as energy sources for soil microorganisms [55].

This priming effect dynamics follows a characteristic pattern: initial stimulation of microbial activity by labile carbon shifts toward negative priming as persistent organic matter becomes protected through biochar's surface interactions and pore entrapment [48]. Concurrently, prolonged amendment exposure drives microbial community succession, favoring taxa adapted to the modified soil environment [54,56]. Biochar can increase the diversity of the soil microbial community, as demonstrated by the increase in the Shannon Index, since, in addition to improving the chemical and physical properties of the soil, biochar particles have a high specific surface area and porosity, which provides a favorable habitat for microorganisms [11].

The greater enzymatic activity observed during the shorter incubation period (10 days) likely reflects an immediate microbial response to the organic substrates supplied by the amendments, which is consistent with the higher SOC values recorded at this time point (Table S1). This peak activity across all

treatments with biochar, followed by subsequent decline, aligns with typical substrate utilization dynamics where microbial activity diminishes as available substrates are depleted [48,54]. Furthermore, studies have indicated that interactions between extracellular enzymes and surface charges of soil minerals may reduce or inactivate their activity due to conformational changes in their structure [52,57,58].

In this study, the observed decrease in acid phosphatase activity over time could potentially be attributed to phosphorus input from the biochar amendment. Soil phosphatase enzymes, synthesized by both plants and soil microbiota, generally exhibit enhanced activity under conditions of phosphorus limitation [19]. This inverse relationship reflects feedback inhibition, where increased soluble phosphate represses enzyme synthesis in microorganisms and, similarly, downregulates phosphatase production in plant roots [59]. Similar results were found by [18], where the addition of wheat straw biochar to soil reduced acid phosphatase activity due to increased soluble phosphate availability. Likewise, PE binder, a component of our BBGFs, has been shown to increase phosphorus availability and consequently decrease soil enzyme activity [42].

The biochar used in this study contained high ash content (50.6%; Table 1), which contributes to pH elevation in tropical soils [20]. This alkaline effect likely explains the observed decrease in acid phosphatase activity, as this enzyme exhibits optimal function between pH 4–6 [60]. By day 40, all biochar-amended treatments had reached pH values exceeding this optimal range (Table S1). The biochar immobilizes P from natural phosphates through its Mg, Ca, and Fe constituents (Table 1), competing with P fixation by Al/Fe (oxy)hydroxides (goethite, hematite, gibbsite) and kaolinite in the clay fraction of weathered tropical soils. This mechanism enhances P bioavailability in the soil system, and the resulting increased soluble P content reduce acid phosphatase activity [3,10].

Overall, the PCA enabled an integrated assessment of most variables analyzed, demonstrating that BBGFs influenced soil nutrient dynamics (Tables S1 and S2). At 10 days of incubation, soils amended with BBGFs-PE and BBGFs-BO were associated with SOC, K, Mg, S, Zn, and Fe, likely due to elevated enzymatic activity during this period. This increase may reflect negative priming effect, where microbial preference for biochar compounds preserved native SOC while promoting the mineralization of biochar-derived carbon and nutrients. The initial incorporation of BBGFs into the soil appears to have stimulated microbial utilization of readily available carbon components from the biochar [61]. Although the biochar exhibited a high C/N ratio (Table 1), its combination with acidic binders (Table 2) and reactive natural phosphate likely enhanced biochar mineralization at 10 days, mitigating nutrient limitations [62].

The addition of BBGFs formulated with 75% CW increased soil P-Meh and P-Res, while increasing Ca content, CEC, and pH. These results paralleled those observed with non-granulated biochar treatments, applied alone or with NP, and support [20] findings on CW's hydrophilic characteristics. The 75% CW binder dosage directly influenced granule structure by reducing interparticle cohesive forces, increasing fertilizer solubility compared to higher doses. In this scenario, a negative effect of biochar on acid phosphatase activity was observed in the BBGFs-CW treatment at the 75% binder dose, associated with a negative correlation in the PCA between soil P levels and enzyme activity. This suggests that native soil microorganisms converted organic phosphates from the fertilizer primarily into bioavailable forms, reducing the demand for phosphatase activity, as previously reported [10,18].

After 40 days, soils amended with BBGFs showed up to a 62.7% increase in CEC (Table S1), as both the biochar components and binding agents provided oxygen-containing functional groups. This aligns

with studies showing biochar's capacity to modify soil properties, improving water retention, nutrient availability and soil structure while regulating pH levels and reducing nutrient leaching [8,63]. The observed CEC enhancement in BBGFs-treated soils further confirms biochar's role in promoting carbon sequestration and optimizing nutrient cycling efficiency. According to [64], CEC is favored by biochars produced at moderate temperatures (<500 °C) from ash-rich feedstocks. Furthermore, biochar application can directly enhance soil CEC in addition to preserving native SOC from microbial mineralization [65].

At 40 days of incubation, as the labile carbon fractions from biochar were depleted, reducing the availability of readily accessible compounds, it is presumed that the increased investment of carbon in enzymes targeting recalcitrant compounds sustained microbial metabolism while decreasing enzymatic activity over time, due to higher energy expenditure [35,61]. As a carbon-rich and recalcitrant additive, biochar contributes to increasing the soil carbon stock, even under positive priming conditions. This reflects the stabilization of biochar-derived carbon, which offsets losses from the mineralization of native SOC [56,66]. On the other hand, soils amended with the BBGFs-CW (75%) treatment maintained a negative priming effect, owing to the lower recalcitrance of this fertilizer, as discussed earlier, which likely contributed to an increase in soil carbon stock.

At 10 and 40 days of soil incubation with BBGFs-PE and BBGFs-BO, the activities of β -glucosidase and arylsulfatase exhibited strong relationships with SOC and S levels, as evidenced by previous research, which demonstrated that these enzymes served as effective bioindicators for detecting changes in soil management systems (such as conservation agriculture in relation to conventional tillage) [18,35,67,68]. However, these associations do not necessarily imply a direct causal link between enzyme activity and soil chemical characteristics. Rather, they likely indicate a broader context in which enhanced soil quality, resulting from effective management practices, boosts nutrient availability, organic matter content, and biological activity, as noted by [69].

Soils treated with BBGFs-PE and BBGFs-BO exhibited a negative correlation with P-Res and P-Meh at 10 and 40 days of incubation, as these fertilizers generally have low water solubility, resulting in limited P availability in the short term, although this availability may increase over time due to the gradual dissolution of the fertilizer and the activity of acid phosphatase enzyme [2,20]. In contrast, soluble phosphate fertilizers release P immediately upon application, but their availability decreases over time due to adsorption by soil particles and conversion into less soluble chemical forms [20,70].

Soil microorganisms perform multiple enzyme-mediated processes that support plant growth and development, including nutrient cycling, pollutant decomposition, soil aggregate formation, and pathogen control [16]. These processes contribute to the sustainability of agricultural production, as the enhancement of soil biological activity improves nutrient recycling and optimizes the utilization of applied fertilizers, leading to greater agronomic efficiency of fertilization [67,69]. Although soil enzymes may originate from plant and animal residues, microbial biomass constitutes their predominant source. Consequently, an increase in soil enzymatic activity can be interpreted as a reflection of heightened biological vitality [19].

This study focused on enzymatic activities as key functional indicators of the soil's biochemical response to the BBGFs. While the results clearly demonstrate the overall impact of the formulations, future research could provide a deeper mechanistic understanding. For instance, linking the observed enzymatic functions to shifts in the microbial community structure would be a valuable next step. Furthermore, future investigations could build upon our findings by including direct quantification of specific compounds, such

as polycyclic aromatic hydrocarbons, to fully characterize the environmental interactions of these novel fertilizers.

5 CONCLUSIONS

The application of BBGFs formulated with alternative binders (BO, PE, and CW) up to a dose of 150% significantly increased the activity of β -glucosidase, acid phosphatase, and arylsulfatase in the soil compared to the controls, particularly within the initial 10-day period. However, enzymatic activity declined by 40 days across all binder treatments, indicating a temporal shift in microbial response.

Incorporating these agro-industrial binders into BBGFs supports sustainable soil management by the valorization of agricultural residues, improvement of soil pH and CEC, and reduction in nutrient losses due to enhanced microbial activity. Such practices contribute substantially to environmentally friendly agriculture in tropical soils.

The use of BO as a binder in BBGFs consistently enhanced the enzymatic activity of β -glucosidase, acid phosphatase, and arylsulfatase, maintaining higher and more stable values over time compared to BBGFs-PE and BBGFs-CW, highlighting its potential as a slow-release amendment for sustainable nutrient cycling in tropical Oxisols. In contrast, BBGFs-PE showed a pronounced initial boost in acid phosphatase activity, while BBGFs-CW exhibited the least impact on enzyme activity.

BO at a 150% dose is recommended both for the production and agricultural application of BBGFs, given its superior capacity to increase β -glucosidase, acid phosphatase, and arylsulfatase activities, as well as improve SOC, CEC, and nutrient availability.

Future research should build upon these findings through long-term field trials to verify their agronomic performance and broader environmental impacts. Such investigations would also benefit from integrating microbial community analysis and direct toxicological assessments to provide a deeper mechanistic understanding of these BBGF formulations.

Supplementary Materials

The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/agronomy15092230/s1>. Figure S1. (A) Kiln-furnace system. (B) Charcoal fines (biochar) from pyrolysis at 450 °C; Table S1. Soil chemical properties after 10 and 40 days of incubation with biochar-based granular fertilizers (BBGFs) produced with different doses of binders' cassava wastewater (CW), pyroligneous extract (PE) and bio-oil (BO). The treatments natural soil (NS), natural phosphate (NP), biochar and natural phosphate (B+NP) and biochar (B) were used as a reference for comparison with the other treatments; Table S2. Soil chemical properties after 10 and 40 days of incubation with biochar-based granular fertilizers (BBGFs) produced with different doses of binders' cassava wastewater (CW), pyroligneous extract (PE) and bio-oil (BO). The treatments natural soil (NS), natural phosphate (NP), biochar and natural phosphate (B+NP) and biochar (B) were used as a reference for comparison with the other treatments; Table S3. Chemical composition of cassava wastewater (CW) used as binder in biochar-based granular fertilizers (BBGFs). References [31,71] are cited in the Supplementary Materials.

Author Contributions

Conceptualization, J.M.d.S.J. and L.A.F. (Luiz Arnaldo Fernandes); methodology, J.M.d.S.J., L.A.F. (Luiz Arnaldo Fernandes), F.C., L.A.F. (Leidivan Almeida Frazão) and R.F.P.; validation, J.M.d.S.J., L.A.F. (Luiz Arnaldo Fernandes), F.C., L.A.F. (Leidivan Almeida Frazão) and R.F.P.; formal analysis, J.M.d.S.J. and L.A.F. (Luiz Arnaldo Fernandes); investigation, J.M.d.S.J.; resources, L.A.F. (Luiz Arnaldo Fernandes), F.C. and L.A.F. (Leidivan Almeida Frazão); data curation, J.M.d.S.J. and L.A.F. (Luiz Arnaldo Fernandes); writing—original draft preparation, J.M.d.S.J.; writing—review and editing, J.M.d.S.J., L.A.F. (Luiz Arnaldo Fernandes), F.C., L.A.F. (Leidivan Almeida Frazão) and R.F.P.; visualization, J.M.d.S.J.; supervision, L.A.F. (Luiz Arnaldo Fernandes), F.C. and L.A.F. (Leidivan Almeida Frazão); project administration, L.A.F. (Luiz Arnaldo Fernandes); funding acquisition, L.A.F. (Luiz Arnaldo Fernandes). All authors have read and agreed to the published version of the manuscript.

Funding

This research was funded by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq/Brazil), the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES/Brazil), the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG/Brazil) and the Center for Carbon Research in Tropical Agriculture (CCARBON) at the Universidade de São Paulo (USP/Brazil), sponsored by the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP/Brazil) under grant 2021/10573-4.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments

The authors acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq/Brazil), the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES/Brazil) and the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG/Brazil) for financial support and scholarships. Special thanks to CNPq for the fellowship for the second author (grants #304127/2023-0), to the Pró-Reitoria de Pesquisa (PRPQ) da Universidade Federal de Minas Gerais (UFMG/Brazil) and to the Laboratório de Química Instrumental (LQI/UFMG).

Conflicts of Interest

The authors declare no conflicts of interest.

References

1. Igalavithana, A.D.; Choi, S.W.; Shang, J.; Hanif, A.; Dissanayake, P.D.; Tsang, D.C.W.; Kwon, J.H.; Lee, K.B.; Ok, Y.S. Carbon dioxide capture in biochar produced from pine sawdust and paper mill sludge: Effect of porous structure and surface chemistry. *Sci. Total Environ.* **2020**, *739*, 139845.
2. Carneiro, J.S.S.; Ribeiro, I.C.A.; Nardis, B.O.; Barbosa, C.F.; Lustosa Filho, J.F.; Melo, L.C.A. Long-term effect of biochar-based fertilizers application in tropical soil: Agronomic efficiency and phosphorus availability. *Sci. Total Environ.* **2021**, *760*, 143955.

3. Pogorzelski, D.; Lustosa Filho, J.F.; Matias, P.C.; Santos, W.O.; Vergütz, L.; Melo, L.C.A. Biochar as composite of phosphate fertilizer: Characterization and agronomic effectiveness. *Sci. Total Environ.* **2020**, *743*, 140604.
4. Basak, B.B.; Sarkar, B.; Saha, A.; Sarkar, A.; Mandal, S.; Biswas, J.K.; Wang, H.; Bolan, N.S. Revamping highly weathered soils in the tropics with biochar application: What we know and what is needed. *Sci. Total Environ.* **2022**, *822*, 153461.
5. Novais, R.F.; Smyth, T.J. *Fósforo em Solo e Planta em Condições Tropicais*; Univesidade Federal de Viçosa: Viçosa, Brazil, 1999; 399p.
6. Santos Júnior, J.M.; Colen, F.; Pegoraro, R.F.; Heinrichs, R.; Frazão, L.A.; Sampaio, R.A.; Fernandes, L.A. Biochar pellets as soil conditioner on the growth of *Urochloa brizantha* BRS Paiaguás. *Rev. Ciênc. Agron.* **2024**, *55*, e20238690.
7. Shoudho, K.N.; Khan, T.H.; Ara, U.R.; Khan, M.R.; Shawon, Z.B.Z.; Hoque, M.E. Biochar in global carbon cycle: Towards sustainable development goals. *Curr. Res. Green. Sustain. Chem.* **2024**, *8*, 100409.
8. Adhikari, S.; Moon, E.; Timms, W. Identifying biochar production variables to maximize exchangeable cations and increase nutrient availability in soils. *J. Clean. Prod.* **2024**, *446*, 141454.
9. Otoni, J.P.; Matoso, S.C.G.; Pérez, X.L.O.; Silva, V.B. Potential for agronomic and environmental use of biochars derived from different organic waste. *J. Clean. Prod.* **2024**, *449*, 141826.
10. Lopes, E.M.G.; Reis, M.M.; Frazão, L.A.; Terra, L.E.M.; Lopes, E.F.; Santos, M.M.; Fernandes, L.A. Biochar increases enzyme activity and total microbial quality of soil grown with sugarcane. *Environ. Technol. Innov.* **2021**, *21*, 101270.
11. Lopes, E.M.G.; Mota, M.F.C.; Santos Júnior, J.M.; Reis, M.M.; Frazão, L.A.; Fernandes, L.A. Biochar alters the soil microbiological activity of sugarcane fields over time. *Sci. Agric.* **2024**, *81*, e20230289.
12. Mir, N.R.; Mir, B.A.; Mavi, M.S.; Kapoor, N. Revitalizing soils: Biochar's battle against heavy metal menace in plants—A review. *Pedosphere*, 2025; *in press*.
13. Wang, H.; Zhang, H.; He, L.; Wang, J.; Wang, S.; Shi, X.; Zhang, X.; Wang, H.; He, F. Environmental behavior of per- and polyfluoroalkyl substances (PFASs) and the potential role of biochar for its remediation: A review. *Biochar* **2025**, *7*, 14.
14. Dong, M.; Jiang, M.; He, L.; Zhang, Z.; Gustave, W.; Vithanage, M.; Niazi, N.K.; Chen, B.; Zhang, X.; Wang, H.; et al. Challenges in safe environmental applications of biochar: Identifying risks and unintended consequence. *Biochar* **2025**, *7*, 12.
15. Mendes, I.C.; Souza, L.M.; Sousa, D.M.G.; Lopes, A.A.C.; Reis Júnior, F.B.; Lacerda, M.P.C.; Malaquias, J.V. Critical limits for microbial indicators in tropical Oxisols at post-harvest: The FERTBIO soil sample concept. *Appl. Soil Ecol.* **2019**, *139*, 85–93.
16. Mendes, I.C.; Sousa, D.M.G.; Dantas, O.D.; Lopes, A.A.C.; Reis Júnior, F.B.; Oliveira, M.I.; Chaer, G.M. Soil quality and grain yield: A win–win combination in clayey tropical oxisols. *Geoderma* **2021**, *388*, 114880.
17. Barbosa, J.Z.; Poggere, G.; Corrêa, R.S.; Hungria, M.; Mendes, I.C. Soil enzymatic activity in Brazilian biomes under native vegetation and contrasting cropping and management. *Appl. Soil Ecol.* **2023**, *190*, 105014.
18. Song, X.; Razavi, B.S.; Ludwig, B.; Zamanian, K.; Zang, H.; Kuzyakov, Y.; Dippold, M.A.; Gunina, A. Combined biochar and nitrogen application stimulates enzyme activity and root plasticity. *Sci. Total Environ.* **2020**, *735*, 139393.
19. Tabatabai, M.A. Soil Enzymes. In *Methods of Soil. Analysis: Microbiological and Biochemical Properties*; Mickelson, S.H., Bigham, J.M., Eds.; Soil Science Society of America Inc.: Madison, WI, USA, 1994; pp. 775–833.

20. Santos Júnior, J.M.; Colen, F.; Frazão, L.A.; Pegoraro, R.F.; Fernandes, L.A. Granulated organomineral fertilizers from by-products of the agricultural and forestry sector. *Sci. Agric.* **2025**, *82*, e20240132.
21. Peng, J.; Zhang, L.; Meulien, E.S.; Bi, X.T.; Lim, J.C.; Chen, W. Waste Plastics as an Effective Binder for Biochar Pelletization. *Energy Fuels* **2021**, *35*, 13840–13846.
22. Schmidt, V.K.O.; Vasconcelos, G.M.D.; Vicente, R.; Carvalho, J.S.; Della-Flora, I.K.; Degang, L.; Oliveira, D.; Andrade, C.J. Cassava wastewater valorization for the production of biosurfactants: Surfactin, rhamnolipids, and mannosylerythritol lipids. *World J. Microbiol. Biotechnol.* **2023**, *39*, 65.
23. Genova, G.; Borruso, L.; Signorini, M.; Mitterer, M.; Niedrist, G.; Cesco, S.; Felderer, B.; Cavani, L.; Mimmo, T. Analyzing soil enzymes to assess soil quality parameters in long-term copper accumulation through a machine learning approach. *Appl. Soil Ecol.* **2024**, *195*, e105261.
24. Schettini, B.L.S.; Jacovine, L.A.G.; Torres, C.M.M.E.; Carneiro, A.C.O.; Villanova, P.H.; Rocha, S.J.S.S.; Rufino, M.P.M.X.; Silva, L.B.; Castro, R.V.O. Furnace-kiln system: How does the use of new technologies in charcoal production affect the carbon balance? *Ind. Crop. Prod.* **2022**, *187*, 115330.
25. ASTM D1762-84; Standard Test Method for Chemical Analysis of Wood Charcoal. ASTM International: West Conshohocken, PA, USA, 2021; 2p.
26. Tedesco, M.J.; Gianello, C.; Bissani, C.A.; Bohnen, H.; Volkweiss, S.J. *Soil, Plants and Other Materials Analysis*, 2nd ed.; Universidade Federal do Rio Grande do Sul: Porto Alegre, Brazil, 1995; 174p.
27. Klasson, K.T. Biochar characterization and a method for estimating biochar quality from proximate analysis results. *Biomass Bioenergy* **2017**, *96*, 50–58.
28. ASTM E1756-08; Standard Test Method for Determination of Total Solids in Biomass. ASTM International: West Conshohocken, PA, USA, 2020; 2p.
29. Schulte, E.E.; Hoskins, B. Recommended soil organic matter tests. In *Recommended Soil Testing Procedures for the Northeastern United States*, 3rd ed.; Sims, J.T., Wolf, A., Eds.; University of Delaware: Newark, NJ, USA, 2011; pp. 63–74.
30. Malavolta, E. *Elements of Plant Mineral Nutrition*; Agronômica Ceres: São Paulo, Brazil, 1980; 252p.
31. Teixeira, P.C.; Donagemma, G.K.; Fontana, A.; Teixeira, W.G. *Manual of Soil Analysis Methods*, 3rd ed.; Embrapa Solos: Rio de Janeiro, Brazil, 2017; 573p.
32. Cheng, J.; Liao, Z.; Hu, S.; Geng, Z.; Zhu, M.; Xu, W. Synthesis of an environmentally friendly binding material using pyrolysis byproducts and modified starch binder for slow-release fertilizers. *Sci. Total Environ.* **2022**, *819*, 153146.
33. Lee, C.L.; Chin, K.L.; Khoo, P.S.; Hafizuddin, M.S.; H'ng, P.S. Production and Potential Application of Pyrolygneous Acids from Rubberwood and Oil Palm Trunk as Wood Preservatives through Vacuum-Pressure Impregnation Treatment. *Polymers* **2022**, *14*, 3863.
34. Mafaldo, I.M.; Araújo, L.M.; Cabral, L.; Barão, C.E.; Noronha, M.F.; Fink, J.R.; Albuquerque, T.M.R.; Lima, M.S.; Vidal, H.; Pimentel, T.C.; et al. Cassava (*Manihot esculenta*) Brazilian cultivars have different chemical compositions, present prebiotic potential, and beneficial effects on the colonic microbiota of celiac individuals. *Food Res. Int.* **2024**, *195*, 114909.
35. Rahmanian, M.; Khadem, A. The effects of biochar on soil extra and intracellular enzymes activity. *Biomass Convers. Biorefinery* **2024**, *14*, 21993–22005.
36. Janu, R.; Mrlik, V.; Ribitsch, D.; Hofman, J.; Sedláček, P.; Bielská, L.; Soja, G. Biochar surface functional groups as affected by biomass feedstock, biochar composition and pyrolysis temperature. *Carbon Resour. Convers.* **2021**, *4*, 36–46.
37. McCall, M.A.; Watson, J.S.; Tan, J.S.W.; Sephton, M.A. Biochar Stability Revealed by FTIR and Machine Learning. *ACS Sustain. Resour. Manag.* **2025**, *2*, 842–852.

38. Frainetti, A.J.; Klinghoffer, N.B. Recent experimental advances on the utilization of biochar as a tar reforming catalyst: A review. *Int. J. Hydrogen Energy* **2023**, *48*, 8022–8044.
39. Lachos-Perez, D.; Martins-Vieira, J.C.; Missau, J.; Anshu, K.; Siakpebru, O.K.; Thengane, S.K.; Morais, A.R.C.; Tanabe, E.H.; Bertuol, D.A. Review on Biomass Pyrolysis with a Focus on Bio-Oil Upgrading Techniques. *Analytica* **2023**, *4*, 182–205.
40. Ibarra, J.V.; Moliner, R.; Bonet, A.J. FT-i.r. investigation on char formation during the early stages of coal pyrolysis. *Fuel* **1994**, *73*, 918–924.
41. Grewal, A.; Abbey, L.; Gunupuru, L.R. Production, prospects and potential application of pyroligneous acid in agriculture. *J. Anal. Appl. Pyrolysis* **2018**, *135*, 152–159.
42. Yuan, Y.; Kong, Q.; Zheng, Y.; Zheng, H.; Liu, Y.; Cheng, Y.; Zhang, X.; Li, Z.; You, X.; Li, Y. Co-application of biochar and pyroligneous acid improved peanut production and nutritional quality in a coastal soil. *Environ. Technol. Innov.* **2022**, *28*, 102886.
43. El-Naggar, A.; Mosa, A.; Ahmed, N.; Niazi, N.K.; Yousaf, B.; Sarkar, B.; Rinklebe, J.; Cai, Y.; Chang, S.X. Modified and pristine biochars for remediation of chromium contamination in soil and aquatic systems. *Chemosphere* **2022**, *303*, 134942.
44. Freddo, A.; Cai, C.; Reid, B.J. Environmental contextualization of potential toxic elements and polycyclic aromatic hydrocarbons in biochar. *Environ. Pollut.* **2012**, *171*, 18–24.
45. Bolan, S.; Sharma, S.; Mukherjee, S.; Kumar, M.; Rao, C.S.; Nataraj, K.C.; Singh, G.; Vinu, A.; Bhowmik, A.; Sharma, H.; et al. Biochar modulating soil biological health: A review. *Sci. Total Environ.* **2024**, *914*, 169585.
46. Dai, Z.; Xiong, X.; Zhu, H.; Xu, H.; Leng, P.; Li, J.; Tang, C.; Xu, J. Association of biochar properties with changes in soil bacterial, fungal and fauna communities and nutrient cycling processes. *Biochar* **2021**, *3*, 239–254.
47. Yin, Y.; Zhang, Z.; Yang, K.; Gu, P.; Liu, S.; Jia, Y.; Zhang, Z.; Wang, T.; Yin, J.; Miao, H. Deeper insight into the effect of salinity on the relationship of enzymatic activity, microbial community and key metabolic pathway during the anaerobic digestion of high strength organic wastewater. *Bioresour. Technol.* **2022**, *363*, 127978.
48. Zhao, K.; Wang, N.; Jiang, S.; Li, F.; Luo, S.; Chen, A.; Li, H.; Lin, X.; Zhang, J.; Zhang, L.; et al. Potential implications of biochar and compost on the stoichiometry-based assessments of soil enzyme activity in heavy metal-polluted soils. *Carbon Res.* **2022**, *1*, 29.
49. Sritongon, N.; Sarin, P.; Theerakulpisut, P.; Riddech, N. The effect of salinity on soil chemical characteristics, enzyme activity and bacterial community composition in rice rhizospheres in Northeastern Thailand. *Sci. Rep.* **2022**, *12*, 20360.
50. Jacobs, D.F.; Timmer, V.R. Fertilizer-induced Changes in Rhizosphere Electrical Conductivity: Relation to Forest Tree Seedling Root System Growth and Function. *New For.* **2005**, *30*, 147–166.
51. Din, M.M.U.; Khan, M.I.; Azam, M.; Ali, M.H.; Qadri, R.; Naveed, M.; Nasir, A. Effect of Biochar and Compost Addition on Mitigating Salinity Stress and Improving Fruit Quality of Tomato. *Agronomy* **2023**, *13*, 2197.
52. Zeng, L.; Zimmerman, A.R.; Huang, R. Adsorption of extracellular enzymes by biochar: Impacts of enzyme and biochar properties. *Geoderma* **2024**, *451*, 117082.
53. Zaid, F.; Al-Awwal, N.; Yang, J.; Anderson, S.H.; Alsunuse, B.T.B. Effects of Biochar-Amended Composts on Selected Enzyme Activities in Soils. *Processes* **2024**, *12*, 1678.
54. Liu, X.A.; Finley, B.K.; Mau, R.L.; Schwartz, E.; Dijkstra, P.; Bowker, M.A.; Hungate, B.A. The soil priming effect: Consistent across ecosystems, elusive mechanisms. *Soil Biol. Biochem.* **2020**, *140*, 107617.

55. Daunoras, J.; Kačergius, A.; Gudiukaitė, R. Role of Soil Microbiota Enzymes in Soil Health and Activity Changes Depending on Climate Change and the Type of Soil Ecosystem. *Biology* **2024**, *13*, 85.
56. Lu, W.; Zha, Q.; Zhang, H.; Chen, H.Y.H.; Yu, J.; Tu, F.; Ruan, H. Changes in soil microbial communities and priming effects induced by rice straw pyrogenic organic matter produced at two temperatures. *Geoderma* **2021**, *400*, 115217.
57. Li, Y.; Koopal, L.K.; Chen, Y.; Shen, A.; Tan, W. Conformational modifications of lysozyme caused by interaction with humic acid studied with spectroscopy. *Sci. Total Environ.* **2021**, *768*, 144858.
58. Zang, Y.; Liu, F.; Li, X.; Sheng, A.; Zhai, J.; Liu, J. Adsorption kinetics, conformational change, and enzymatic activity of β -glucosidase on hematite (α -Fe₂O₃) surfaces. *Colloids Surf. B Biointerfaces* **2020**, *193*, 111115.
59. Reid, M.S.; Bielecki, R.L. Response of *Spirodela oligorrhiza* to Phosphorus Deficiency. *Plant Physiol.* **1970**, *46*, 609–613.
60. Wojewódzki, P.; Lemanowicz, J.; Debska, B.; Haddad, S.A. Soil Enzyme Activity Response under the Amendment of Different Types of Biochar. *Agronomy* **2022**, *12*, 569.
61. Zhang, Y.; Dang, Y.; Wang, J.; Huang, Q.; Wang, X.; Yao, L.; Vinay, N.; Yu, K.; Wen, X.; Xiong, Y.; et al. A synthesis of soil organic carbon mineralization in response to biochar amendment. *Soil Biol. Biochem.* **2022**, *175*, 108851.
62. Abban-Baidoo, E.; Manka'abusi, D.; Apuri, L.; Marschner, B.; Frimpong, K.A. Biochar addition influences C and N dynamics during biochar co-composting and the nutrient content of the biochar co-compost. *Sci. Rep.* **2024**, *14*, 23781.
63. Dey, S.; Purakayastha, T.J.; Sarkar, B.; Rinklebe, J.; Kumar, S.; Chakraborty, R.; Datta, A.; Lal, K.; Shivay, Y.S. Enhancing cation and anion exchange capacity of rice straw biochar by chemical modification for increased plant nutrient retention. *Sci. Total Environ.* **2023**, *886*, 163681.
64. Domingues, R.R.; Sánchez-Monedero, M.A.; Spokas, K.A.; Melo, L.C.A.; Trugilho, P.F.; Valenciano, M.N.; Silva, C.A. Enhancing Cation Exchange Capacity of Weathered Soils Using Biochar: Feedstock, Pyrolysis Conditions and Addition Rate. *Agronomy* **2020**, *10*, 824.
65. El-Naggar, A.; Lee, S.S.; Awad, Y.M.; Yang, X.; Ryu, C.; Rizwan, M.; Rinklebe, J.; Tsang, D.C.W.; Ok, Y.S. Influence of soil properties and feedstocks on biochar potential for carbon mineralization and improvement of infertile soils. *Geoderma* **2018**, *332*, 100–118.
66. Zhou, J.; Wen, Y.; Liu, C.; Blagodatskaya, E.; Kuzyakov, Y.; Zeng, Z.; Jones, D.L.; Zang, H. Quantifying apparent and real priming effects based on inverse labelling. *Appl. Soil Ecol.* **2024**, *195*, 105234.
67. Chaer, G.M.; Mendes, I.C.; Dantas, O.D.; Malaquias, J.V.; Reis Júnior, F.B.; Oliveira, M.I.L. Evaluating C trends in clayey Cerrado Oxisols using a four-quadrant model based on specific arylsulfatase and β -glucosidase activities. *Appl. Soil Ecol.* **2023**, *183*, 104742.
68. Passinato, J.H.; Amado, T.J.C.; Kassam, A.; Acosta, J.A.A.; Amaral, L.P. Soil Health Check-Up of Conservation Agriculture Farming Systems in Brazil. *Agronomy* **2021**, *11*, 2410.
69. Pawlowski, E.; Sobucki, L.; Barbosa, J.G.P.; Handte, V.G.; Vieira, I.B.; Brunetto, G.; Mendes, I.C.; Jacques, R.J.S. Relationships between yield, enzymatic activity, and chemical properties across different soil layers and phenological stages of grapevines in southern Brazil. *Appl. Soil Ecol.* **2024**, *204*, 105732.
70. Lustosa Filho, J.F.; Carneiro, J.S.S.; Barbosa, C.F.; Lima, K.P.; Leite, A.A.; Melo, L.C.A. Aging of biochar-based fertilizers in soil: Effects on phosphorus pools and availability to *Urochloa brizantha* grass. *Sci. Total Environ.* **2020**, *709*, 136028.
71. Ministério da Agricultura, Pecuária e Abastecimento (MAPA). *Manual de Métodos Analíticos Oficiais para Fertilizantes e Corretivos*; MAPA: Brasília, Brazil, 2017; 240p.

APÊNDICE A

Supplementary Material

Biochar-based granular fertilizers with agroindustrial binders enhance enzymatic activity and nutrient cycling in tropical Oxisols

José Mendes dos Santos Júnior ^{*}, Luiz Arnaldo Fernandes ¹, Fernando Colen ¹, Leidivan Almeida Frazão ¹ and Rodinei Facco Pegoraro ¹

¹ Institute of Agrarian Sciences, Federal University of Minas Gerais (UFMG), Montes Claros, MG 39404547, Brazil; larnaldo@ufmg.br (L.A.F.); fernandocolen@ica.ufmg.br (F.C.); lafracao@ufmg.br (L.A.Fr.); rodinei@ufmg.br (R.F.P.)

* Correspondence: josemendesjunior@ufmg.br



Figure S1. (A) Kiln-furnace system; (B) Charcoal fines (biochar) from pyrolysis at 450 °C.

Table S1. Soil chemical properties^a after 10 and 40 days of incubation with biochar-based granular fertilizers (BBGFs) produced with different doses of binders' cassava wastewater (CW), pyrolygneous extract (PE) and bio-oil (BO). The treatments natural soil (NS), natural phosphate (NP), biochar and natural phosphate (B+NP) and biochar (B) were used as a reference for comparison with the other treatments.

Treatments	pH (H ₂ O)		P-Meh. (mg kg ⁻¹)		P-Res. (mg kg ⁻¹)		SOC (dag kg ⁻¹)		CEC (cmol _c kg ⁻¹)	
	10	40	10	40	10	40	10	40	10	40
NS	6.5 A	4.9 A*	0.9 A	0.9 A	1.9 A	7.8 A*	0.1 A	0.1 A	1.0 A	0.9 A
NP	5.8 B	5.6 B	174.2 B	204.8 B*	142.6 B	104.2 B*	0.2 B	0.4 B*	1.5 B	1.4 B
B+NP	6.8 C	7.2 C	200.4 C	186.6 C	67.4 C	91.1 C*	0.3 C	0.4 C	2.4 C	2.5 C
B	6.6 D	7.1 D	5.2 D	4.0 D*	11.8 D	9.3 D	0.6 D	0.4 D*	1.8 D	1.3 D*
CW75	6.0 abcABD	6.4 aCD	24.0 a	21.1 a*	11.0 aD	22.8 a*	0.3 bBC	0.3 bcBCD	1.7 bcBD	2.0 b*
CW100	5.5 bcB	6.5 aCD*	4.2 d	1.1 d*	10.7 aD	22.0 ab*	0.5 aD	0.2 cA*	1.7 bcBD	2.7 aC*
CW125	6.3 abABCD	6.7 aCD	7.3 b	3.0 b*	5.0 bc	17.2 bc*	0.2 cABC	0.2 cA	1.4 c	2.3 abC*
CW150	5.8 abcB	6.5 aCD*	2.2 e	1.0 de*	3.9 c	17.8 bc*	0.2 cABC	0.6 a*	1.5 bcBD	2.1 abC*
PE75	6.2 abcABCD	6.5 aCD	5.1 cD	3.5 bD*	4.8 bc	17.5 bc*	0.3 bcBC	0.2 cA	1.5 bcBD	1.9 b*
PE100	5.9 abcABD	6.3 aB	1.4 fg	1.0 de*	3.0 c	16.0 c*	0.5 aD	0.5 aBCD	1.5 bcBD	2.1 abC*
PE125	6.4 abABCD	6.5 aCD	2.1 e	0.9 de*	4.6 bc	18.0 bc*	0.4 ab	0.5 aBCD	1.4 c	2.2 abC*
PE150	6.5 aABCD	6.6 aCD	1.1 hA	0.7 e*	4.0 c	16.0 c*	0.2 cABC	0.3 bcBCD	1.5 bcBD	2.4 abC*
BO75	5.9 abcABD	6.9 aCD*	1.6 f	1.7 c	4.0 c	17.8 bc*	0.5 aD	0.2 cA*	1.8 abBD	1.4 cBD*
BO100	6.1 abcABD	6.3 aBD	2.1 e	1.2 d*	6.4 b	17.4 bc*	0.3 bcBC	0.3 bcBCD	1.8 abBD	1.4 cBD*
BO125	5.4 cB	6.1 aB*	2.1 e	0.7 e*	4.3 bc	19.8 abc*	0.5 aD	0.4 abBCD	1.8 abBD	1.4 cBD*
BO150	5.6 abcB	6.5 aCD*	1.4 fg	1.3 cd	4.5 bc	17.2 bc*	0.3 bcBC	0.3 bcBCD	2.1 aCD	1.4 cBD*

^aAccording to [31]: P-Meh.: Mehlich phosphorus (Mehlich-1 extractor); P-Res.: resin phosphorus (anion exchange resin); CEC: cation exchange capacity at pH 7; SOC: soil organic carbon, measured via loss on ignition (Schulte and Hoskins, 2011). Means followed by the same lowercase letter in the columns do not differ from each other by the Tukey test ($p < 0.05$). Uppercase letters indicate the comparison of treatments against four specific references by the Dunnett test ($p < 0.05$), where A = NS (Natural soil), B = NP (Natural phosphate), C = B+NP (Biochar + Natural phosphate), and D = B (Biochar). The presence of a corresponding uppercase letter (A, B, C, or D) on a treatment mean indicates it does not differ statistically from that specific reference treatment. An asterisk (*) in the 40-day value indicates a significant difference from the 10-day value for the same treatment by the t-test ($p < 0.05$).

Table S2. Soil chemical properties^a after 10 and 40 days of incubation with biochar-based granular fertilizers (BBGFs) produced with different doses of binders' cassava wastewater (CW), pyroligneous extract (PE) and bio-oil (BO). The treatments natural soil (NS), natural phosphate (NP), biochar and natural phosphate (B+NP) and biochar (B) were used as a reference for comparison with the other treatments.

Treatments	K (mg kg ⁻¹)		Ca (cmol _c kg ⁻¹)		Mg (cmol _c kg ⁻¹)		S (mg kg ⁻¹)		Fe (mg kg ⁻¹)		Zn (mg kg ⁻¹)	
	10	40	10	40	10	40	10	40	10	40	10	40
NS	13.7 A	7.8 A*	0.3 A	0.2 A	0.1 A	0.1 A	1.9 A	1.5 A*	115.4 A	110.9 A	0.3 A	0.2 A*
NP	13.7 B	9.4 B*	0.7 B	1.0 B*	0.1 B	0.1 B	2.7 B	3.3 B*	58.2 B	47.7 B*	0.6 B	0.7 B*
B+NP	48.7 C	58.8 C*	1.6 C	2.0 C*	0.2 C	0.2 C	5.4 C	3.9 C*	75.1 C	51.1 C*	1.0 C	0.6 C*
B	48.5 D	48.6 D	1.2 D	0.8 D*	0.2 D	0.1 D*	3.9 D	2.2 D*	125.7 D	115.4 D	0.4 D	0.2 D*
CW75	41.9 ab	29.1 f*	0.7 bB	1.2 b*	0.1 bAB	0.2 aC*	4.3 bD	3.2 cdB*	167.1 bc	229.0 a*	0.7 fBC	0.3 gAD*
CW100	38.1 bcd	36.5 de	0.6 bcB	0.9 cdD*	0.1 bAB	0.2 aC*	3.8 cD	3.3 cdB*	189.4 a	195.5 b	0.3 gABD	0.3 gAD
CW125	36.3 cde	26.5 fg*	0.6 bcB	1.5 a*	0.1 bAB	0.2 aC*	3.1 dB	2.3 eD*	144.6 d	220.2 a*	0.3 gABD	0.7 fBC*
CW150	32.9 def	25.1 g*	0.5 c	1.2 b*	0.1 bAB	0.2 aC*	3.9 cD	3.0 dB*	172.5 ab	191.4 bc	0.3 gABD	0.2 gAD*
PE75	32.3 ef	27.0 fg*	0.6 bcB	0.8 deD*	0.1 bAB	0.2 aC*	4.1 bcD	3.1 dB*	140.3 d	105.4 gA*	1.4 e	1.0 f*
PE100	30.4 f	36.8 d*	0.7 bB	1.0 cB*	0.2 aCD	0.2 aC	4.8 a	3.6 abcBC*	148.9 cd	168.4 d*	2.3 c	2.8 c*
PE125	41.5 bc	33.6 e*	0.9 a	1.2 b*	0.2 aCD	0.2 aC	3.4 d	4.0 aC*	133.4 de	171.9 cd*	4.4 b	3.7 b*
PE150	35.1 def	28.5 f*	0.8 abB	1.3 b*	0.2 aCD	0.2 aC	3.3 d	3.4 bcdB	116.9 eA	156.7 de*	4.7 b	4.1 a*
BO75	38.1 bcd	47.1 aD*	0.7 bB	1.0 cB*	0.2 aCD	0.2 aC	4.3 bD	3.6 abcBC*	115.5 eA	144.3 ef*	1.9 cd	1.4 e*
BO100	31.3 ef	42.3 b*	0.7 bB	1.0 cB*	0.2 aCD	0.2 aC	4.5 ab	3.3 cdB*	134.6 de	130.5 f	1.8 d	1.5 e*
BO125	40.8 bc	39.0 cd	0.6 bcB	0.7 eD*	0.2 aCD	0.2 aC	4.4 b	3.9 abC*	130.5 de	123.2 fgD	5.9 a	2.0 d*
BO150	44.1 a	40.0 bc	0.7 bB	0.8 deD	0.2 aCD	0.2 aC	4.7 ab	3.3 cdB*	139.3 d	143.9 ef	5.9 a	2.1 d*

^aAccording to [31]: K, Fe, and Zn: Mehlich-1 extractor; S: monocalcium phosphate in acetic acid extractor; Ca and Mg: KCl extractor (1 mol L⁻¹). Means followed by the same lowercase letter in the columns do not differ from each other by the Tukey test ($p < 0.05$). Uppercase letters indicate the comparison of treatments against four specific references by the Dunnett test ($p < 0.05$), where A = NS (Natural soil), B = NP (Natural phosphate), C = B+NP (Biochar + Natural phosphate), and D = B (Biochar). The presence of a corresponding uppercase letter (A, B, C, or D) on a treatment mean indicates it does not differ statistically from that specific reference treatment. An asterisk (*) in the 40-day value indicates a significant difference from the 10-day value for the same treatment by the t-test ($p < 0.05$).

Table S3. Chemical composition of cassava wastewater (CW) used as binder in biochar-based granular fertilizers (BBGFs).

Properties ^a	%
OC	1.8
Total N	<0.5
P ₂ O ₅	<1.0
K ₂ O	<1.0
Total Ca	<0.5
Total Mg	<0.5
Total S	<1.0
Total Fe	<0.05
Total Zn	<0.05
Total B	<0.1
C:N ratio	3.6
Total Cu	<0.05
Total Mn	<0.05

^aAccording to [71]: OC = Organic carbon: oxidation with K₂Cr₂O₇ (volumetric); Total N: Kjeldahl method; P₂O₅: spectrophotometric method using molybdovanadophosphoric acid; K₂O: acid digestion with HCl and H₂O₂; Ca, Mg, Fe, Zn, Cu, and Mn: nitric-perchloric acid digestion; S: alkaline extraction with KOH and oxidation with H₂O₂; B: HCl extraction.

4.3 Artigo 3 – Unlocking residual phosphorus in tropical soils: The role of agro-industrial binders in biochar-based granular fertilizers efficiency and soil health

Este artigo foi elaborado conforme as normas da revista **Pedosphere** (versão preliminar).

Unlocking residual phosphorus in tropical soils: The role of agro-industrial binders in biochar-based granular fertilizers efficiency and soil health

Abstract

Phosphorus (P) fixation in highly weathered tropical soils necessitates the development of fertilizer technologies that synchronize nutrient release with plant demand. This study evaluated the agronomic effectiveness and soil health implications of biochar-based granular fertilizers (BBGFs) formulated with eucalyptus biochar and reactive natural phosphate (NP) (3:1 w/w), combined with three agro-industrial binders: cassava wastewater (CW), pyroligneous extract (PE), and bio-oil (BO). A greenhouse experiment with *Urochloa brizantha* BRS Paiaguás in a sandy-loam Oxisol assessed binder doses (75%, 100%, 125%, and 150%) against soluble P (SP), NP, and powdered biochar controls (with and without NP) over five cropping cycles. BBGFs formulated with PE at 125% and 150% binder doses promoted total plant biomass and relative agronomic effectiveness (96.8% and 101.3%, respectively) equivalent to the SP. Specifically, the 150% PE binder dose increased total P uptake by 6.5% compared to the reference treatment and maintained high P use efficiency. In contrast, BBGFs formulated with BO constrained biomass production at high binder doses due to granule hydrophobicity, although they achieved the highest Soil Quality Index (SQI) (0.539). BBGFs formulated with CW exhibited a release lag phase, and agronomic recovery occurred only from the fourth cycle onwards. Regarding soil traits, all BBGFs increased pH, organic carbon, and exchangeable bases compared to mineral fertilization alone. These findings indicate that BBGFs-PE at optimized doses effectively replace SP fertilizers, sustain long-term P availability, and enhance biological soil quality in tropical agroecosystems.

Keywords: slow-release fertilizer, phosphorus use efficiency, soil quality index, pyroligneous extract, bio-oil, cassava wastewater.

INTRODUCTION

Phosphorus (P) deficiency is a primary constraint for crop production in highly weathered tropical soils, such as Oxisols. In these environments, the predominance of iron and aluminum (hydr)oxides, coupled with high acidity, results in a high P fixation capacity (Novais and Smyth, 1999). Consequently, a large fraction of soluble phosphate fertilizers applied to the soil becomes rapidly unavailable to plants due to precipitation and specific adsorption reactions (Marschner and Rengel, 2023). This phenomenon leads to low P recovery efficiency, typically below 20% of the applied dose in the first growing season (Solanki et al., 2015). To compensate for this low efficiency, farmers often apply P fertilizer rates exceeding crop removal, resulting in the accumulation of legacy P pools that are difficult to mobilize (Khan et al., 2025). Therefore, developing fertilizer technologies that synchronize P release with plant demand is essential for ensuring sustainable production (Carneiro et al., 2021; Han et al., 2025; Hidayat and Samitsu, 2026).

A promising strategy to mitigate P fixation is the association of phosphate sources with carbon-rich matrices, specifically biochar (Cheng et al., 2024; Haider et al., 2022; Hou et al., 2024). Biochar is defined as a carbon-rich solid material obtained from the thermochemical conversion of biomass in an oxygen-limited environment (pyrolysis) (Joseph et al., 2021). Beyond its role in carbon sequestration, biochar acts as a soil conditioner by neutralizing acidity and supplying exchangeable bases (Santos Júnior et al., 2024; Vega et al., 2025).

When used as a matrix for fertilizers (Biochar-based fertilizers – BBFs), it can physically protect phosphate particles within its porous structure, retarding direct contact with soil sorption sites (Han et al., 2025; Hou et al., 2024). Previous studies have demonstrated that BBFs can promote higher biomass yields and PUE compared to soluble sources, particularly in the medium- to long-term, due to a slow-release profile that enhances the residual effect of fertilization (Borges et al., 2020; Carneiro et al., 2021; Lustosa Filho et al., 2020; Pogorzelski et al., 2020; Santos et al., 2019; Santos Júnior et al., 2024).

However, the agronomic efficiency of biochar-based granular fertilizers (BBGFs) relies heavily on the physicochemical integrity of the granules, which is modulated by the binders used during the granulation process. Recent advances have focused on utilizing agro-industrial byproducts, such as cassava wastewater (CW), pyroligneous extract (PE), and bio-oil (BO), as functional binders (Cheng et al., 2022; Chen et al., 2025; Lu et al., 2023; Santos Júnior et al., 2025a; Santos Júnior et al., 2025b; Yuan et al., 2022). Unlike inert materials, these byproducts contain organic acids, phenolic compounds, and labile carbon that can stimulate microbial activity and alter nutrient release kinetics (Santos Júnior et al., 2025b; Suo et al., 2025; Vilas-Boas et al., 2025; Yuan et al., 2022). In a previous study, we demonstrated that these binders significantly influence the physical quality of granules and initial plant growth (Santos Júnior et al., 2025a). Nevertheless, the long-term impact of specific binder properties, ranging from hydrophilic (CW, PE) to hydrophobic (BO) matrices, on P residual availability and soil biological health remains unclear.

In this study, we hypothesized that BBGFs formulated with agro-industrial binders provide a sustained P supply superior to soluble sources in the long term, thereby improving PUE and soil quality in a tropical Oxisol. The objectives of this work were: (i) to evaluate the agronomic effectiveness and residual effect of BBFs formulated with agro-industrial binders on *Urochloa brizantha* biomass yield and P uptake dynamics over five successive cropping cycles; (ii) to determine the phosphorus use efficiency (PUE) and the impact of these fertilizers on soil P availability compared to soluble sources; and (iii) to assess the

implications of using bioactive binders on soil health, integrating chemical fertility and enzymatic activity into a Soil Quality Index (SQI).

MATERIALS AND METHODS

Production and characterization of biochar-based fertilizers

Detailed information regarding the feedstock preparation, pyrolysis conditions, and physicochemical characterization of the biochar-based fertilizers is available in our previous studies (Santos Júnior et al., 2025a; Santos Júnior et al., 2025b). Briefly, the biochar (charcoal fines) was obtained from the slow pyrolysis of *Eucalyptus urograndis* wood at 450 °C, with a heating rate of 0.1 C° min⁻¹ and a residence time of six days to ensure complete carbonization (Schettini et al., 2022).

Biochar pH and electrical conductivity (EC) were determined using 1.0 g of biochar in 20 mL of deionized water after shaking for 1.5 h on an orbital shaker (Rajkovich et al., 2012). Bulk density was assessed by weighing the biochar compacted for 1 min in a 10 mL graduated cylinder (Santos et al., 2019). Proximate analysis (moisture, volatile matter, ash, and fixed carbon) followed the ASTM D1762-84 standard. Total carbon and nitrogen contents were quantified using the wet oxidation and Kjeldahl methods, respectively. Oxygen and hydrogen contents were estimated based on correlations established by Klasson (2017). Total nutrient contents were determined by wet digestion, validated for biochar analysis by Enders and Lehmann (2012). For this, samples were digested using a nitric-perchloric acid mixture (3:1 v/v) under heating. Finally, the digested material was diluted with deionized water, and elements were quantified, according to Malavolta et al. (1997): P by the colorimetric method; S by barium chloride turbidimetry; K and Na by flame photometry (Micronal B 462); and other nutrients by atomic absorption spectrometry (Varian AAS 240 FS). The chemical and physical properties of the biochar used in this experiment are summarized in Table 1.

TABLE 1
Selected physical and chemical properties of the biochar obtained from eucalyptus wood charcoal fines.

Biochar	
pH	8.96 (0.01)
EC (μS cm ⁻¹)	786.33 (5.94)
Density (kg dm ⁻³)	0.61 (0.01)
Ash (%)	50.66 (1.06)
VM (%)	23.67 (4.60)
Moisture (%)	4.91 (1.18)
FC (%)	20.76 (2.48)
C (%)	50.75 (2.3)
H (%)	1.96 (0.31)
O (%)	7.81 (2.21)
Total N (g kg ⁻¹)	1.99 (0.05)
C/N	255.03 (5.91)
P (g kg ⁻¹)	3.29 (0.03)
K (g kg ⁻¹)	1.08 (0.05)
Ca (g kg ⁻¹)	50.66 (4.33)
Mg (g kg ⁻¹)	4.26 (0.24)
S (g kg ⁻¹)	3.57 (0.30)
Na (g kg ⁻¹)	0.86 (0.03)
Fe (g kg ⁻¹)	17.52 (0.45)

Zn (mg kg ⁻¹)	27.21 (0.09)
Mn (mg kg ⁻¹)	479.49 (12.74)
Cu (mg kg ⁻¹)	17.88 (0.27)

EC: Electrical conductivity; VC: Volatile matter; FC: Fixed carbon. Values in parentheses indicate the 95% confidence intervals (n = 4).

The binders were sourced from distinct agro-industrial waste streams. CW was collected from starch processing facilities in Montes Claros, MG, Brazil. Both PE and BO were recovered as condensable byproducts from the slow pyrolysis kiln-furnace system. The pyrolytic vapors were condensed and subjected to a six-month static decantation period to facilitate gravitational phase separation. Subsequently, the fractions were isolated: the aqueous supernatant was collected as PE, whereas the dense, hydrophobic, and viscous sediment (pyrolysis tar) was harvested as BO. The binders were characterized for pH and EC directly in liquid samples (CW and PE) or in a 1:5 aqueous extract (BO). Total solids content was determined by drying at 103 °C according to ASTM E1756-08. Selected properties of the binders are also provided in Table 2.

TABLE 2
Selected properties of the agro-industrial binders used in the fertilizer formulations.

Binder	pH	EC	TS
	-	$\mu\text{S cm}^{-1}$	g L^{-1}
BO	2.76 (0.18)	1386.67 (37.34)	115.20 (4.09)
PE	3.31 (0.08)	9963.33 (26.67)	71.93 (1.19)
CW	4.34 (0.13)	567.67 (4.16)	230.80 (26.20)

CW: Cassava wastewater; PE: Pyroligneous extract; BO: Bio-oil; EC: Electrical conductivity. Values in parentheses indicate the 95% confidence intervals (n = 3).

The BBGFs consisted of a mixture of biochar and reactive natural phosphate (NP; 27% total P₂O₅ and 8.1% P₂O₅ soluble in 2% citric acid) at a 3:1 ratio (w/w). Granulation was performed in a disk granulator operating at 32.98 rad s⁻¹ by spraying the specific binders onto the Biochar-NP mixture. Binder quantity was determined as a percentage of the physical mixture weight at proportions of 75, 100, 125, and 150%. For example, for the 75% dose, 1 kg of the mixture (750 g biochar + 250 g NP) was combined with 750 mL of binder, with increments of 250 mL for each 25% increase. Finally, the granules were oven-dried at 65 °C for 72 h until constant weight. The produced fertilizers were identified based on the binder used: BBGFs-CW, BBGFs-PE, and BBGFs-BO.

The surface morphology of the biochar and BBGFs was evaluated by scanning electron microscopy (SEM, Zeiss EVO MA10). Micrographs were obtained for the biochar and for the BBGFs prepared with binder doses of 75% and 150% to characterize the structural changes promoted by the binders (CW, PE, and BO).

Greenhouse pot experiment

The experiment was conducted in a greenhouse using soil samples collected from the 0-20 cm layer of a dystrophic sandy-loam Oxisol (Red Yellow Latosol, according to the Brazilian Soil Classification System) under native Cerrado vegetation (Brazilian Savanna), in Montes Claros, Minas Gerais, Brazil (16°41'2.03" S, 43°50'19.28" W, altitude 646 m). The soil was air-dried and passed through a 2-mm sieve. Chemical characterization prior to the experiment indicated high acidity (pH_{water} of 5.4) and low natural

fertility, with available P of 1.50 mg kg⁻¹ and K of 12.60 mg kg⁻¹ (Mehlich-1 method). Exchangeable Ca²⁺ and Mg²⁺ concentrations were 0.31 and 0.14 cmol_c kg⁻¹ (1 mol L⁻¹ KCl extraction), respectively. The soil presented high aluminum saturation (50.9%) with exchangeable Al³⁺ of 0.50 cmol_c kg⁻¹ (1 mol L⁻¹ KCl extraction), and a total soil organic carbon (SOC) content of 5.4 g kg⁻¹ (Walkley and Black, 1934). Other physicochemical properties were determined according to standard methods (Teixeira et al., 2017) (Table S1).

The experimental design was a randomized block with three replications, arranged in a 4 x 3 + 4 factorial scheme. The treatments comprised four binder proportions for granules production (75, 100, 125, and 150% relative to the mixture weight) and three binder types (CW, PE, and BO). Additionally, four control treatments were established: (i) Soluble P (SP), receiving potassium phosphate (KH₂PO₄) as a positive reference; (ii) Natural Phosphate (NP); (iii) a physical mixture of biochar and NP (B+NP); and (iv) biochar only (B).

Experimental units consisted of pots filled with 1.5 dm³ of soil. Soil acidity was corrected using a mixture of calcium carbonate (CaCO₃) and magnesium carbonate (MgCO₃) at a Ca:Mg molar ratio of 3:1 to raise the base saturation (V%) to 70%. The soil was incubated with the carbonates for 30 days, maintaining moisture at approximately 80-90% of the field capacity. After this period, the soil was air-dried, and the treatments were mixed with the whole soil volume to supply 200 mg kg⁻¹ of P, according to Novais et al. (1991) for greenhouse experiments. Next, the treated soil was left to rest for 5 days before sowing to allow the applied amendments to react and stabilize.

Ten seeds of *Urochloa brizantha* cv. *BRS Paiaguás* (Paiaguás grass) were sown per pot, and seedlings were thinned to five uniform plants at 13 days after emergence. The grass was cultivated for five successive cropping cycles, totaling 165 days. Unlike fixed-interval harvesting, cutting management was determined by light interception targets (95%) as established in our previous study (Santos Júnior et al., 2024). Specifically, plants were harvested to a residual height of 20 cm above the soil surface whenever the average plant height reached 40 cm to allow regrowth. After each harvest, nutrient replenishment was performed via fertigation with N and K (100 mg kg⁻¹), according to fertility recommendations for plants growth in greenhouse experiments (Novais et al., 1991).

Harvested shoots were rinsed with distilled water and oven-dried at 65 °C until constant weight to determine shoot dry matter (SDM). Following the fifth harvest, stubble and roots were separated from the soil by wet sieving (2-mm mesh) and processed similarly to quantify stubble (SBDM) and root dry matter (RDM). Subsequently, all plant tissues were ground and subjected to nitric-perchloric digestion (Malavolta et al., 1997). P was determined by colorimetry, K by flame photometry, and Ca and Mg by atomic absorption spectrometry. Finally, nutrient uptake was calculated as the product of nutrient concentration and the respective dry mass yield.

Relative Agronomic Effectiveness (RAE) was calculated to compare the dry matter production of each treatment against the soluble reference. The calculation followed the equation described by Carneiro et al. (2021):

$$RAE (\%) = \left(\frac{SDM_{BBGF}}{SDM_{SP}} \right) \times 100$$

in which SDM_{BBGF} is the accumulated shoot dry matter production (sum of the five cropping cycles) in a given BBGF treatment (g per pot); and SDM_{SP} is the accumulated shoot dry matter production of the soluble P reference treatment (KH_2PO_4) (g per pot).

Phosphorus uptake efficiency (PUpE), Phosphorus Utilization Efficiency (PUtE), and Phosphorus Use Efficiency (PUE) were calculated based on the total nutrient balance of the system (shoots + stubble + roots), adapted from Moll et al. (1982) and Hajari et al. (2015). The indices were obtained using the following equations:

$$PUpE (\%) = \left(\frac{P_{acc}}{P_{supplied}} \right) \times 100$$

$$PUtE (g g^{-1}) = \left(\frac{TPB}{P_{acc}} \right)$$

$$PUE (g g^{-1}) = \frac{PUpE}{100} \times PUtE$$

in which P_{acc} is the sum of P accumulation in the shoots (all cropping cycles), stubble, and roots (mg per pot); $P_{supplied}$ is the dose of P applied via fertilization (mg per pot); and TPB is the total plant dry biomass (shoots + roots + stubble), expressed in mg per pot.

Approximately 200 g of soil were collected from each pot after homogenization for chemical analysis. Soil pH, SOC, exchangeable cations (Ca^{2+} and Mg^{2+}), and available P and K were determined following the same standard procedures described for the initial soil characterization (Teixeira et al., 2017). Additionally, available P was extracted by the ion-exchange resin method (van Raij et al., 1986) to evaluate the labile P pool without the acidic dissolution effect of the Mehlich extractant. Potential acidity (H+Al) was determined by volumetric titration with NaOH (0.025 mol L^{-1}) after extraction with calcium acetate (0.5 mol L^{-1} , pH 7.0), allowing the calculation of CEC, sum of bases (SB) and V% as follows: $CEC (\text{cmol}_c \text{ kg}^{-1}) = H + Al + Ca^{2+} + Mg^{2+} + (K^+/391)$; $SB (\text{cmol}_c \text{ kg}^{-1}) = Ca^{2+} + Mg^{2+} + (K^+/391)$, and $V\% = ([Ca^{2+} + Mg^{2+} + (K^+/391)] / CEC \times 100)$.

Soil quality index

The Soil Quality Index (SQI) was calculated using a weighted additive framework adapted for tropical Oxisols by Mendes et al. (2021). This model integrates chemical (FERT) and biological (BIO) indicators into three primary soil functions: (i) Nutrient Cycling (F1), assessed by the activities of β -glucosidase, arylsulfatase, and acid phosphatase; (ii) Nutrient Storage (F2), represented by SOC and CEC; and (iii) Nutrient Supply (F3), encompassing acidity indicators (pH, H+Al, Al^{3+}) and nutrient availability (P, K^+ , Ca^{2+} , Mg^{2+} , and V%).

Enzymatic activities used for the F1 function were obtained from our previous study (Santos Júnior et al., 2025b), in which a dystrophic Oxisol was incubated with the BBGFs in 100 cm^3 pots. Briefly, air-dried soil samples collected at 10 and 40 days were analyzed with specific substrates, according to Tabatabai (1994), without the use of toluene. Subsequently, the amount of p-nitrophenol (PNP) released from the enzymatic reaction was determined, expressed as $\text{mg PNP kg}^{-1} \text{ soil h}^{-1}$, by UV-visible spectrophotometry. The mean activity values observed at 10 and 40 days of incubation were used as inputs for the index calculation.

Indicator values were transformed into unitless scores (0 to 1) using scoring functions. For β -glucosidase, arylsulfatase, SOC, CEC, and chemical attributes, scores (SS) were calculated using the non-

linear Standardized Scoring Functions (SSF) described by Wymore (1993), with threshold parameters indicated by Mendes et al. (2021):

$$SS = \frac{1}{1 + \left(\frac{B - L}{x - L}\right)^{2S(B + x - 2L)}}$$

in which x is the soil indicator value; B is the baseline value where the score equals 0.5; L is the lower threshold value; and S is the slope of the tangent to the curve at the baseline.

For acid phosphatase, scores were adapted using a linear function based on the activity limits reported by Lopes et al. (2015) for clayey Oxisols. The upper critical limit (CL) was established at 495 mg PNP kg⁻¹ soil h⁻¹, corresponding to the maximum activity observed for air-dried samples in that study. The score was computed as:

$$S_{\text{Phosp}} = \frac{x_{\text{activity}}}{\text{CL}} \text{ if } x < \text{CL}; \text{ and } S_{\text{Phosp}} = 1.0 \text{ if } x > \text{CL}$$

in which x is the acid phosphatase activity value.

Function scores (SF) were computed by summing the weighted scores of each indicator. Finally, the SQI_{FERTBIO} was calculated by summing the weighted scores of each function:

$$\text{SQI}_{\text{FERTBIO}} = (\text{SF}_1 \times 0.33) + (\text{SF}_2 \times 0.33) + (\text{SF}_3 \times 0.33)$$

in which the weights were equally distributed among functions, considering their equivalent importance for the functioning of weathered tropical soils.

Statistical analysis

Data normality was verified using the Shapiro–Wilk test. Data were subjected to analysis of variance (ANOVA) using the F-test ($p < 0.05$). When significant differences were observed, means were compared by Tukey's test ($p < 0.05$). For the effect of binder doses, regression analysis was performed, selecting the best models based on the significance of parameters ($p < 0.05$) and the highest coefficient of determination (R^2). Comparisons between the BBGFs treatments and the control treatments were performed using Dunnett's test ($p < 0.05$). Statistical analyses were conducted using R software, version 4.2.2.

RESULTS

Morphological analysis by scanning electron microscopy (SEM)

The micrographs obtained by SEM analysis at different magnifications of the biochar and BBGFs are shown in Figs. 1 – 4. The biochar exhibited particles of various sizes with smooth and rough surface regions, featuring organized longitudinal channels and tubular pores (Fig. 1a). This material presented a degraded matrix and a porous structure, where exposed macropores and fragments within the pores were identified (Fig. 1b).

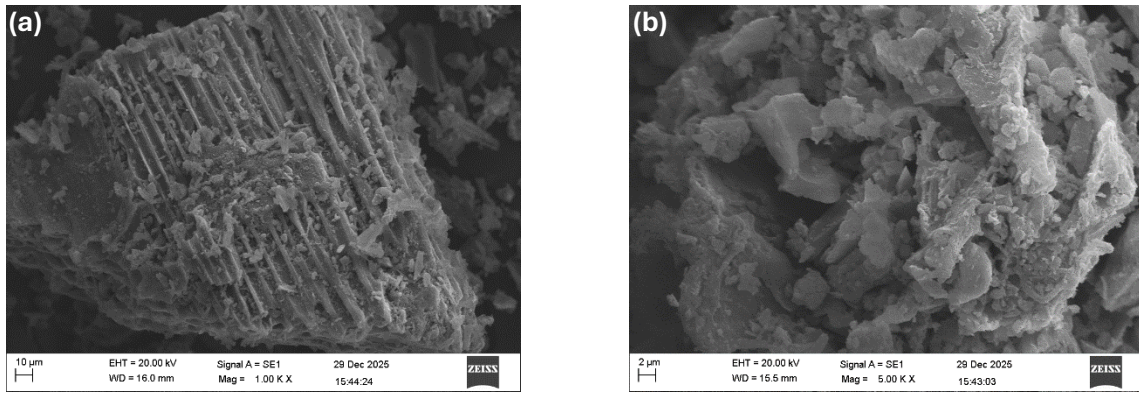


Fig. 1 Scanning electron microscope (SEM) images of the biochar at 50x (a) and 500x (b) magnifications.

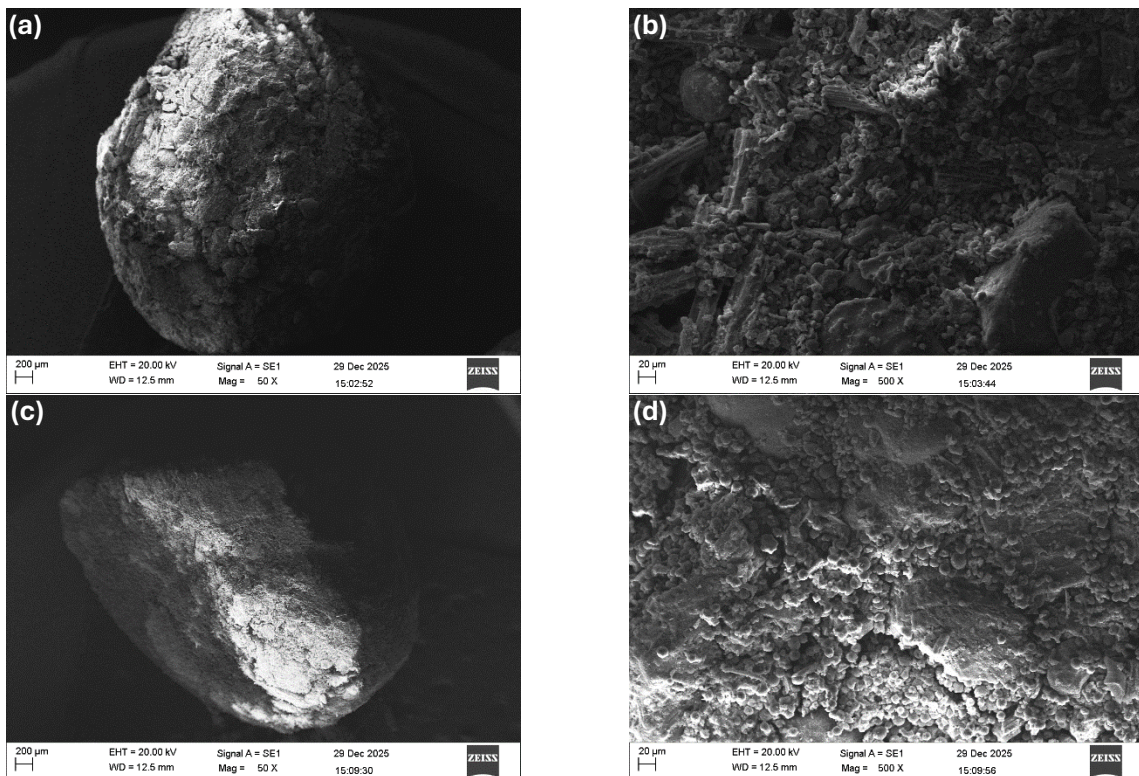


Fig. 2 Scanning electron microscope (SEM) images of BBGF-CW at 75% (a, b) and 150% (c, d) binder doses (50x and 500x magnifications, respectively).

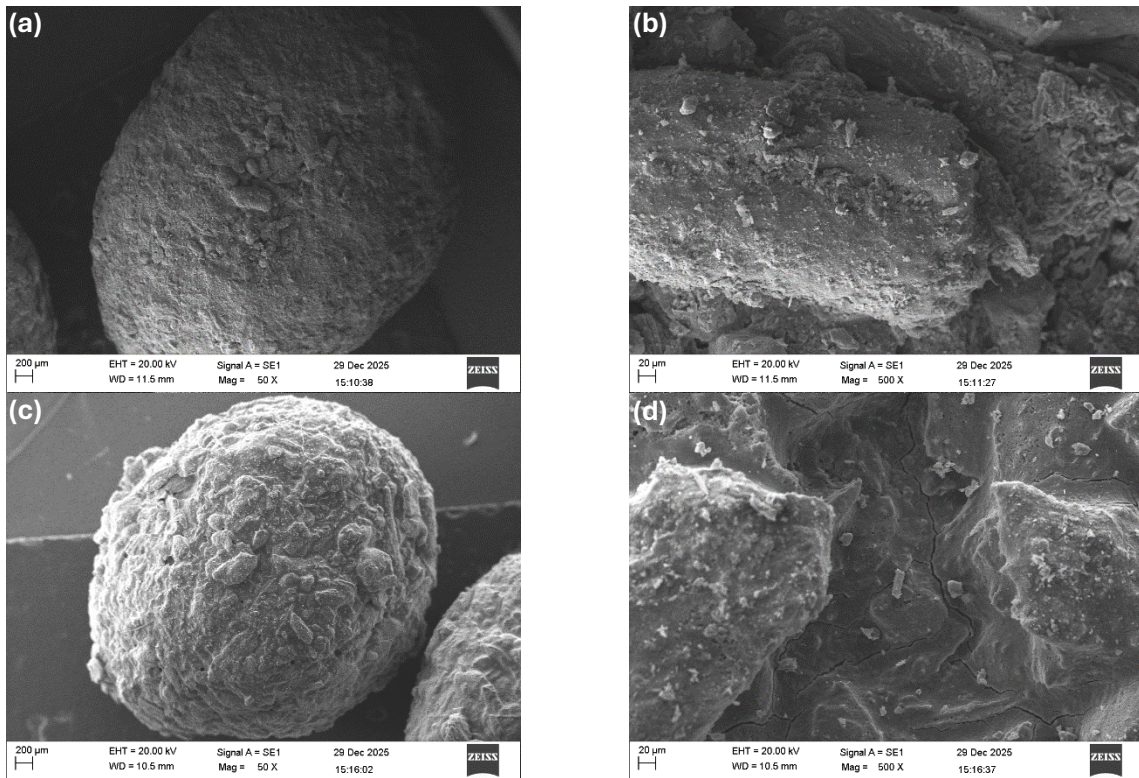


Fig. 3 Scanning electron microscope (SEM) images of BBGF-PE at 75% (a, b) and 150% (c, d) binder doses (50x and 500x magnifications, respectively).

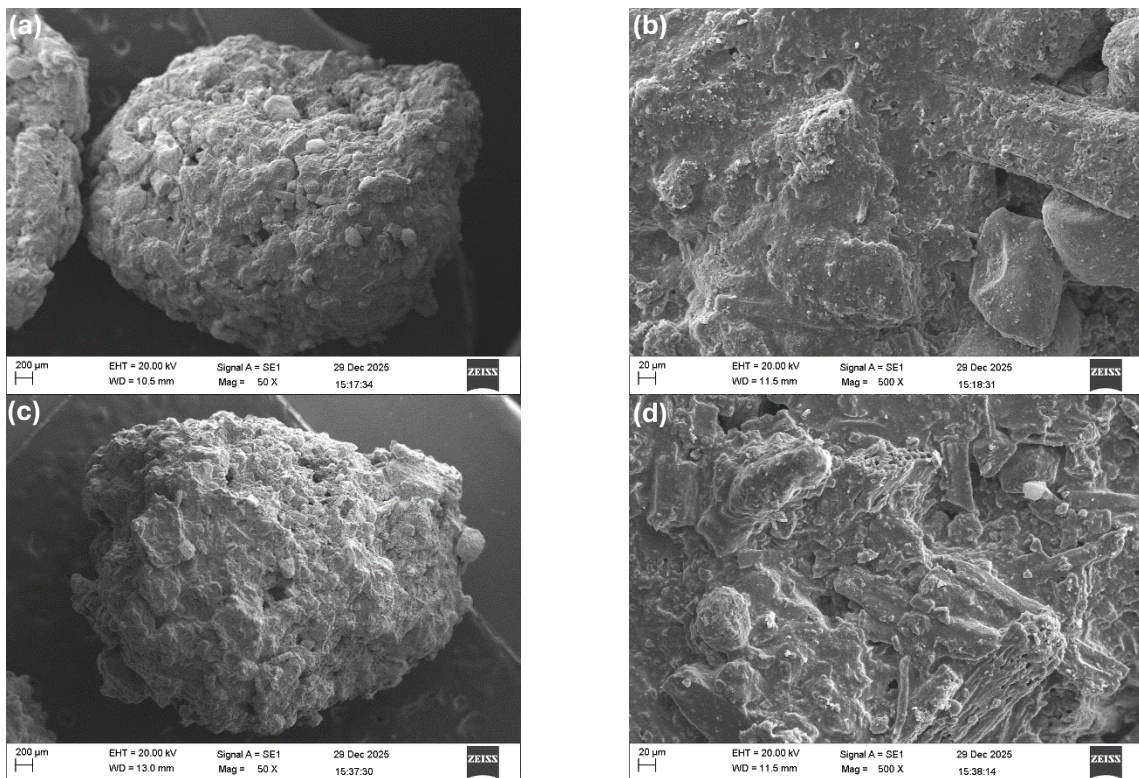


Fig. 4 Scanning electron microscope (SEM) images of BBGF-BO at 75% (a, b) and 150% (c, d) binder doses (50x and 500x magnifications, respectively).

For the BBGF-CW at 75% binder dose (Fig. 2), the surface exhibited agglomerates of various sizes and the presence of cavities (Fig. 2a). At higher magnification, a discontinuous arrangement between the biochar and NP particles was identified, featuring binder deposits and the formation of small globular precipitates (Fig. 2b). The BBGF-CW at 150% binder dose displayed a more uniform surface with a reduced presence of cavities compared to the 75% binder dose (Fig. 2c). At the higher dose, the biochar and NP particles were more effectively coated by the binder, although porosity was observed across the structure (Fig. 2d).

Regarding the BBGF-PE (Fig. 3), granules at the 75% binder dose showed a uniform surface morphology with a visible coating on the biochar and NP matrix (Fig. 3a-b). While precipitates and porosity were observed at the lower dose, the 150% binder dose presented a rigid and compact surface arrangement characterized by transverse cracks and reduced cavity sizes identified across the structure (Fig. 3c and 3d).

Regarding the BBGF-BO (Fig. 4), granules at both binder doses exhibited a heterogeneous surface morphology, featuring particles of various sizes agglomerated (Fig. 4a and 4c). At the 75% binder dose, biochar and NP fragments were identified, with larger cavities observed within the granules (Fig. 4b). In contrast, the 150% binder dose promoted a more compact arrangement, in which the biochar honeycomb-like structure appeared embedded within a rigid binder matrix, although smaller cavities remained visible across the structure (Fig. 4d).

Soil chemical analysis

After 165 days of Paiaguás grass cultivation, soil pH was significantly altered by the different treatments (Table S2). All BBGFs treatments increased soil pH compared to the SP fertilization (pH of 5.88), regardless of binder dose (Fig. 5a). The highest values were observed for BBGFs-CW and BBGFs-BO (6.40 and 6.38, respectively), which were statistically equivalent to the powdered B control (Fig. 5a). In contrast, the BBGFs-PE treatment presented a pH of 6.26, being comparable to the B+NP treatment (Fig. 5a).

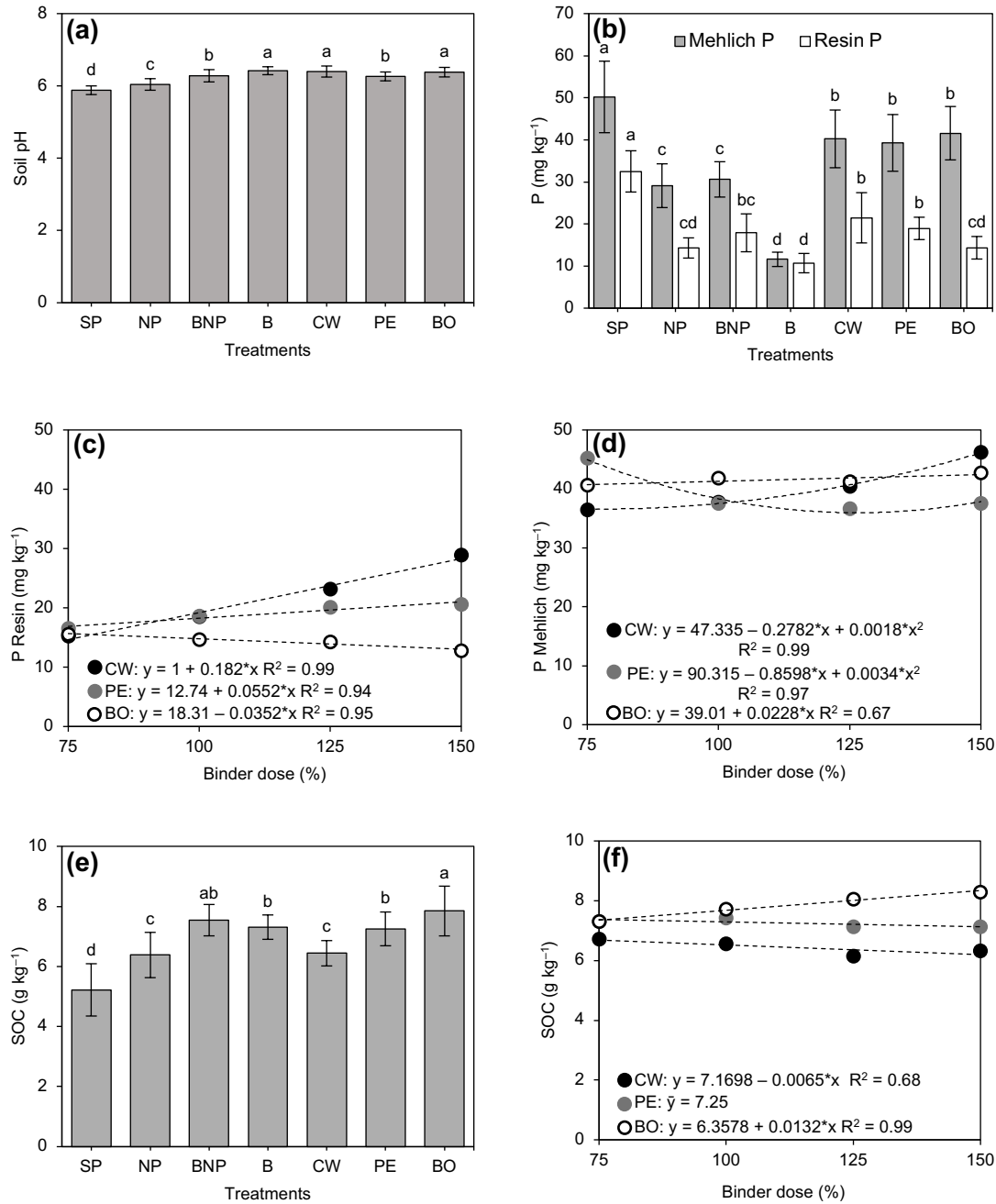


Fig. 5 Soil pH (a), P availability extracted by Mehlich-1 and ion-exchange resin (b), and soil organic carbon (SOC) (e) after five cropping cycles of Paiaguás grass, regardless of binder dose; and regression analysis for P-Resin (c), P-Mehlich (d), and SOC (f) as a function of binder doses in biochar-based granular fertilizers (BBGFs). CW: Cassava wastewater; PE: Pyroligneous extract; BO: Bio-oil; SP: Soluble phosphate; NP: Natural phosphate; B+NP: Biochar + NP; B: Biochar. Bars indicate mean $\pm$ standard deviation. Means followed by the same letter do not differ from each other by Tukey's test ($p < 0.05$).

Regarding soil P status, the SP fertilization resulted in the highest available P levels by both Mehlich-1 and Resin extractors (50.2 and 32.5 mg kg⁻¹, respectively) (Fig. 5b). For the Mehlich-1 extractor, BBGFs-CW, BBGFs-PE, and BBGFs-BO were statistically equivalent (from 39.3 to 41.6 mg kg⁻¹) (Fig. 5b). Conversely, the Resin method revealed a distinct pattern among the granular organomineral sources. While BBGFs-CW and BBGFs-PE maintained similar P levels (21.48 and 18.95 mg kg⁻¹, respectively), the BBGFs-BO treatment exhibited lower availability (14.35 mg kg⁻¹), being statistically comparable to the NP, B+NP and B controls (14.3, 17.9 and 10.7 mg kg⁻¹, respectively) (Fig. 5b). Concerning binder dose effects,

Resin P levels for BBGFs-PE and BBGFs-CW fitted to positive linear models, indicating increased availability with higher binder doses, whereas BBGFs-BO exhibited a negative linear response (Fig. 5c). In contrast, Mehlich-1 P levels for BBGFs-PE and BBGFs-CW were best described by quadratic models, while BBGFs-BO followed a positive linear response (Fig. 5d).

SOC levels were significantly enhanced by all BBGFs treatments relative to SP fertilization, with increments ranging from 17.82% to 59% (Fig. 5e and Table S2). Additionally, the highest SOC value was recorded for BBGFs-BO at 150% dose (8.3 g kg⁻¹), reflecting a positive linear response to binder dose (Fig. 5f).

Regarding soil exchangeable bases, Ca levels were significantly lower for the NP control (1.80 cmol_c kg⁻¹) compared to the other BBGFs treatments, regardless of binder dose (Table S2). In contrast, exchangeable Mg levels did not differ among treatments (Table S2). As for soil exchangeable K, the analysis regardless of binder dose revealed that the SP treatment promoted the highest K levels (84.90 mg kg⁻¹). Conversely, the BBGFs were equivalent to the NP, B+NP, and B controls (Table S2). Among the BBGFs treatments, the BBGFs-PE at the 150% dose exhibited the highest soil exchangeable K levels (Table S2).

Soil Quality Index (SQI_{FERTBIO}) and soil functional indicators

The soil functional indicators (F1, F2, and F3) and the integrated Soil Quality Index (SQI_{FERTBIO}) were influenced by the BBGFs binder type and doses, as shown in Fig. 6. The nutrient cycling function (F1) scores varied among the BBGFs binders. The highest F1 values were observed for BBGFs-BO, followed by BBGFs-PE and BBGFs-CW (Fig. 6a). The BBGF-BO at 150% dose presented the highest F1 score (0.686), representing an increase of approximately 15% and 25% when compared to BBGF-PE and BBGF-CW at the same dose, respectively (Fig. 6a). Regression analysis indicated that F1 scores were best described by a linear model for all formulations (Fig. 6b).

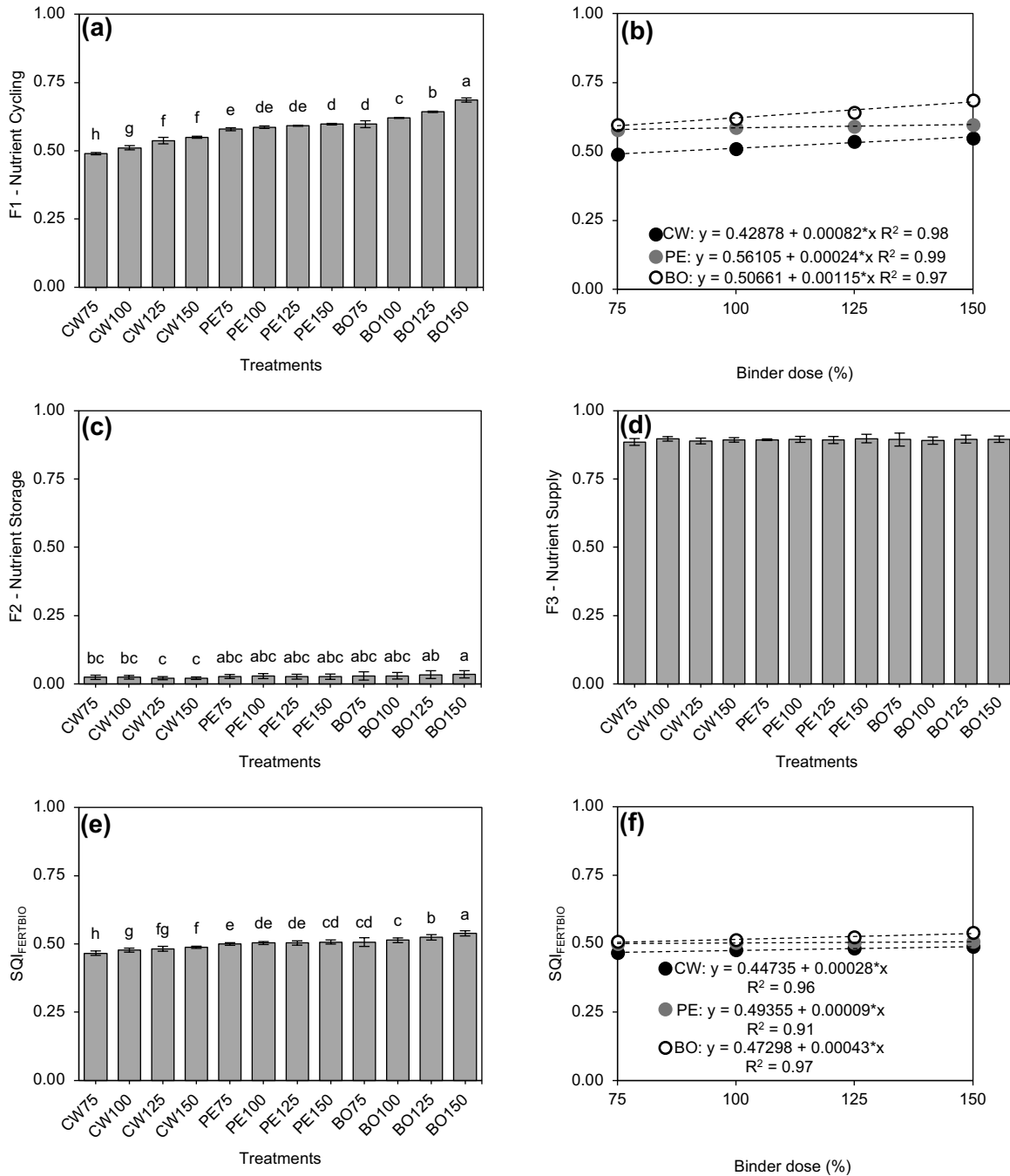


Fig. 6 Scores of soil functions: nutrient cycling (F1) (a), nutrient storage (F2) (c), and nutrient supply (F3) (d); and the Soil Quality Index ($SQI_{FERTBIO}$) (e) of soils fertilized with biochar-based granular fertilizers (BBGFs). Regression analysis for F1 (b) and $SQI_{FERTBIO}$ (f) as a function of binder doses in BBGFs. CW: Cassava wastewater; PE: Pyrolygneous extract; BO: Bio-oil. Bars indicate mean $\pm$ standard deviation. Means followed by the same letter do not differ from each other by Tukey's test ($p < 0.05$).

Regarding the nutrient storage function (F2), the BBGF-BO at 150% dose presented the highest value (0.035), which differed from BBGFs-CW but did not differ from BBGFs-PE treatments (Fig. 6c). For the nutrient supply function (F3), there was no significant difference among the BBGFs treatments, with values ranging from 0.88 to 0.90 regardless of the binder or dose (Fig. 6d).

The $SQI_{FERTBIO}$ followed the trend observed for F1. The BBGF-BO at 150% dose presented the highest SQI (0.539), which differed from the other BBGFs treatments, being 2.8% to 15.5% higher when compared to the remaining formulations (Fig. 6e). The SQI values for BBGFs-PE ranged from 0.500 to

0.507, with no significant difference among the 100%, 125%, and 150% doses (Fig. 6e). Regression analysis indicated that SQI values were best described by a linear model as a function of binder doses for all BBGFs treatments (Fig. 6f).

Paiaguás grass biomass production and relative agronomic effectiveness

The response of Paiaguás grass in successive cultivations is shown in Fig. 7 and Fig. 8. The overall performance under BBGFs and control treatments is presented in Fig. 7, while the regression analysis as a function of binder doses is detailed in Fig. 8. SDM yield varied according to the cropping cycles and binder doses. In the first cropping cycle, regardless of binder doses, the application of B+NP and soluble P source resulted in the highest SDM yields (1.76 and 1.70 g per pot, respectively) (Fig. 7a). In contrast, regression analysis indicated no significant effect of binder doses for BBGFs formulated with CW, PE, or BO, which presented mean yields of 0.28, 0.29, and 0.27 g per pot, respectively (Fig. 8a).

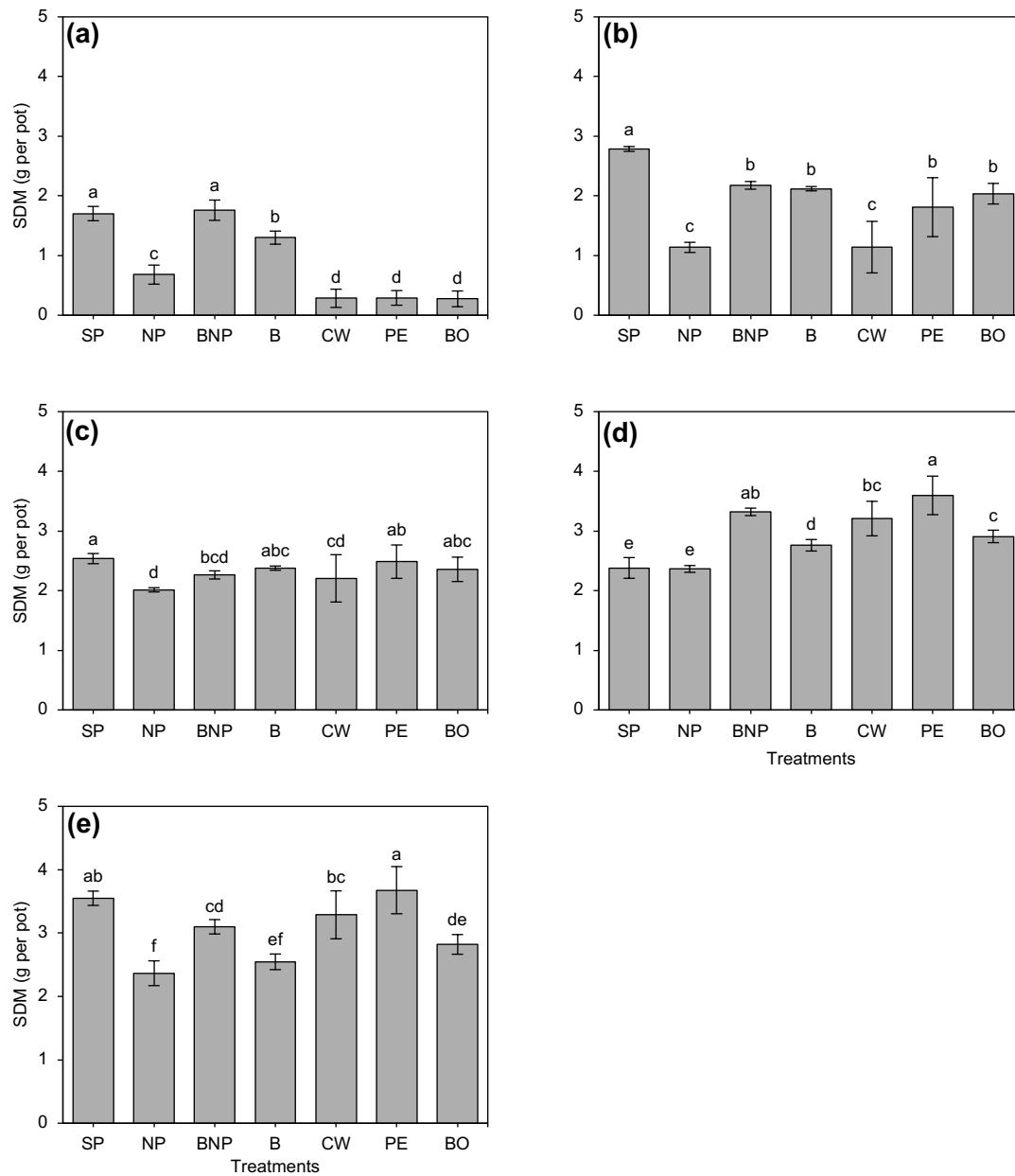


Fig. 7 Shoot dry matter (SDM) of Paiaguás grass in the first cropping cycle (a), second cycle (b), third cycle (c), fourth cycle (d), and fifth cycle (e), regardless of binder dose. CW: Cassava wastewater; PE: Pyrolygneous extract; BO: Bio-oil; SP: Soluble phosphate; NP: Natural phosphate; B+NP: Biochar + NP; B: Biochar. Bars indicate mean $\pm$ standard deviation. Means followed by the same letter do not differ from each other by Tukey's test ($p < 0.05$).

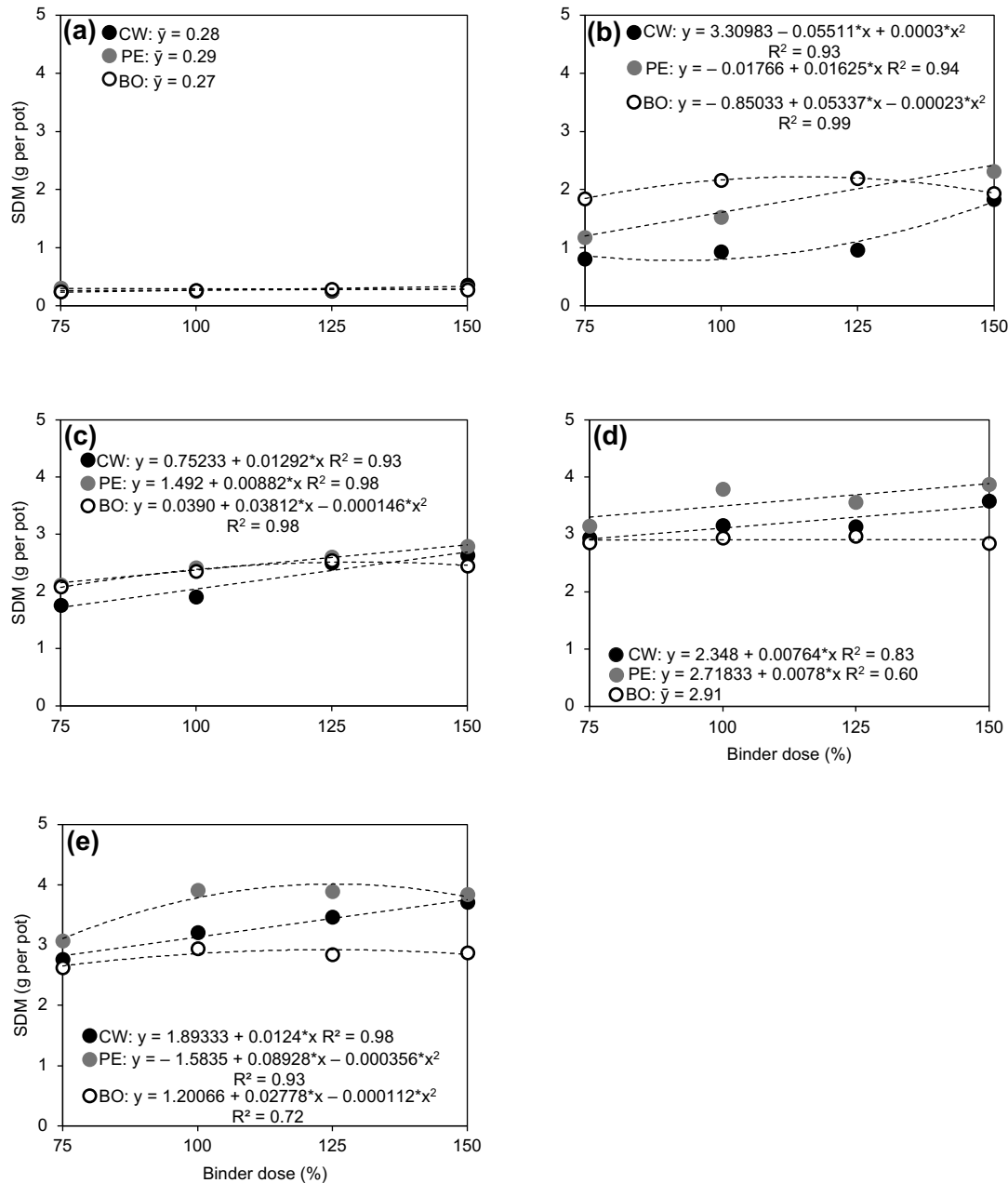


Fig. 8 Shoot dry matter (SDM) of Paiaguás grass as a function of binder doses in biochar-based granular fertilizers (BBGFs) during the first (a), second (b), third (c), fourth (d), and fifth (e) cropping cycles. CW: Cassava wastewater; PE: Pyroligneous extract; BO: Bio-oil.

In the second cropping cycle, regardless of the binder dose, BBGFs-PE and BBGFs-BO promoted higher SDM yields compared to NP fertilization, representing increments of 59.3% and 79.2%, respectively (Fig. 7b). These treatments did not differ from B and B+NP fertilization (Fig. 7b). However, the highest absolute SDM yield was recorded for the SP fertilization (2.79 g per pot) (Fig. 7b). Regarding binder doses, SDM response to PE was best described by a linear increase (Fig. 8b). Conversely, BBGFs-BO fitted a quadratic model, with the maximum estimated yield (2.22 g per pot) observed at the 115% binder dose (Fig. 8b).

From the third harvest onwards, BBGFs-CW and BBGFs-PE promoted SDM yields equal to or higher than those obtained by the biochar powdered controls (B and B+NP), with significant gains ranging from 1.82% to 53.40% (Fig 7c–e). Specifically in the third cropping cycle, the SDM production under BBGFs-PE

and BBGFs-BO treatments was equivalent to the SP application (Fig. 7c). These treatments exhibited linear and quadratic responses to binder doses, respectively, where the maximum SDM for BO was estimated at the 130% dose (2.53 g per pot) (Fig. 8c). Furthermore, despite exhibiting lower mean SDM production relative to these treatments (Fig. 8c), the BBGFs-CW response was best described by a linear model with an upward trend, achieving its highest SDM value at the 150% dose (2.64 g per pot) (Fig. 8c).

In the fourth cropping cycle, all BBGFs outperformed the soluble source regardless of the binder dose (Fig. 7d), with SDM increments ranging from 20% to 63%, approximately. During this cycle, BBGFs-CW and BBGFs-PE exhibited a linear pattern in response to binder dosage, whereas BBGFs-BO showed no significant variation, with a mean of 2.91 g per pot (Fig. 8d). Conversely, in the fifth cropping cycle, SDM yields for BBGFs-PE and BBGFs-CW were equivalent to the SP treatment (Fig. 7e). Additionally, BBGFs-PE outperformed the NP, B, and B+NP controls regardless of binder dose, showing yield increments of 55.39%, 44.40%, and 18.63%, respectively (Fig. 7e). Regarding dose effects, the response of BBGFs-PE and BBGFs-BO was best represented by quadratic models, reaching estimated maximum yields of 4.00 g and 2.90 g, respectively, at doses of approximately 125%, whereas BBGFs-CW fitted a linear model (Fig. 8e).

Relative agronomic effectiveness (RAE), based on the accumulated SDM of the five cropping cycles, is presented in Fig. 9. The BBGFs-PE applied at 125% and 150% doses presented RAE values of 96.84% and 101.29%, respectively, and did not differ from the SP reference and B+NP control (Fig. 9a). For BBGFs-CW, the highest dose (150%) resulted in a RAE of 93.72%, which did not differ from the B+NP treatment (Fig. 9a). Regression analysis indicated that RAE for BBGFs-CW and BBGFs-PE increased linearly with binder doses (Fig. 9b). BBGFs-BO was best described by a quadratic model, reaching a maximum at 120% (Fig. 9b).

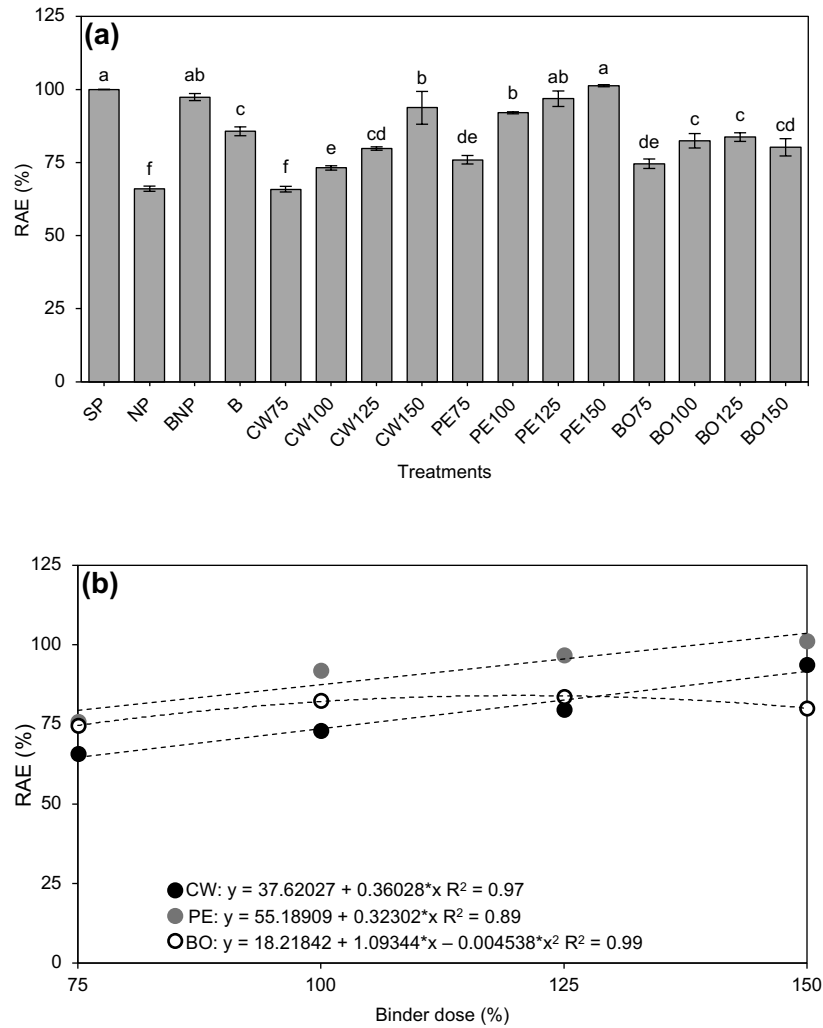


Fig. 9 Relative agronomic effectiveness (RAE) of biochar-based granular fertilizers (BBGFs) applied to Paiaguás grass (a), and RAE as a function of binder doses in BBGFs (b). CW: Cassava wastewater; PE: Pyrolygneous extract; BO: Bio-oil; SP: Soluble phosphate; NP: Natural phosphate; B+NP: Biochar + NP; B: Biochar. Bars indicate mean $\pm$ standard deviation. Means followed by the same letter do not differ from each other by Tukey's test ($p < 0.05$).

SBDM yield was highest for the SP treatment (7.28 g per pot), when compared to BBGFs treatments (Table S3). Although the binder dose did not significantly affect SBDM, all BBGFs treatments exhibited superior yields compared to the NP control, showing increments from 48.97% to 92.55% (Table S3). RDM production was highest for the powdered biochar controls (B and B+NP), which surpassed the SP treatment (4.45 g per pot) by over 55% (Fig. 10a), yielding the highest root-to-total shoot ratios (0.43 and 0.39, respectively) (Table S3). Furthermore, BBGFs-PE at the 150% binder dose outperformed the SP fertilization in RDM yield, resulting in a 23.82% increase (Fig. 10a). Compared to the NP control (3.58 g per pot), superior RDM values were observed for BBGFs-CW at the 75% and 150% doses and for all BBGFs-PE doses tested (Fig. 10a). Conversely, lower root-to-total shoot ratios were observed for the SP treatment (0.21) and BBGFs-BO at doses ranging from 100% to 150% (0.25-0.26) (Table S3).

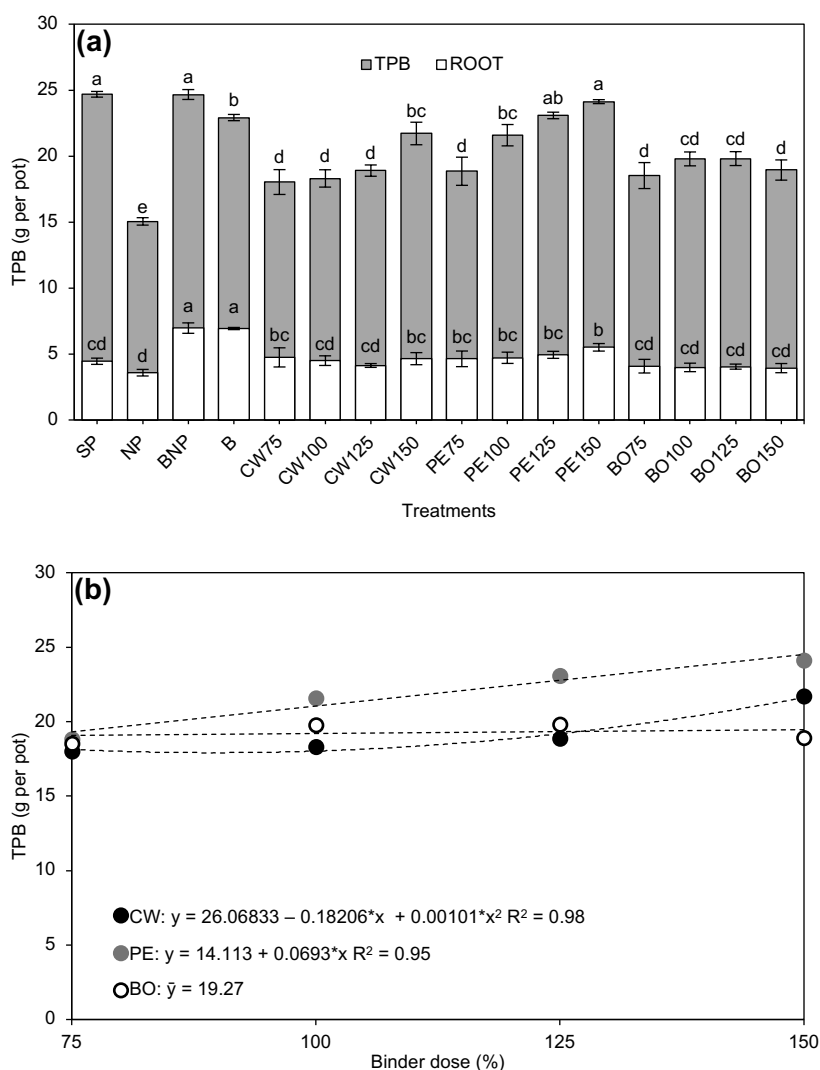


Fig. 10 Total plant biomass (TPB) and root dry matter (RDM) of Paiaguás grass (a), and TPB production as a function of binder doses in biochar-based granular fertilizers (BBGFs) (b). CW: Cassava wastewater; PE: Pyrolygneous extract; BO: Bio-oil; SP: Soluble phosphate; NP: Natural phosphate; B+NP: Biochar + NP; B: Biochar. Gray bars represent TPB and white bars indicate RDM. Bars indicate mean $\pm$ standard deviation. Means followed by the same letter do not differ from each other by Tukey's test ($p < 0.05$). Statistical comparisons were performed separately for TPB (top letters) and RDM (bottom letters).

Despite lower SDM yields in the first cropping cycle compared to SP treatment, the cumulative analysis reveals a recovery trend for granular fertilizers, where BBGFs-PE, specifically, compensated for this initial deficit, resulting in a TPB equivalent to the soluble source (Fig. 10a). Paiaguás grass TPB under BBGFs-PE at 125% and 150% binder doses was equivalent to the SP and B+NP fertilizations, reaching yields of 23.08 and 24.13 g per pot, respectively (Fig. 10a). Accordingly, BBGFs-PE fitted to a positive linear model, indicating continuous biomass gains with increasing doses (Fig. 10b). In contrast, BBGFs-CW was best described by a quadratic model, whereas BBGFs-BO showed no significant response to dose, averaging 19.27 g per pot (Fig. 10b).

Nutrient uptake

P uptake by Paiaguás grass was significantly influenced by the interaction between fertilizer source and cropping cycles (Fig. 11 and Fig. 12). In the first cropping cycle, P uptake in the SP treatment

outperformed the other sources (6.56 mg per pot), showing levels approximately 7-fold higher than those observed for the BBGFs treatments (Fig. 11a). Conversely, the application of BBGFs resulted in limited P acquisition during this initial period, with no significant differences observed among the binder doses (Fig. 12a).

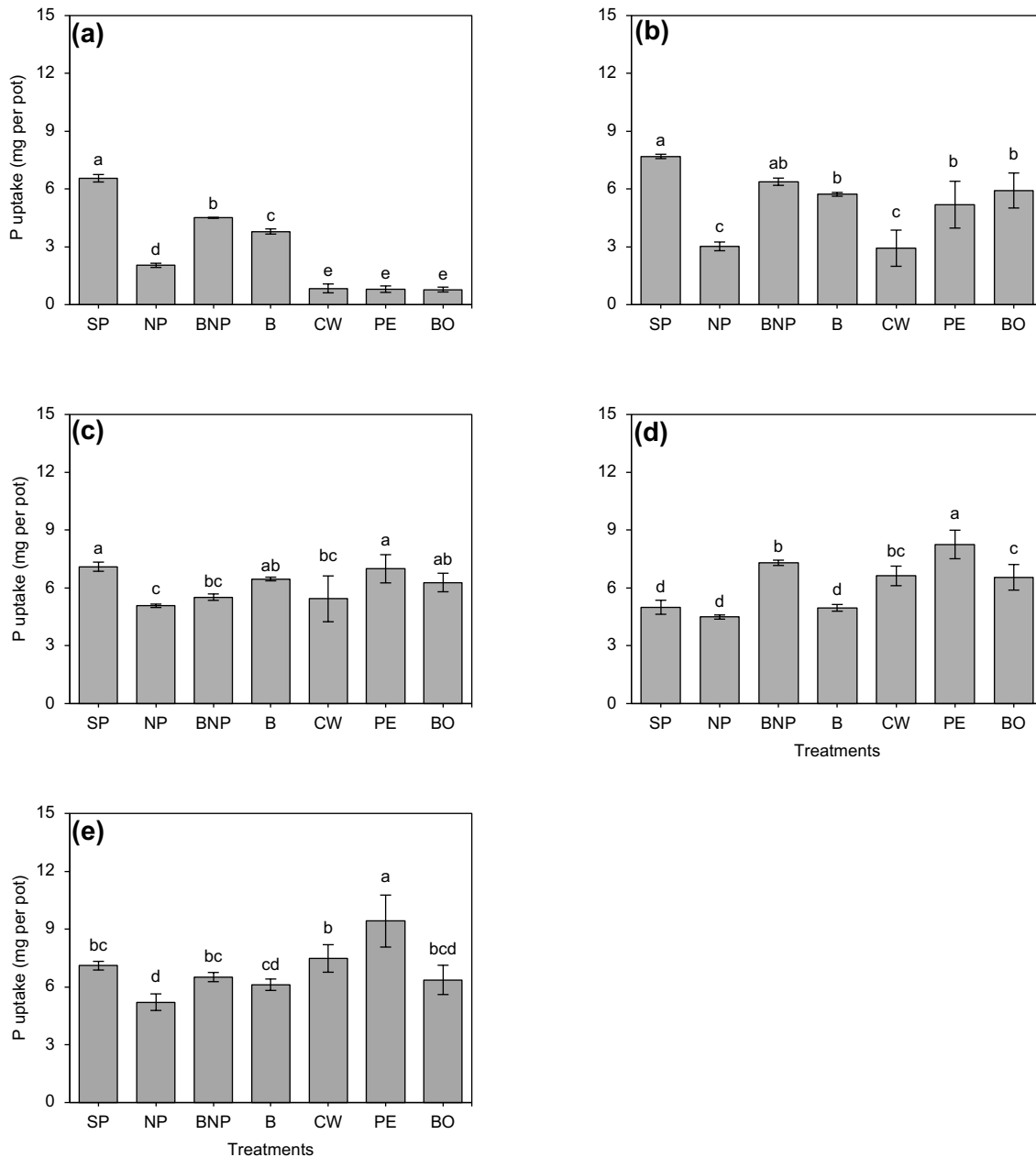


Fig. 11 P uptake by Paiaguás grass in the first cropping cycle (a), second cycle (b), third cycle (c), fourth cycle (d), and fifth cycle (e), regardless of binder dose. CW: Cassava wastewater; PE: Pyroligneous extract; BO: Bio-oil; SP: Soluble phosphate; NP: Natural phosphate; B+NP: Biochar + NP; B: Biochar. Bars indicate mean $\pm$ standard deviation. Means followed by the same letter do not differ from each other by Tukey's test ($p < 0.05$).

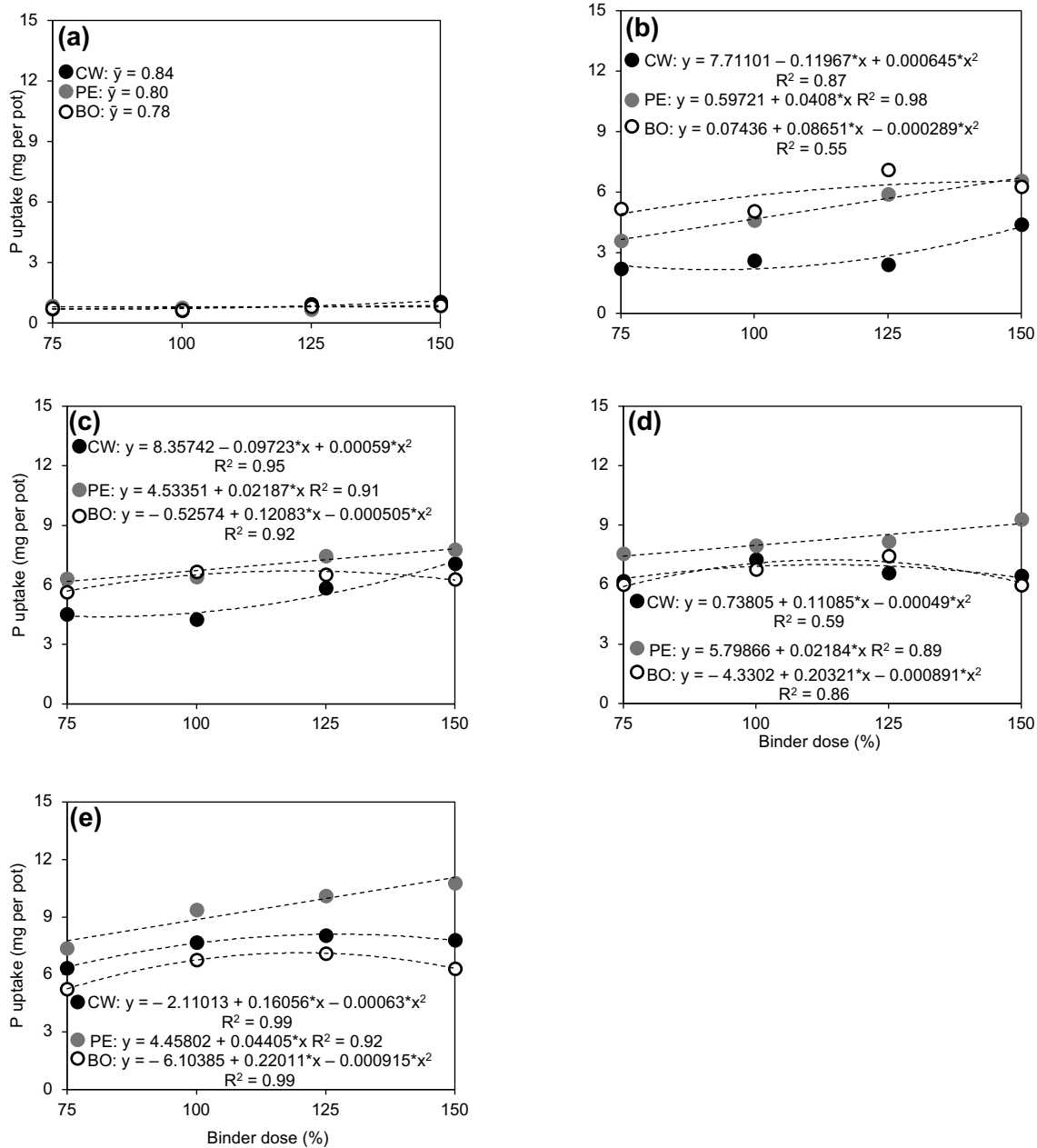


Fig. 12 P uptake by Paiaguás grass as a function of binder doses in biochar-based granular fertilizers (BBGFs) during the first (a), second (b), third (c), fourth (d), and fifth (e) cropping cycles. CW: Cassava wastewater; PE: Pyrolygneous extract; BO: Bio-oil.

From the second cropping cycle onwards, the P uptake response to binder doses for BBGFs-PE was best described by a positive linear model, whereas a quadratic model provided the best fit for BBGFs-CW and BBGFs-BO (Fig. 12b–e). In the second cropping cycle, the SP treatment maintained the highest P uptake (7.69 mg per pot) (Fig. 11b). In contrast, P accumulation for the BBGFs treatments remained significantly lower in relation to soluble source, ranging from 2.23 to 7.13 mg per pot (Table S4). Regardless of the binder doses, the BBGFs-PE and BBGFs-BO treatments did not differ from the B and B+NP control treatments in powder form (Fig. 11b).

P uptake for BBGFs-CW treatments exhibited a quadratic response with an upward trend in the second and third cycles, peaking at the highest doses with values of 4.43 and 7.08 mg per pot, respectively (Fig. 12b and c). In the subsequent cycles (fourth and fifth), the maximum uptake was reached at estimated

binder doses of 113% and 127%, accumulating 7.01 and 8.12 mg per pot (Fig. 12d and e). Regarding BBGFs-BO, the maximum P uptake from the second to the fifth cropping cycle was observed at estimated doses of approximately 149%, 120%, 114%, and 120%, corresponding to accumulations of 6.55, 6.70, 7.26, and 7.13 mg per pot, respectively (Fig. 12b–e).

It should be highlighted that in the third, fourth, and fifth cropping cycles, the highest P uptake by Paiaguás grass was found for the BBGFs-PE treatment at the 150% dose, reaching 7.79, 9.30, and 10.79 mg per pot, respectively (Fig. 12c–e and Table S4). These values represent increases of approximately 10%, 86%, and 52% when compared with the SP treatment. Additionally, regardless of the binder dose, from the third cropping cycle onwards, BBGFs-PE and BBGFs-BO promoted P uptake levels equal to or higher than those obtained with SP fertilization (Fig. 11c–e), whereas uptake under BBGFs-CW treatments was comparable to or exceeded the SP treatment starting from the fourth cropping cycle (Fig. 11d and e).

Overall, P uptake was approximately 6.5% higher in the BBGF-PE 150% treatment compared to the SP treatment (Fig. 13a). Furthermore, the BBGF-PE at the 125% dose did not differ from the SP, B+NP and B controls (Fig. 13a). Regarding the regression analysis for total P uptake, the BBGFs-PE fitted a positive linear model, indicating continuous gains within the tested range (Fig. 13b). Conversely, BBGFs-BO presented a quadratic response with a negative coefficient, reaching the maximum P accumulation at the estimated dose of 120% (Fig. 13b). Finally, BBGFs-CW was described by a quadratic model with a positive coefficient, exhibiting an upward trend where the maximum uptake was obtained at the highest dose applied (Fig. 13b).

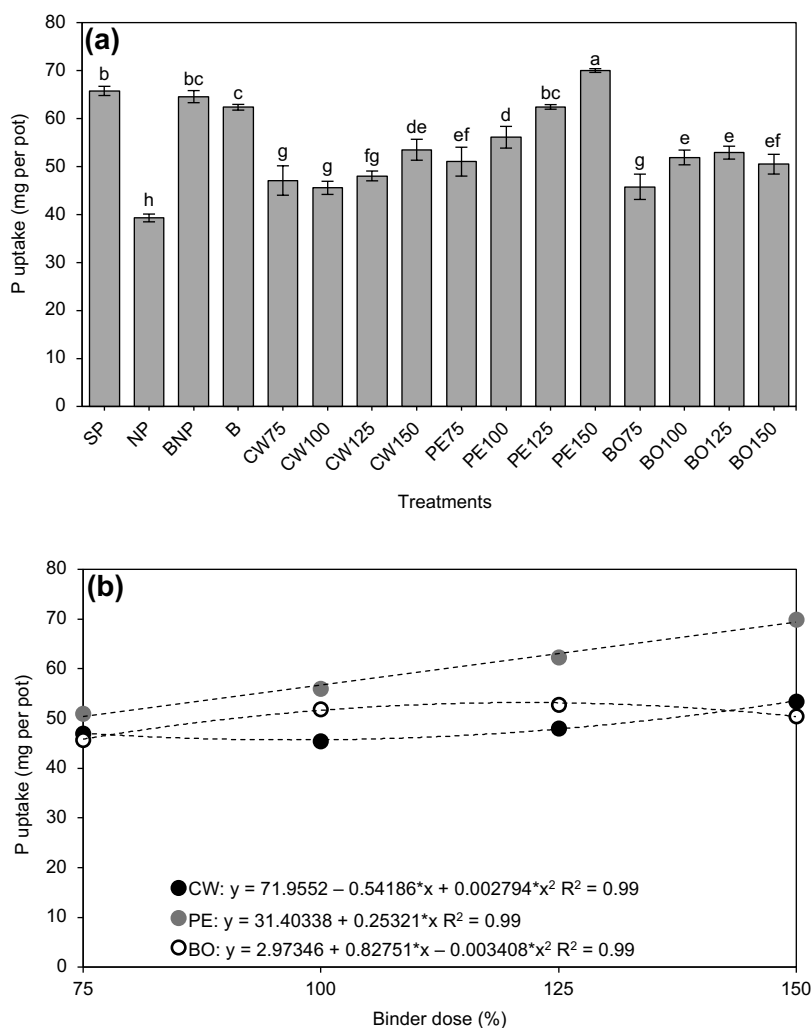


Fig. 13 Total P uptake by Paiaguás grass (a), and total P uptake as a function of binder doses in biochar-based granular fertilizers (BBGFs) (b). CW: Cassava wastewater; PE: Pyroligneous extract; BO: Bio-oil; SP: Soluble phosphate; NP: Natural phosphate; B+NP: Biochar + NP; B: Biochar. Bars indicate mean $\pm$ standard deviation. Means followed by the same letter do not differ from each other by Tukey's test ($p < 0.05$).

The uptake of Ca, Mg, and K by plants over the cycles is presented in Tables S5, S6, and S7, respectively. Overall, a similar acquisition pattern was observed for these nutrients. In the first cropping cycle, all BBGFs resulted in limited uptake rates, with values significantly lower than those of the SP treatment and biochar controls (B and B+NP). However, from the second cycle onwards, nutrient capture in BBGFs treatments increased progressively. By the final harvests (fourth and fifth cycles), BBGFs-PE treatments applied at doses ranging from 100% to 150% promoted uptake rates comparable to or higher than the SP control specifically for Ca, Mg, and K.

Regarding total Ca uptake, high doses of BBGFs-PE (125% and 150%) promoted values of 172.33 and 172.15 mg per pot, respectively, which were equivalent to the SP (171.56 mg per pot), B+NP (178.18 mg per pot) and B (174.87 mg per pot) treatments (Fig. 14a). In contrast, total Ca accumulation for BBGFs-CW and BBGFs-BO remained significantly lower than the SP and biochar controls (B and B+NP), regardless of the binder dose applied (Fig. 14a). Regression analysis for total Ca uptake revealed a positive

linear trend for BBGFs-PE and BBGFs-BO, whereas BBGFs-CW was described by a quadratic model with a positive term (Fig. 14b).

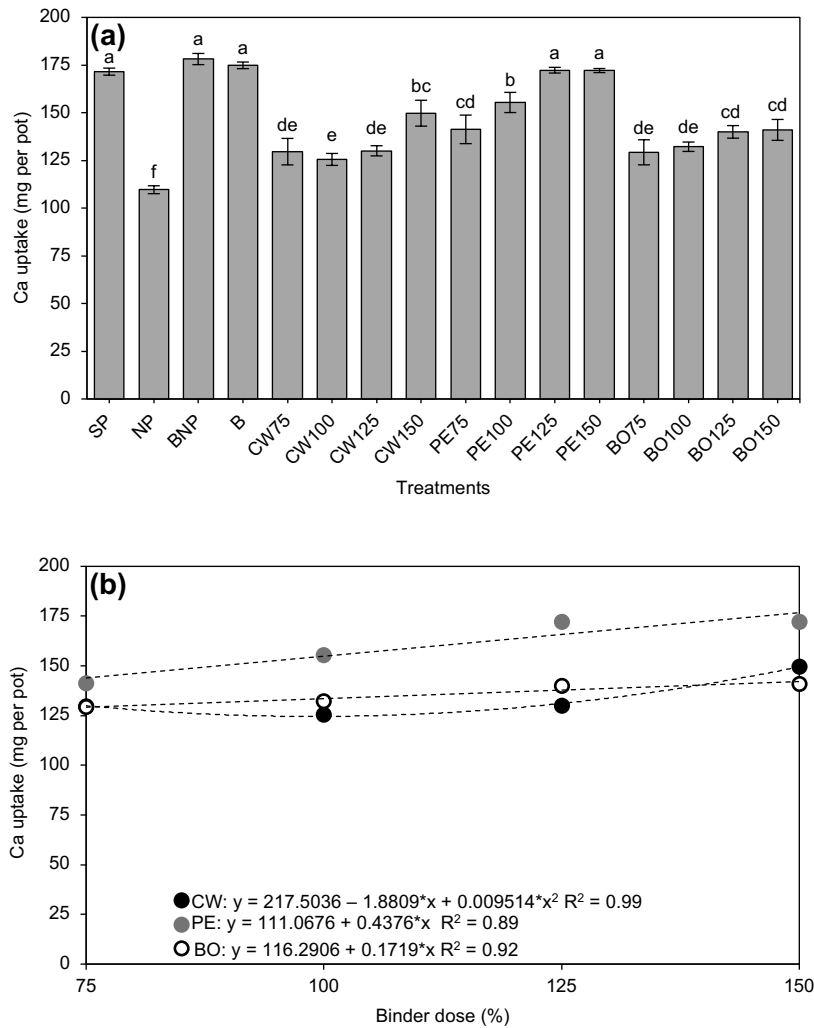


Fig. 14 Total Ca uptake by Paiaguás grass (a), and total Ca uptake as a function of binder doses in biochar-based granular fertilizers (BBGFs) (b). CW: Cassava wastewater; PE: Pyrolygneous extract; BO: Bio-oil; SP: Soluble phosphate; NP: Natural phosphate; B+NP: Biochar + NP; B: Biochar. Bars indicate mean $\pm$ standard deviation. Means followed by the same letter do not differ from each other by Tukey's test ($p < 0.05$).

For total Mg uptake, the BBGFs-PE treatment at the 150% dose significantly outperformed the soluble P source. This accumulation was approximately 8.6% higher than that of the reference treatment (Fig. 15a). BBGFs-PE at the 125% dose also achieved high accumulation and did not differ significantly from the SP, B+NP and B controls (Fig. 15a). Total Mg uptake data for BBGFs-PE fitted a positive linear model (Fig. 15b). Conversely, BBGFs-CW fitted a quadratic model, whereas BBGFs-BO showed no significant differences among the binder doses, being represented by the average value of 87.32 mg per pot (Fig. 15b).

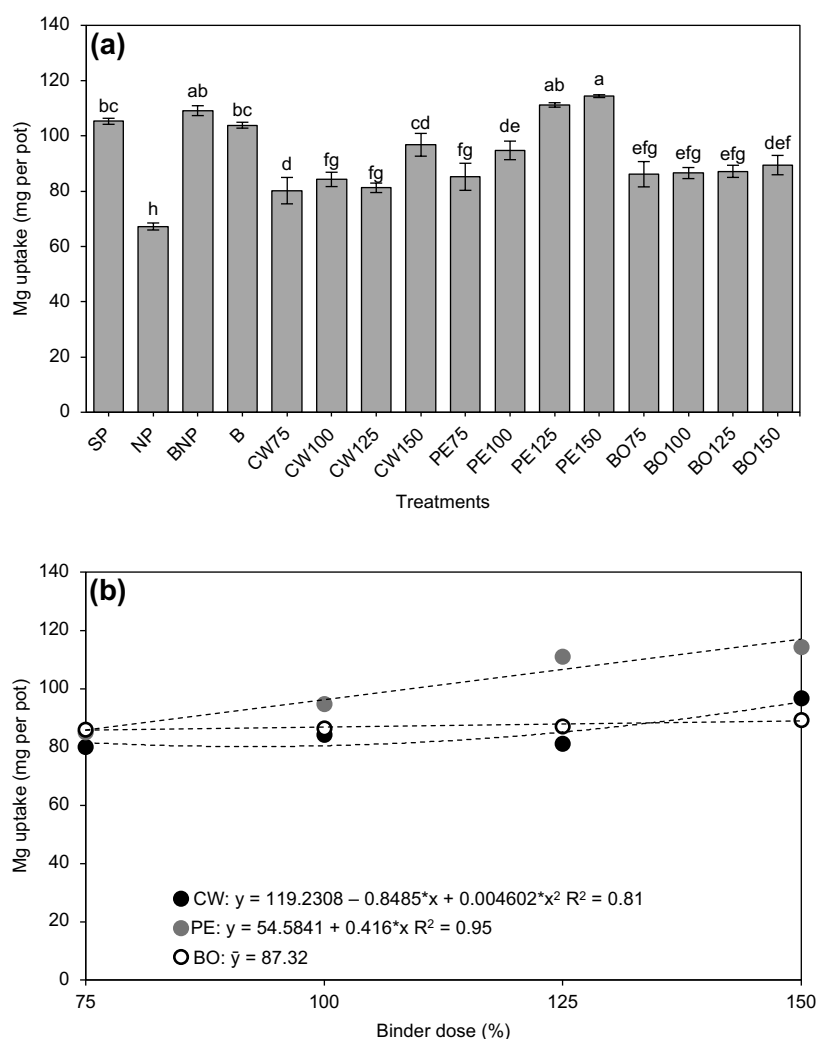


Fig. 15 Total Mg uptake by Paiaguás grass (a), and total Mg uptake as a function of binder doses in biochar-based granular fertilizers (BBGFs) (b). CW: Cassava wastewater; PE: Pyroligneous extract; BO: Bio-oil; SP: Soluble phosphate; NP: Natural phosphate; B+NP: Biochar + NP; B: Biochar. Bars indicate mean $\pm$ standard deviation. Means followed by the same letter do not differ from each other by Tukey's test ($p < 0.05$).

Regarding total K uptake, BBGFs-PE at 125% and 150% doses resulted in accumulations of 772.53 and 768.09 mg per pot, respectively (Fig. 16a). These values were equivalent to the SP (812.12 mg per pot), B+NP (812.11 mg per pot) and B (789.61 mg per pot) treatments (Fig. 16a). In contrast, the other BBGFs promoted significantly lower total K accumulation (Fig. 16a). According to the regression analysis, total K uptake for BBGFs-PE and BBGFs-BO was best described by a quadratic model with a negative term, while BBGFs-CW fitted a quadratic model with a positive term (Fig. 16b).

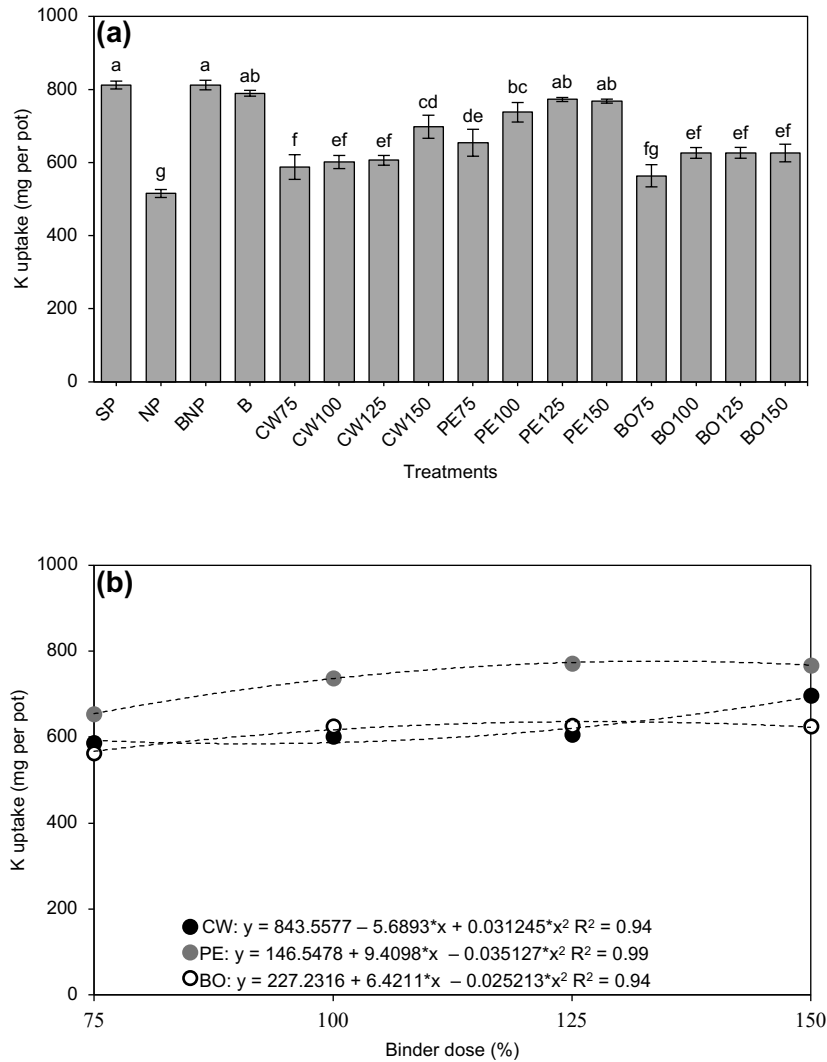


Fig. 16 Total K uptake by Paiaguás grass (a), and total K uptake as a function of binder doses in biochar-based granular fertilizers (BBGFs) (b). CW: Cassava wastewater; PE: Pyroligneous extract; BO: Bio-oil; SP: Soluble phosphate; NP: Natural phosphate; B+NP: Biochar + NP; B: Biochar. Bars indicate mean $\pm$ standard deviation. Means followed by the same letter do not differ from each other by Tukey's test ($p < 0.05$).

Phosphorus use efficiency

Phosphorus use efficiency (PUE) and its components, PUpE and PUE, are presented in Fig. 17 and Fig. 18. Regarding PUpE, the BBGFs-PE treatment at the 150% dose presented the highest value (23.34%), which was significantly higher than the SP treatment (21.92%) (Fig. 17a). BBGFs-PE at the 125% dose (20.81%) did not differ from the SP, B+NP (21.52%) and B (20.78%) controls (Fig. 17a). In contrast, PUpE for BBGFs-CW and BBGFs-BO was generally lower than the biochar controls (B and B+NP) and the SP treatment, regardless of the dose applied (Fig. 17a). Regression analysis indicated that PUpE for BBGFs-PE fitted a positive linear model (Fig. 18a). BBGFs-CW was best described by a quadratic model with a positive term, whereas BBGFs-BO fitted a quadratic model with a negative term, reaching the maximum estimated value at the dose of 121% (Fig. 18a).

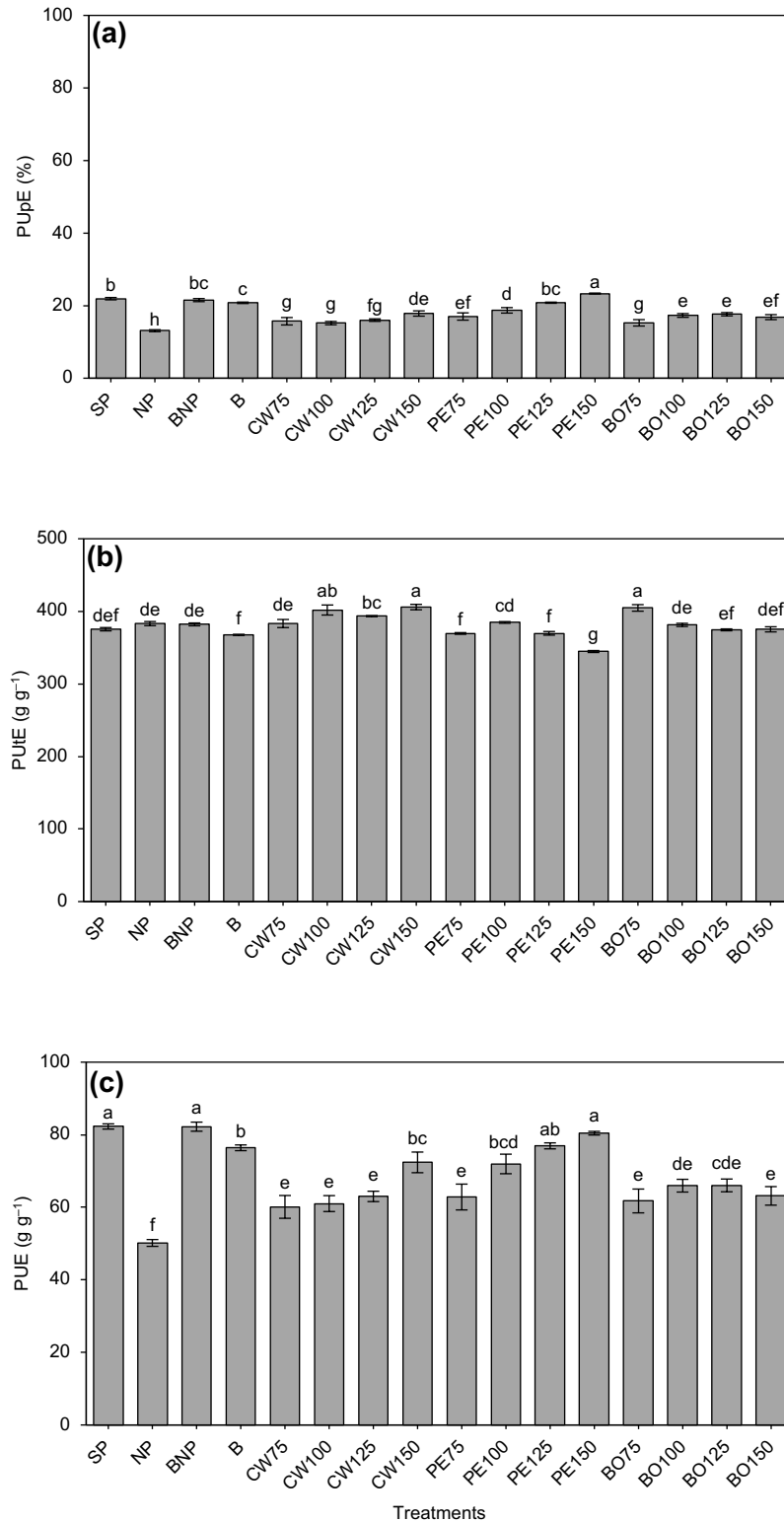


Fig. 17 P uptake efficiency (PUpE) (a), P utilization efficiency (PUtE) (b), and P use efficiency (PUE) (c) of biochar-based granular fertilizers (BBGFs) and reference treatments applied to Paiaguás grass. CW: Cassava wastewater; PE: Pyrolygneous extract; BO: Bio-oil; SP: Soluble phosphate; NP: Natural phosphate; B+NP: Biochar + NP; B: Biochar. Bars indicate mean $\pm$ standard deviation. Means followed by the same letter do not differ from each other by Tukey's test ($p < 0.05$).

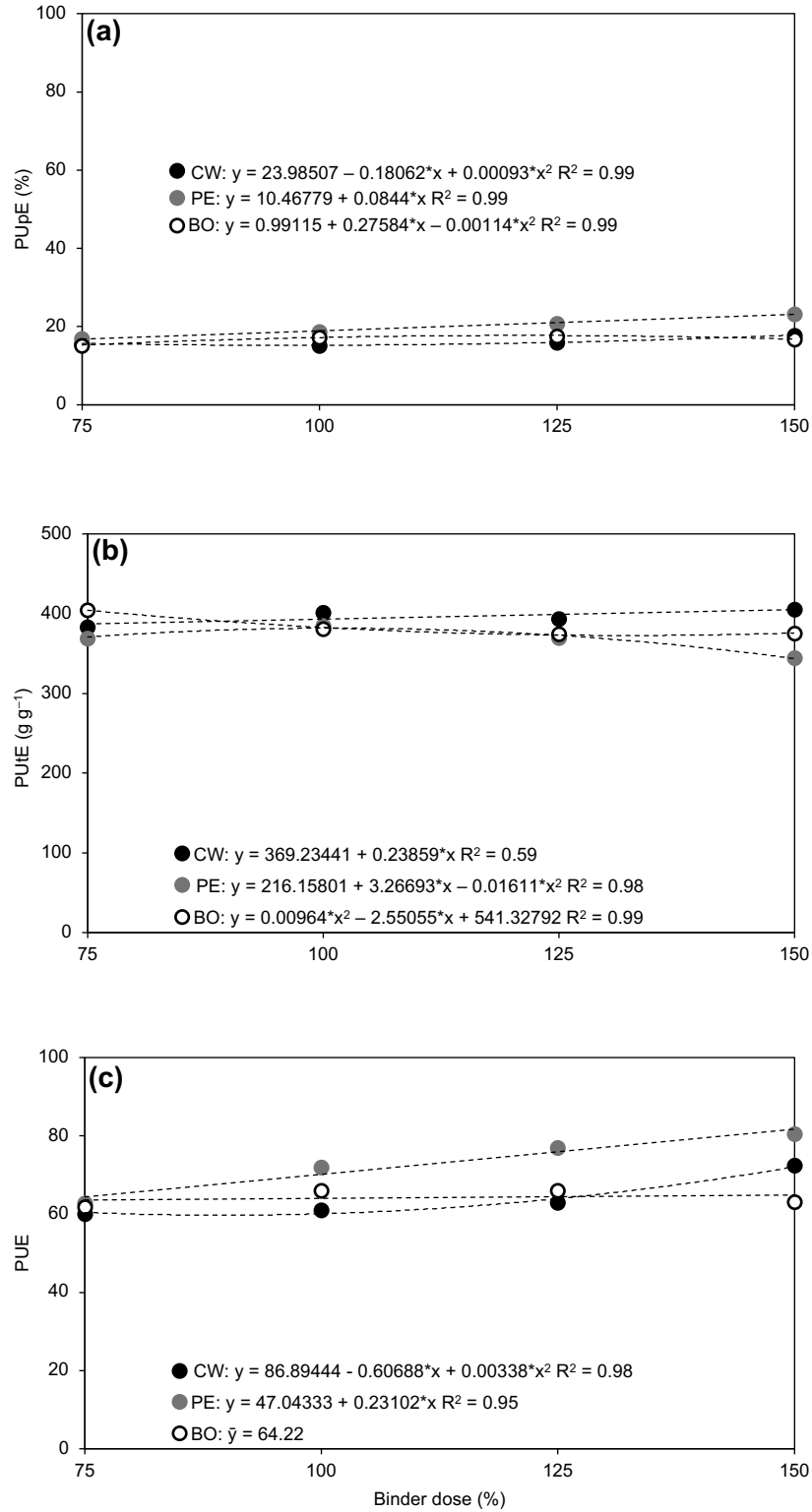


Fig. 18 P uptake efficiency (PUpE) (a), P utilization efficiency (PUtE) (b), and P use efficiency (PUE) (c) as a function of binder doses in biochar-based granular fertilizers (BBGFs). CW: Cassava wastewater; PE: Pyroligneous extract; BO: Bio-oil.

Regarding PUE, the BBGFs-CW treatment at the 150% dose (405.89 g g^{-1}) and BBGFs-BO at the 75% dose (404.72 g g^{-1}) presented the highest values, which were significantly higher than the SP treatment (375.37 g g^{-1}) (Fig. 17b). In contrast, BBGFs-PE at the 150% dose resulted in the lowest PUE (344.62 g g^{-1}), which was lower than the SP treatment, representing a decrease of approximately 8.2% (Fig. 17b). Regression analysis revealed that PUE for BBGFs-CW fitted a positive linear model (Fig. 18b). BBGFs-PE was described by a quadratic model with a negative term, reaching the maximum estimated value at the dose of 101%, whereas BBGFs-BO fitted a quadratic model with a positive term (Fig. 18b).

For PUE, the application of BBGFs-PE at the highest dose (150%) resulted in 80.42 g g^{-1} , which did not differ from the SP (82.28 g g^{-1}) and B+NP (82.22 g g^{-1}) control treatments (Fig. 17c). Conversely, BBGFs-CW and BBGFs-BO showed lower PUE values compared to the soluble source and B+NP treatment, although BBGFs-CW at the 150% dose (72.38 g g^{-1}) did not differ from the B control (Fig. 17c). Regression analysis indicated that PUE for BBGFs-PE increased linearly with binder doses (Fig. 18c). BBGFs-CW was better described by a quadratic model, whereas BBGFs-BO did not present a significant fit, showing an average PUE of 64.22 g g^{-1} across all doses (Fig. 18c).

DISCUSSION

Morphological characterization of biochar-based granular fertilizers (BBGFs)

The micrographs of the biochar revealed organized longitudinal channels and tubular pores (Fig. 1a), which probably resulted from the release of volatile matter and the thermal decomposition of the biomass during the pyrolysis process (Muraro et al., 2026; Sahoo et al., 2021). Additionally, the presence of fragments and the partial filling and obstruction of the pore spaces (Fig. 1b) can be explained by the high ash content (Table 1) of this material (Edeh et al., 2023; Wang et al., 2025a). These mineral residues, concentrated during pyrolysis, may block pores, and contribute to chemical interactions with metal cations within the fertilizer matrix (Wang et al., 2019).

Regarding the BBGFs, the identification of precipitates on the surface (Figs. 2–4) suggests the formation of P compounds during the granulation process (Fang et al., 2020). These precipitates probably result from the reaction between P from the NP and the metal ions available in the biochar ash. According to Han et al. (2025), the drying process is critical for the internal enrichment of P and the formation of stable complexes within the porous structure. This interaction, combined with the effect of the acidic binders (Table 2), promotes the filling and obstruction of the pore spaces (Santos Júnior et al., 2025a) and creates physical protection (Pogorzelski et al., 2020). As noted by Lustosa Filho et al. (2019), the reduced P solubility in such a matrix is beneficial for tropical soils because it prevents the saturation of sorption sites and the formation of P-saturated zones, where rapid P fixation occurs. Thus, P release follows a combined process of dissolution and diffusion to regulate nutrient diffusion (Carneiro et al., 2021; Cheng et al., 2024).

The 150% binder dose promotes a more compact and uniform surface morphology (Figs. 2c and d, 3c and d, and 4c and d). This higher concentration results in a densified matrix where biochar and NP particles are effectively embedded. According to Hidayat and Samitsu (2026), such coatings reduce the specific surface area and average pore diameter, which limits the accessible diffusion pathways. This structural reorganization acts as a stable barrier that restricts water transport into the fertilizer core and minimizes nutrient leaching (Cheng et al., 2024).

Furthermore, the aromaticity of BO and PE binders, coupled with chemical interactions between reactive carbonyl groups and metal ions (Cheng et al., 2022), increases the bond strength and provides superior granule rigidity compared to BBGFs-CW (Santos Júnior et al., 2025a; Santos Júnior et al., 2025b). Consequently, these features transform the BBGFs into a smart fertilizer capable of sustaining P supply throughout the growth season (Lustosa Filho et al., 2019; Santos Júnior et al., 2025a).

Soil properties

The significant increase in soil pH across all BBGFs treatments, reaching values up to 6.40 (Fig. 5a), demonstrates the high neutralization potential of the BBGFs. This liming effect is directly attributed to the high ash content (50.66%) and alkalinity (pH 8.96) of the eucalyptus biochar (Table 1). The thermal decomposition of biomass during pyrolysis concentrates basic cations (Ca^{2+} , Mg^{2+} , K^{+}) in the form of carbonates and oxides, which, upon contact with the soil solution, neutralize the active acidity (Teng et al., 2025; Vega et al., 2025).

The maintenance of soil pH in the weak acidity range (Ribeiro et al., 1999) throughout the five cropping cycles suggests that BBGFs attenuated the acidifying potential of the top-dressing fertilization. The preferential uptake of nitrate (NO_3^-) by Paiaguás grass, the predominant form of nitrogen in the soil, resulting from the nitrification process of ammonium (NH_4^+), promotes the release of OH^- ions by the roots to maintain electrostatic balance, effectively increasing soil pH (Neumann and Ludewig, 2023). In this context, biochar acts as a strategic reservoir for NO_3^- within its multi-layered structure and porosity, facilitating steady plant uptake and reducing leaching (Khan et al., 2023). Additionally, capillary forces and H-bonding within biochar micropores may have attenuated the immediate availability of acidifying ions in the soil solution, providing a superior buffering effect compared to the SP treatment (pH 5.88), where such physical-chemical protection was absent (Idbella et al., 2024).

The lower soil pH observed for BBGFs-PE (6.26) compared to BBGFs-CW (6.40) and BBGFs-BO (6.38) reflects the chemical interaction between the binder's acidity and the biochar's mineral fraction during granulation. The aqueous nature and high electrical conductivity of the PE binder (Table 2) facilitated the rapid diffusion of organic acids, promoting the partial pre-neutralization of the biochar's carbonates and oxides during the granulation and drying stages (Cheng et al., 2022; Santos Júnior et al., 2025a). In contrast, the hydrophobic nature of BO provided a protective matrix for the basic components, while for CW, the higher binder pH, and high solids content (Table 2) offered a less aggressive chemical environment (Santos Júnior et al., 2025a). Specifically, the starch-based solids in CW promote the formation of a binder network that may increase the path length for chemical diffusion (Chen et al., 2025; Salimi et al., 2023).

After Paiaguás grass cultivation, all biochar treatments-maintained soil available P levels significantly higher than the original soil levels (Table S1). This increase can be attributed to the addition of phosphorus by the treatments and to possible effects of biochar on the availability of this nutrient. For example, the presence of calcium and magnesium ions can favor the formation of Ca-P and Mg-P associations (Lustosa Filho et al., 2020; Khan et al., 2025). These associations are characterized by weaker chemical bonds and higher solubility compared to the insoluble Fe-P and Al-P complexes typically formed in acidic tropical soils (Khan et al., 2025). Furthermore, the alkaline nature and high specific surface area of the biochar contributed to increasing soil pH, facilitating the release of P previously adsorbed to soil colloids or Al and Fe oxides (Hou et al., 2024; Joseph et al., 2021).

Soil available P extracted by Mehlich-1 was considered adequate ($30.1\text{--}45.0\text{ mg kg}^{-1}$) for all BBGFs treatments (Ribeiro et al., 1999). The higher P availability observed by the Mehlich-1 method ($\approx 40\text{ mg kg}^{-1}$) compared to the resin method ($14\text{--}21\text{ mg kg}^{-1}$) reflects the distinct chemical mechanisms of these extractors in soils amended with NP. According to Quaggio et al. (2022), the available resin P was considered medium ($16\text{--}40\text{ mg kg}^{-1}$) for BBGFs-CW and BBGFs-PE, and low ($5\text{--}15\text{ mg kg}^{-1}$) for the BBGFs-BO treatment. The acidic solution of Mehlich-1 promotes the dissolution of sparingly soluble Mg-P and Ca-P minerals, such as apatite-type compounds present in the BBGFs matrix, which are not readily available for plant uptake (van Raij, 2019). Conversely, the resin method involves an exchange extraction mechanism, which is regulated by the diffusion rate of phosphate ions from the BBGFs into the soil solution (Freitas et al., 2013).

In contrast to Carneiro et al. (2021), who reported lower Mehlich-1 values due to the high P buffering capacity of clayey soils that exhausts the extractor's acidity (600 g kg^{-1}), the lower clay content of our Oxisol (120 g kg^{-1}) likely preserved the solubilization power of the acid. Consequently, Mehlich-1 accessed non-labile P pools that the resin method could not extract.

Regression models revealed distinct extraction dynamics as a function of BBGFs binder dose for soil available P by Mehlich-1. For BBGFs-PE and BBGFs-CW, the responses were best described by quadratic models. In BBGFs-PE, the reduction in extractable P with increasing doses indicates an efficiency threshold within the granule's functional network. This behavior is attributed to the high density of oxygen-containing functional groups ($-\text{OH}$ and $-\text{COOH}$) (Santos Júnior et al., 2025b), which facilitate phosphate retention through cation bridging and greater polarity (Cheng et al., 2022; Jin et al., 2023), creating a saturation threshold that effectively traps P within the matrix. Conversely, the increase in available P for BBGFs-CW suggests that the starch-based binder's acidity facilitated localized NP solubilization, while its more permeable and hydrophilic matrix ensured greater P accessibility (Cheng et al., 2022; Lu et al., 2023; Santos Júnior et al., 2025b). Finally, BBGFs-BO exhibited a positive linear response, as its recalcitrant structure provided physical shielding, allowing P recovery to scale proportionally with binder mass (Cheng et al., 2022; Santos Júnior et al., 2025a; Santos Júnior et al., 2025b).

The significant reduction in P-resin for BBGFs-BO (14.35 mg kg^{-1}) compared to BBGFs-CW (21.48 mg kg^{-1}) and BBGFs-PE (18.95 mg kg^{-1}) is primarily driven by the hydrophobic diffusion barrier of the BO binder. The rigid surface arrangement integrated into a dense organic matrix, as identified via SEM (Fig. 4), aligns with the superior crushing strength and granule density established in our previous work (Santos Júnior et al., 2025a). Such a physical configuration provides effective shielding against water penetration and nutrient solubilization, while the high concentration of high-molecular-weight aromatic compounds promotes the immobilization of P through physicochemical occlusion (Cheng et al., 2022; Santos Júnior et al., 2025b). The linear reduction in P-resin availability as the BO binder dose increases reinforces the evidence for this structural shielding (Wang et al., 2025b).

Soil organic carbon (SOC) content was enhanced by all BBGFs treatments compared to SP fertilization, reflecting the contribution of the biochar-binder matrix to the soil carbon pool because the pyrogenic carbon compounds from biochar (Borges et al., 2020). The linear SOC enrichment observed for BBGFs-BO is driven by the aromatic nature and recalcitrant structure of the BO binder (Cheng et al., 2022; Santos Júnior et al., 2025b). Under tropical edaphoclimatic conditions, such stable carbon forms are essential to resist the rapid mineralization rates that typically exhaust organic residues *in natura* (Liu et al.,

2024; Vega et al., 2025; Yang et al., 2024). Furthermore, the BO matrix likely induced a negative priming effect, where the persistence of aromatic compounds facilitates carbon sequestration by protecting native soil organic matter (Song et al., 2024; Santos Júnior et al., 2025b).

Conversely, the lower SOC content in BBGFs-CW reflects the labile nature of the unmodified starch binder. The low crystallinity and amylose content of native starch promote water absorption and swelling, which disrupts the ordered crystalline structure (Cai et al., 2023; Chen et al., 2025; Salimi et al., 2023; Wang et al., 2025b). This mechanism expedites the progression through the nutrient release stages: water absorption (lag phase), constant release (steady-state), and depletion (degradation phase) (Salimi et al., 2023). This prompt transition provides an immediate carbon source for soil microorganisms. Consequently, the availability of these labile substrates induced a positive priming effect, accelerating the turnover of labile biochar fractions and native soil carbon (Santos Júnior et al., 2025b; Vega et al., 2025; Wang et al., 2022).

According to Chen et al. (2025), the interaction between the starch binder and water promotes the expansion of the polymeric network. While this initial expansion facilitates nutrient release, the structure subsequently undergoes a rearrangement. This process leads to a smoother and more regulated nutrient diffusion over time.

It is important to consider that the application of biochar may compensate for soil carbon depletion compared to the application of chemical fertilizers alone, which often results in decreased SOC, degraded soil structure, and the ultimate deterioration of soil productivity (Haider et al., 2022; Li et al., 2024; Yang et al., 2024). This is especially significant given that soil constitutes a major terrestrial C reservoir, where minor fluctuations in soil C stocks can significantly impact atmospheric C levels and influence climate change (Smith, 2012).

The superior SOC content in BBGF-BO at higher doses (125 and 150%) compared to powder biochar treatments reflects a difference in bioaccessibility. While biochar in powder form provides higher surface area and porosity for microbial habitats and supplies direct nutrients for bacterial growth, it also increases the exposure of labile carbon fractions to microbial enzymes (Liu et al., 2024). In highly weathered tropical soils, this exposure facilitates mineralization. On the other hand, the granular structure of BBGF-BO provides physical protection, where the aromatic BO binder acts as a shield (Cheng et al., 2022; Hidayat and Samitsu, 2026; Santos Júnior et al., 2025b).

The high carbon/nitrogen ratio of the biochar used in the present study (Table 1) likely delayed native carbon mineralization, particularly when combined with higher doses of PE and BO (Santos Júnior et al., 2025b). Wood-derived biochar enhances carbon sequestration because it contains low amounts of easily oxidizable organic fractions (Haider et al., 2022; Otoni et al., 2024). This underscores the potential of BBGFs as a strategy for sustainable agriculture and a viable alternative to offset greenhouse gas emissions.

For exchangeable Ca^{2+} and Mg^{2+} , the soil content was classified as medium $1.21\text{--}2.40\text{ cmol}_c\text{ kg}^{-1}$ for Ca^{2+} and $0.46\text{--}0.90\text{ cmol}_c\text{ kg}^{-1}$ for Mg^{2+}) across all treatments (Ribeiro et al., 1999). These contents can be attributed to the initial acidity correction performed with calcium and magnesium carbonates, which established a baseline fertility. However, the significantly superior Ca^{2+} content in BBGFs treatments compared to the NP control suggests the supplemental addition of this nutrient by the biochar itself. Considering the high calcium concentration in the biochar (Table 1), the granules acted as a direct source of Ca^{2+} released during the experimental period.

Beyond their role as essential nutrients, Ca^{2+} and Mg^{2+} contribute to the slower release mechanism of the organomineral fertilizer. These cations stabilize mineral nutrients within the biochar matrix through electrostatic surface attraction, precipitation, or ion exchange, and by increasing the pore structure, which forms a greater number of adsorption sites (Haider et al., 2022). Consequently, this interaction impacts the availability of P, creating an environment that regulates the nutrient release rate (Cancellier et al., 2025; Han et al., 2025; Santos Júnior et al., 2024).

The exchangeable K^+ content in the SP treatment was higher primarily because the reference fertilizer used (potassium phosphate) is a highly soluble source containing K. In contrast, despite the low K content of the eucalyptus wood biochar (Table 1), as reported in other studies (Bilias et al., 2023; Otoni et al., 2024; Vega et al., 2025; Xu et al., 2025), the BBGFs maintained soil levels classified as adequate ($71 - 120 \text{ mg kg}^{-1}$) (Ribeiro et al., 1999).

The maintenance of these levels is attributed to the interaction between the biochar matrix and a portion of the K supplied via top-dressing. This phenomenon involves the physical protection of soluble fractions within the micropores and the complex pore geometry of the wood biochar, which creates a tortuous path that limits water access and hinders diffusion (Fachini et al., 2022; Pogorzelski et al., 2020). Additionally, the strong electrostatic attraction between the negatively charged biochar surface and positively charged elements contributes to the retention of these ions (Bilias et al., 2023; Fachini et al., 2022; Haider et al., 2022).

This specific dynamic also elucidates the higher soil K content observed for BBGFs-PE at the 150% dose compared to the other BBGFs treatments (Table S2). In this formulation, the PE binder probably provided additional functional groups that favor electrostatic interactions, enhancing the retention of K^+ ions on the biochar-binder matrix and preventing their rapid depletion (Bilias et al., 2023; Cheng et al., 2022; Vilas-Boas et al., 2025). Consequently, this mechanism modulates nutrient availability, promoting K uptake by plants (discussed later).

Biochar-Based Granular Fertilizers (BBGFs) on soil health indicators ($\text{SQL}_{\text{FERTBIO}}$)

The application of the Soil Quality Index ($\text{SQL}_{\text{FERTBIO}}$) demonstrated that binder selection is a critical driver of soil health recovery in tropical Oxisols. While all BBGFs exhibited comparable chemical effectiveness (F3), nutrient cycling function (F1) and nutrient storage (F2) were distinctively modulated by the physicochemical nature of the binders.

The soil function F1 was the most sensitive component of the index, differentiating the organomineral sources where chemical attributes could not. The superiority of BBGFs-BO at 150% is linked to the specific chemical composition of the BO. As previously discussed, the BO binder presents a high concentration of recalcitrant carbon forms, including aromatic hydrocarbons and heterocyclic compounds, which act as a continuous substrate for enzymatic activity (Santos Júnior et al., 2025b; Song et al., 2024; Vilas-Boas et al., 2025). Specifically, the heavy fraction of the pyrolytic condensate shows a lower H/C ratio, reflecting the abundance of complex aromatic structures derived from lignin degradation processes during pyrolysis (Vilas-Boas et al., 2025). These characteristics confer high viscosity to the BO binder, which is responsible for the rigid structure of the granules formulated with this binder (Cheng et al., 2022; Santos Júnior et al., 2025a).

Although possessing lower recalcitrance than the BO binder, the BBGFs-PE exhibited intermediate performance, significantly outperforming the BBGFs-CW. This response is driven by the distinct chemical nature of the PE binder, which provides a balanced input of carbon forms. While the CW binder is rapidly mineralized, the PE delivers a combination of labile organic compounds, such as carboxaldehydes and organic acids, along with a reserve of phenolic structures (Ouattara et al., 2024; Santos Júnior et al., 2025b; Vilas-Boas et al., 2025).

Furthermore, the PE binder is rich in oxygen-containing functional groups (e.g., $-OH$ and $-COOH$), which are known to enhance nutrient retention through cation complexation and hydrogen bonding with ions (Cheng et al., 2022; Vilas-Boas et al., 2025). Thus, the BBGFs-PE creates a chemical environment that stimulates enzymatic activity more sustainably than simple carbohydrates, without inducing the immediate substrate depletion observed in the BBGFs-CW treatments.

The soil function F1 scores fell within the moderate range (0.42–0.62) for all BBGFs-CW and BBGFs-PE treatments, regardless of the binder dose, as well as for BBGFs-BO at 75% and 100% doses. Notably, BBGFs-BO treatments at 125% and 150% doses were classified as adequate (>0.62). This interpretation was based on the relative cumulative yield framework, which incorporates SOC into the index calculation, according to Mendes et al. (2021).

It is important to highlight that while the original $SQL_{FERTBIO}$ framework proposed by Mendes et al. (2021) relied exclusively on β -glucosidase and arylsulfatase activities to calculate the soil function F1, this study incorporated acid phosphatase as a complementary indicator. This inclusion is justified by the vital role of this enzyme in hydrolyzing organic P compounds, facilitating release from organic matter, a critical process in soils amended with organomineral sources (Barbosa et al., 2023; Tantriani et al., 2025).

Literature indicates that phosphatase activity is highly sensitive to the type of fertilization and management practices (Barbosa et al., 2023; Hou et al., 2024; Lopes et al., 2021; Rocabruna et al., 2024; Tantriani et al., 2025). While exclusive inorganic P fertilization often inhibits acid phosphatase activity due to feedback inhibition mechanisms (Janes-Bassett et al., 2022; Lopes et al., 2021), the combined use of organic and inorganic sources, as found in BBGFs, tends to stimulate it (Janes-Bassett et al., 2022; Rocabruna et al., 2024). This aligns with our previous findings (Santos Júnior et al., 2025b), where soil incubation with BBGFs resulted in a peak of enzymatic activity in the initial days followed by stabilization at sustained levels. This pattern indicates that the organic components of the binders and biochar stimulate microbial biomass turnover, maintaining a dynamic equilibrium that ensures continuous P mineralization, rather than the suppression observed with mineral fertilizers alone.

Regarding the sampling depth, although Mendes et al. (2021) prioritized the 0–10 cm layer, the 0–20 cm depth was adopted in this study as it represents the standard layer widely used for routine soil sampling and analysis, consistent with several investigations (Lopes et al., 2021; Santos Júnior et al., 2025b; Wang et al., 2022; Yan et al., 2022).

The F2 function estimates the size of the soil's nutrient reservoir, a property strictly governed by soil texture and the quantity and quality of organic matter. In this framework, F2 was assessed using SOC and CEC as key indicators. Consequently, the superior F2 scores observed in the BBGFs-PE and mainly BBGFs-BO treatments, compared to the BBGFs-CW treatments, are attributed to the higher carbon content and recalcitrance inherent to the binder structure. This carbon input played a decisive role in driving the

index, particularly given that no significant differences were observed for CEC among the treatments (Table S2).

In this context, the soils treated with BBGFs-BO at 125% and 150% doses exhibited the highest SOC among the BBGFs treatments, reaching 8.10 and 8.30 g kg⁻¹, respectively. Although these values represent a substantial increase compared to the original soil and the SP treatment (Table S1 and S2), they fall within the low interpretation class (4.1–11.6 g kg⁻¹) (Ribeiro et al., 1999). This behavior is characteristic of sandy soils, where organic carbon is highly prone to losses via runoff and leaching, attributed to the high susceptibility to erosion and low CEC (Cancellier et al., 2025).

No significant differences were observed for the soil function F3 among the evaluated BBGFs treatments, with all formulations exhibiting average scores of approximately 0.89. According to the interpretative framework proposed by Mendes et al. (2021), these values classify the soil functionality as adequate (> 0.70). Since F3 integrates indicators of nutrient availability (P, Ca, Mg, K) and soil acidity (pH, Al³⁺, and H+Al), these results confirm the dual role of the BBGFs. Besides effectively solubilizing and supplying nutrients, the formulations acted as soil correctives, neutralizing acidity and optimizing the chemical environment for plant development, regardless of the binder used.

Regarding the SQI_{FERTBIO}, the BBGFs treatments exhibited a positive linear response to binder application doses. This linear trend is driven by the cumulative input of organic carbon and nutrients inherent to the increased binder doses. The low-molecular-weight organic acids present in the binders facilitate nutrient release through solubilization processes (Cheng et al., 2022; Suo et al., 2025). Furthermore, these organic inputs likely intensified the complexity and connectivity of the soil microbial networks (Hou et al., 2024; Suo et al., 2025; Yuan et al., 2022). Notably, the BBGFs-BO at 150% dose presented the highest index compared to the other BBGFs treatments, a performance attributed to its distinct physicochemical characteristics, as previously discussed.

All BBGF formulations, regardless of binder dose, were classified within the moderate range (0.46–0.65) (Mendes et al., 2021). This classification reveals a critical functional dynamic: the coexistence of high enzymatic activity (F1) and adequate chemical fertility (F3) in a soil with intrinsically low nutrient reservoir capacity, attributed to its sandy texture and low SOC content. This pattern indicates that the organomineral management is actively enhancing soil health, overcoming the natural limitations of the soil matrix (Mendes et al., 2019; Mendes et al., 2021; Santos Júnior et al., 2025b).

Furthermore, the application of the SQI_{FERTBIO} framework to a sandy-loam soil imposes a rigorous threshold. This occurs because, compared to the clayey Oxisols used for the index calibration, coarse-textured soils provide less physical protection for enzymes and organic matter, while also presenting intrinsic chemical limitations. However, these results suggest a progressive restoration of soil functionality. The obtained SQI scores indicate that, over a longer timeframe, the adopted organomineral management may enhance SOC, soil aggregation, and nutrient cycling efficiency.

Microbial indicators represent the active soil fraction and are significantly more sensitive to early changes in soil quality than chemical or physical attributes (Barbosa et al., 2023; Mendes et al., 2019). Given the limitations of routine chemical analyses in capturing the full benefits of sustainable management practices (Mendes et al., 2021), there is an increasing demand from farmers and agricultural professionals for biological metrics to complement standard fertility diagnoses.

In commercial agriculture, soil management decisions are frequently driven by operational and economic constraints, often at the expense of agronomic parameters. In this context, the $SQL_{FERTBIO}$ index serves as a valuable tool to guide decision-making regarding management practices. By demonstrating that productivity can be aligned with biological enhancement, the index reinforces the importance of maintaining healthy soils to sustain high-yielding crops over time, moving beyond a purely productivist approach (Mendes et al., 2019; Mendes et al., 2021).

Plant growth and agronomic efficiency of fertilizers

The biomass plant production over the five cropping cycles revealed distinct release patterns between the soluble source and the BBGFs. In the first cropping cycle, the SP treatment and the biochar powdered treatments (B and B+NP) outperformed the BBGFs, regardless of the binder used. This initial superiority of SP is expected and attributed to the immediate availability of phosphate ions in the soil solution, readily meeting the initial demand of the plants.

Moreover, the B+NP treatment showed SDM yield comparable to the SP treatment in the first cropping cycle, a performance attributed to the physical form of the amendment. Unlike the granular formulations, the powdered biochar presents a high specific surface area, which maximizes soil-particle contact (Santos Júnior et al., 2024). Upon application, the influx of water into the biochar pores rapidly dissolves soluble mineral compounds and labile organic fractions present on the outer and inner surfaces (Joseph et al., 2021). This process increases the concentration of cations, anions, and dissolved organic carbon in the soil solution, providing an immediate nutrient flush that supports early plant growth (Santos Júnior et al., 2025b; Song et al., 2024), often exhibiting release dynamics similar to soluble fertilizers (Lustosa Filho et al., 2019).

Another contributing factor is the biological response induced by the fine-textured biochar. The incorporation of powdered biochar stimulates microbial activity by increasing porosity and aeration (Khan et al., 2023; Vega et al., 2025; Wang et al., 2022). However, this increased activity is likely driven by a negative priming effect, where the microbial community preferentially targets the labile carbon components of the biochar rather than native soil organic matter (Guo et al., 2024; Idbella et al., 2024; Santos Júnior et al., 2025b). This preferential utilization of readily available carbon accelerates the mineralization of biochar-associated nutrients, ensuring their immediate availability for plant uptake during the initial growth stages (Ahmed et al., 2024).

In the second cropping cycle, the SP treatment still promoted higher SDM yields compared to granular formulations, a response driven by the immediate availability of soluble P forms in the soil solution. The lower performance of BBGFs is related to the slow solubilization kinetics of the NP entrapped within the granule matrix (Pogorzelski et al., 2020; Santos Júnior et al., 2025a). Conversely, the BBGFs-PE and BBGFs-BO treatments resulted in biomass yields equivalent to those obtained with B and B+NP treatments. This performance is attributed to the chemical nature of these binders, specifically their low pH and high load of organic acids (Cheng et al., 2022; Ouattara et al., 2024; Yuan et al., 2022). These compounds induce localized acidification within the granule microsite, accelerating NP dissolution and ensuring a sustained release of nutrients over time.

From the third cropping cycle onwards, BBGFs generally promoted SDM yields equal to or higher than the SP treatment, confirming their residual efficiency. The exception was the BBGFs-BO treatment, which exhibited lower SDM production in the final cycle compared to the soluble source.

The peak SDM yield observed for BBGFs-BO in the third cropping cycle suggests that, at optimal doses, the binder provided a synchronized release of nutrients and labile organic compounds, supporting plant growth (Idbella et al., 2024; Joseph et al., 2021). However, the recurring quadratic behavior with a negative coefficient observed in the second, third, and fifth cycles indicates a dose-dependent limitation. Specifically, higher doses of the BO binder likely induced excessive granule hydrophobicity (Santos Júnior et al., 2025a).

Unlike the hydrophilic PE binder, the BO is composed of aromatic hydrocarbons (pyrolytic tar) (Cheng et al., 2022; Vilas-Boas et al., 2025). Consequently, increasing the binder dose thickens the hydrophobic coating around the fertilizer matrix. This dense coating network acts as an excessive physical barrier, impeding soil water infiltration into the granule pores (Cancellier et al., 2025; Hidayat and Samitsu, 2026; Salimi et al., 2023). Since diffusion is the primary mechanism for P transport (Marschner and Rengel, 2023), this hydraulic restriction prevented the dissolution of the inner NP particles, reducing nutrient release and compromising biomass production at the highest binder doses.

Conversely, the BBGFs-PE exhibited a predominantly linear positive response to binder doses across most cropping cycles. According to Lustosa Filho et al. (2020), such linear crop response indicates that the slow-release P profile was insufficient to saturate plant P uptake in the short term, resulting in a steady physiological response to binder application.

This performance is governed by the specific chemical interplay between the binder and the phosphate source. The PE binder is rich in oxygen-containing functional groups that promote phosphate retention through cation bridges and hydrogen bonding (Ahmed et al., 2024; Cheng et al., 2022; Jin et al., 2023; Santos Júnior et al., 2025b). In contrast to the specific adsorption on soil oxides, these interactions are energetically weaker (reversible adsorption), creating a labile P pool that is readily desorbed and taken up by plants. Furthermore, physical properties played a decisive role. As characterized in our previous study (Santos Júnior et al., 2025a), granules formulated with PE binder possess significantly lower crushing strength compared to those with BO binder, favoring the diffusive transport of nutrients from the inner matrix to the rhizosphere.

The distinct temporal pattern of BBGFs-CW, characterized by low initial SDM yields followed by a significant recovery relative to BBGFs-PE and BBGFs-BO, suggests that nutrient availability was governed by concurrent biological and chemical mechanisms. Biologically, the CW binder contains high concentrations of labile organic compounds (Cai et al., 2023; Chen et al., 2025; Salimi et al., 2023). Upon application to the nutrient-poor Oxisol, this carbon input likely stimulated rapid microbial proliferation, leading to the temporary immobilization of available nutrients in the microbial biomass, thereby restricting plant uptake in the first two cycles (Song et al., 2024; Suo et al., 2025; Yan et al., 2022).

Chemically, the solubilization dynamics were constrained by the binder's pH. As demonstrated in our previous study (Santos Júnior et al., 2025a), the high acidity of PE and BO binders overcame the biochar alkalinity, creating an acidic microsite favorable for NP solubilization. In contrast, the BBGFs-CW exhibits a higher pH due to the formation of $\text{Ca}(\text{OH})_2$ complexes, which maintained the granule alkalinity (Cai et al., 2023; Cheng et al., 2022; Santos Júnior et al., 2025a). This alkaline environment limits the acid dissolution

of apatite minerals in the short term. However, as the labile carbon was depleted and the microbial community underwent turnover (Suo et al., 2025; Yuan et al., 2022), the immobilized nutrients were released back into the soil solution, driving the significant increase in SDM observed for BBGFs-CW in the final stages of the experiment.

A sharp decrease in SDM production was observed for the SP treatment in the fourth cropping cycle. This reduction is attributed to the cumulative P extraction from successive cultivations, which depleted the readily available pool (Carneiro et al., 2021; Santos Júnior et al., 2024). Furthermore, the long-term contact of SP with the soil enhances specific adsorption reactions (aging), progressively converting labile P into non-labile forms attached to Fe and Al oxides (Lustosa Filho et al., 2020).

However, the subsequent SDM yield recovery in the fifth cycle probably occurred due to the plant's adaptive physiological response to P deprivation. Facing the severe depletion observed in the preceding cycle, the root system likely enhanced the secretion of acid phosphatases and organic carboxylates (Neumann and Ludewig, 2023; Rocabrana et al., 2024). These exudates facilitate the mobilization of P from moderately labile inorganic pools or organic fractions, allowing the plant to sustain growth despite the low concentration of soluble P in the soil solution (Tantriani et al., 2025).

Moreover, during the initial period of high P availability, excess inorganic phosphate was likely stored in vacuoles. When external P became limiting, these vacuolar reserves were remobilized to the cytosol and translocated from roots and stubble to support shoot regrowth, a critical homeostatic strategy to mitigate P starvation (Hawkesford et al., 2023).

The high RAE values observed for BBGFs-PE demonstrate the feasibility of substituting exclusive soluble sources with biochar-based formulations in sandy loam soils. Notably, the BBGFs-PE applied at 125% (96.8%) and 150% (101.3%) doses did not differ from the SP treatment. These findings align with Borges et al. (2020) and Pogorzelski et al. (2020), who reported that organomineral fertilizers can match the agronomic efficiency of soluble phosphates in soils with low-to-medium P-fixing capacity. In these formulations, the biochar matrix acts as a physical conditioner and reservoir of exchangeable cations, while the hydrophilic nature of the binder facilitates the progressive solubilization of the entrapped NP, ensuring a P supply synchronized with crop demand.

The linear increase in RAE for BBGFs-PE and BBGFs-CW indicates that the P release mechanism was governed by a steady-supply profile rather than saturation. This linear response suggests that the fertilizer provided nutrients at a rate that met the plant's cumulative uptake without exceeding the soil's adsorption capacity or the plant's physiological sink (Lustosa Filho et al., 2019). This behavior contrasts with the rapid initial release of soluble sources, which often leads to higher fixation losses or luxury consumption in the early stages, reducing overall efficiency in the long term (Cancellier et al., 2025; Carneiro et al., 2021; Hajari et al., 2015; Lustosa Filho et al., 2019). Conversely, the quadratic response of BBGFs-BO highlights a physical limitation imposed by the binder's nature, as previously discussed. At doses above 120%, the dense coating likely imposed a diffusion restriction, limiting P release kinetics below the crop's potential demand.

The distinct biomass allocation patterns observed reflect physiological adjustments to P availability and the specific interactions between the carbonaceous matrix and the binder properties. The SP treatment exhibited the highest SBDM but the lowest root-to-shoot ratio (0.21). This allocation strategy aligns with the resource optimization hypothesis, where plants under high nutrient availability prioritize photosynthate

partitioning towards aboveground biomass, limiting root system expansion (Hawkesford et al., 2023). Unlike P-efficient phenotypes that maximize root length to explore larger soil volumes under nutrient restriction (Tantriani et al., 2025), the plants in the SP treatment operated under luxury consumption in the early cycles, resulting in a less developed root system that likely compromised P acquisition when the labile pool was depleted.

Conversely, treatments containing powdered biochar (B and B+NP) yielded the highest RDM, surpassing the SP treatment by over 55%. This vigorous root proliferation suggests a stimulation mechanism beyond simple nutrient supply. As observed in this study, the high ash content (Table 1) and surface charges of the biochar neutralized soil acidity and reduced Al toxicity (Santos Júnior et al., 2025b), creating a more favorable chemical environment for root elongation (Joseph et al., 2021; Santos Júnior et al., 2025a). Biochars produced at high temperatures (> 400 °C) possess a capacity for electron transfer in the rhizosphere, which can increase root membrane potential and stimulate branching (Ahmed et al., 2024).

The BBGFs-PE, particularly at the 150% dose, integrated these benefits, promoting significantly higher RDM than the SP treatment (+23.8%) while achieving superior stubble production compared to the NP treatment. This performance indicates that the hydrophilic nature of the PE binder facilitated the release of bioactive organic compounds that stimulate root development, as previously observed in bean crops (Santos Júnior et al., 2025a). The synergy between the chemical conditioning of the biochar and the bio-stimulation of the binder resulted in a balanced allocation between shoot and root biomass.

In contrast, the lower root-to-shoot ratios observed for BBGFs-BO (0.25–0.26) suggest limitations imposed by the binder's properties. The compact structure of these granules likely created a diffusion barrier that restricted water influx and the dissolution of mineral elements (Cheng et al., 2022; Hidayat and Samitsu, 2026; Pogorzelski et al., 2020). Additionally, the high concentration of polyaromatic compounds in the BO binder may have exerted a residual phytotoxic effect. Although the biochar matrix can mitigate toxicity through physical encapsulation or chemical adsorption (Santos Júnior et al., 2025b), this mechanism was seemingly insufficient to fully counteract the inhibitory effects on root proliferation at high binder doses.

The cumulative analysis of TPB consolidates the agronomic potential of the tested formulations. Despite the initial superiority of the soluble source, the BBGFs-PE and the physical mixture (B+NP) demonstrated a systemic recovery, achieving TPB yields equivalent to the SP treatment. This equalization confirms that the granular matrix formulated with the hydrophilic binder maintained structural integrity while permitting efficient nutrient diffusion throughout the five cycles (Chen et al., 2025). Unlike the soluble source, which is prone to rapid exhaustion or fixation (Lustosa Filho et al., 2020), the BBGFs-PE functioned as a steady-state nutrient delivery system. The positive linear response to binder doses further suggests that the PE binder enhanced the granule's physicochemical stability without occluding the porosity essential for root interception and P uptake (Han et al., 2025).

In contrast, the distinct dose-response behaviors of BBGFs-CW and BBGFs-BO highlight specific limiting factors. The BBGFs-BO showed no significant response to binder doses, confirming that the BO binder created a recalcitrant coating that effectively locked a portion of the P regardless of the applied dose, preventing the compensatory growth observed in other treatments. Meanwhile, the quadratic behavior of BBGFs-CW, with a recovery only at the highest dose (150%), aligns with the interactions described by Cai et al. (2023). At lower doses, the calcium-rich binder likely promoted the formation of stable calcium-phosphate precipitates and dense calcium-starch cross-linked networks that temporarily delayed

solubilization. However, at the 150% dose, the cumulative acidity and the higher input of labile carbon introduced by the binder likely stimulated a microbial priming effect sufficient to destabilize these structures, supporting late-stage biomass accumulation (Guo et al., 2024).

*Phosphorus dynamics: Uptake and Use Efficiency by *Paiguás* grass*

In the first cropping cycle, the SP treatment promoted a P uptake approximately 7-fold higher than the BBGFs treatments. This disproportionate uptake, unaccompanied by a proportional biomass increase, characterizes a concentration effect typical of high-solubility sources. This confirms that the immediate availability of phosphate ions saturated the soil solution (Carneiro et al., 2021; Hou et al., 2024), exceeding the plant's metabolic sink capacity. However, the sharp decline in P uptake for SP treatment from the third cycle onwards reflects the rapid depletion of the labile P pool and the progressive fixation of remaining P onto soil oxides (Borges et al., 2020; Lustosa Filho et al., 2020).

In contrast, the BBGFs-PE exhibited a continuous supply profile. While initial uptake was lower, the formulation demonstrated superior residual efficiency, fitting a positive linear model across cycles. This cumulative performance resulted in a total P uptake of 70.01 mg per pot at the 150% dose, significantly outperforming the SP treatment (65.76 mg per pot) by approximately 6.5%. This inversion indicates a high degree of synchronization between nutrient release and crop demand (Lu et al., 2023; Pogorzelski et al., 2020). This synchronization is quantitatively confirmed by the Phosphorus Uptake Efficiency (PUpE), where BBGFs-PE at 150% binder dose achieved 23.34%, significantly surpassing the SP treatment (21.92%). As evidenced by the high P accumulation in roots for BBGFs-PE at 150% binder dose (19.82 mg per pot) compared to SP treatment (15.58 mg per pot) (Table S4), this efficiency is directly linked to the extensive root system intercepting P slowly diffusing from the hydrophilic granules (Cheng et al., 2022; Cheng et al., 2024; Xu et al., 2025). Furthermore, the organic acids in the PE binder likely enhanced the mobilization of P fractions associated with the biochar matrix (Ahmed et al., 2024; Suo et al., 2025).

Moreover, this performance is attributed to a synergistic physiological effect. The presence of Mg in the biochar is critical because the active uptake of P by roots relies on plasma membrane H^+ -ATPases. The specific substrate for these pumps is the Mg-ATP complex (Hawkesford et al., 2023). Consequently, the supplemental Mg provided by the biochar ensures that a higher proportion of cytoplasmic ATP is complexed, optimizing the generation of the proton electrochemical gradient required to drive phosphate cotransport against the concentration gradient.

Crucially, the agronomic efficiency of BBGFs-PE is also driven by the amelioration of the chemical rhizosphere environment. The alkalinity of the biochar and the presence of polar surface sites played a decisive role in reducing Al toxicity and hydrogen ion concentration (Joseph et al., 2021). This alleviation likely occurs through cation exchange, precipitation of Al as $Al(OH)_3$ due to pH increase, and complexation of Al by oxygen-containing functional groups (Santos Júnior et al., 2024; Vega et al., 2025). By maintaining soil pH near the optimal range (approx. 6.5) (Joseph et al., 2021; Vega et al., 2025), the biochar matrix prevented the fixation of P by Al and Fe oxides, preserving P availability for uptake.

Regarding Phosphorus Utilization Efficiency (PUtE), the lower values observed for BBGFs-PE compared to the nutrient-restricted treatments (BBGFs-CW and BBGFs-BO treatments) align with the inverse relationship described by Hajari et al. (2015). The high P availability in the BBGFs-PE treatment (confirmed by the high PUpE) likely led to higher tissue P concentrations without a proportional biomass

increase (Law of Diminishing Returns). Conversely, the high PUE observed for BBGFs-CW and BBGFs-BO treatments reflects a physiological response where plants maximize internal conversion efficiency under restricted nutrient supply conditions (Tantriani et al., 2025).

The integration of these components resulted in a high Phosphorus Use Efficiency (PUE) for BBGFs-PE at 150% binder dose statistically equivalent to the soluble source and B+NP controls. This linear response validates that the optimized biochar-binder matrix converted a low-solubility source (NP) into an agronomically efficient fertilizer comparable to soluble sources.

For the BBGFs-BO, total P uptake followed a quadratic trend with a negative coefficient, confirming a yield gap driven by transport limitations. As observed by Cancellier et al. (2025), excessive barrier properties can restrict diffusion rates below daily requirements during peak growth. Meanwhile, the distinct lag phase and upward trend of BBGFs-CW indicate a biological banking mechanism, where the formation of stable starch-calcium complexes delayed solubilization (Cai et al., 2023), ensuring a residual effect in the final cycles.

Calcium, Magnesium and Potassium uptake

The total uptake of Ca, Mg, and K generally followed the biomass accumulation patterns. Although basal liming was uniformly applied to raise V% to 70%, the BBGFs-PE treatments (125% and 150% doses) promoted total cation accumulations equivalent to or higher than the SP treatment. This indicates that the BBGFs formulations provided nutritional benefits extending beyond soil acidity correction.

Regarding total Ca uptake, high doses of BBGFs-PE (125% and 150%) promoted values equivalent to the SP treatment (approx. 172 mg per pot). While the SP treatment relied on the initial dissolution of carbonates from liming, the BBGFs functioned as a supplemental reservoir. The eucalyptus wood biochar contains a high ash content (50.66%) and an exceptionally high Ca concentration (50.66 g kg⁻¹) (Table 1). The biochar ash is rich in bases, particularly calcium carbonate, which acts similarly to soil acidity correctors but with a gradual release profile (Joseph et al., 2021; Santos Júnior et al., 2024). More importantly, the BBGFs altered the nutrient allocation strategy. As evidenced in Table S5, the Ca accumulation in roots for the BBGFs-PE 150% treatment (48.46 mg per pot) and B control (63.75 mg per pot) was significantly higher than in the SP treatment (37.82 mg per pot). This confirms that the organomineral matrix improved the rhizosphere environment, enhancing root interception capacity. Since Ca²⁺ moves primarily by mass flow and has low mobility in the phloem (Marschner and Rengel, 2023), this superior root acquisition was decisive for the total uptake observed in the final cycles.

A similar trend was observed for Mg. The BBGFs-PE treatment at the 150% dose (114.38 mg per pot) significantly outperformed the soluble P source (105.28 mg per pot). Since the SP treatment relied solely on the initial soil/lime Mg supply, this superior accumulation is directly linked to the supplemental Mg provided by the biochar (4.26 g kg⁻¹) (Table 1). The linear response of BBGFs-PE (Fig. 15b and Table S6) confirms a synchronized delivery system. Physiologically, this concurrent supply is critical, as Mg is an essential cofactor for the Mg-ATP complex required for H⁺-ATPase activity (Hawkesford et al., 2023). Conversely, the lack of response for BBGFs-BO suggests that the hydrophobic barrier restricted the release of matrix-associated Mg.

For total K uptake, a distinct mechanism governed by retention rather than direct supply was observed. Despite the low K content of the biochar (1.08 g kg⁻¹) (Table 1) compared to the K-rich source in

the SP treatment (KH_2PO_4), the BBGFs-PE at 125% and 150% doses achieved accumulation levels equal to the SP treatment. Notably, in the fourth cycle, K uptake for BBGFs-PE at 100% was nearly double that of the SP treatment (Table S7). This efficiency is attributed to the physicochemical interaction between the biochar-binder matrix and the K supplied via top-dressing. In sandy-loam soils with low CEC, K is highly mobile and prone to losses (Marschner and Rengel, 2023). The PE binder, rich in oxygen-containing functional groups (Ouattara et al., 2024; Yuan et al., 2022) and likely contributed humic substances to the matrix composition. These substances act as chelating agents, forming stable complex molecules with metal ions (Fachini et al., 2022). This sponge effect allowed the granules to temporarily adsorb K^+ ions supplied via fertigation.

This is corroborated by the root data (Table S7), where the B control and BBGFs-PE at 150% binder dose accumulated significantly more K in the roots (286.21 and 227.42 mg per pot, respectively) compared to the SP treatment (202.92 mg per pot), indicating a retention mechanism in the rhizosphere zone. The quadratic model with a negative coefficient for BBGFs-PE (Fig. 16b) indicates that this retention capacity reached an optimum at an estimated binder dose of approximately 134%, beyond which the physical sealing of pores might hinder ionic exchange.

Regarding the dose-response, the regression analysis for total K uptake revealed a quadratic model with a negative coefficient (Fig. 16b). This trend implies an efficiency threshold at an estimated binder dose of approximately 134%. Beyond this level, the high density of oxygen-containing functional groups introduced by the excess binder likely increased the electrostatic adsorption energy (Ouattara et al., 2024; Yuan et al., 2022). Consequently, this strong chemical retention may have restricted the desorption rate of K^+ into the soil solution, limiting its immediate availability for plant uptake.

CONCLUSIONS

The agronomic efficiency of BBGFs in tropical Oxisols is governed by the physicochemical properties of the binder used in the granulation process. The superior performance of formulations containing PE binder, compared to CW and BO binders, is attributed to the hydrophilic nature and acidity of this binder, which facilitate the progressive solubilization of phosphate within the biochar matrix, reducing direct contact with soil sorption sites. Unlike soluble sources that suffer from rapid fixation and depletion, these hydrophilic granules function as a steady-state delivery system, ensuring synchronized P supply and superior accumulation of Ca, Mg, and K in plant tissue.

Conversely, the use of hydrophobic binders like BO creates a trade-off between carbon sequestration and nutrient availability, where the formation of a recalcitrant coating restricts P diffusion despite maximizing the proposed SQL and carbon storage. Therefore, among the formulations tested, BBGFs-PE at 125 and 150% binder doses is recommended as the most effective alternative for combining agronomic efficiency with soil quality improvement in sandy-loam tropical Oxisols. Further research under field conditions is required to validate the long-term dynamics of these P fractions and their economic viability at farm scale.

REFERENCES

- American Society for Testing and Materials (ASTM). 2021. Standard test method for chemical analysis of wood charcoal. D1762-84. West Conshohocken, PA, USA.
- American Society for Testing and Materials (ASTM). 2020. Standard test method for determination of total solids in biomass. E1756-08. West Conshohocken, PA, USA.
- Ahmed N, Tu P, Deng L, Chachar S, Chachar Z, Deng L. 2024. Optimizing the dual role of biochar for phosphorus availability and arsenic immobilization in soils. *Sci Total Environ.* **957**: 177810.
- Barbosa J Z, Poggere G, Corrêa R S, Hungria M, Mendes I C. 2023. Soil enzymatic activity in Brazilian biomes under native vegetation and contrasting cropping and management. *Appl Soil Ecol.* **190**: 105014.
- Biliás F, Kalderis D, Richardson C, Barbayiannis N, Gasparatos D. 2023. Biochar application as a soil potassium management strategy: A review. *Sci Total Environ.* **858**: 159782.
- Borges B M M N, Strauss M, Camelo P A, Sohi S P, Franco H C J. 2020. Re-use of sugarcane residue as a novel biochar fertiliser - Increased phosphorus use efficiency and plant yield. *J Clean Prod.* **262**: 121406.
- Cai Q, Li X, Ding X, Wang H, Hu X. 2023. Effects of quercetin and Ca(OH)_2 addition on gelatinization and retrogradation properties of Tartary buckwheat starch. *LWT-Food Sci Technol.* **178**: 114488.
- Cancellier E L, Degryse F, da Silva R C, Baird R, Guelfi D, McLaughlin M J. 2025. Bio-based polyurethane coatings for controlled-release phosphorus fertilizers: Synthesis, characterization and effect on P use efficiency. *Sci Total Environ.* **1000**: 180403.
- Carneiro J S S, Ribeiro I C A, Nardis B O, Barbosa C F, Lustosa Filho J F, Melo L C A. 2021. Long-term effect of biochar-based fertilizers application in tropical soil: Agronomic efficiency and phosphorus availability. *Sci Total Environ.* **760**: 143955.
- Chen M, Han J, Shi P, Wang J, Wang Y, Tian F, Wu Z. 2025. Preparation of biochar slow-release phosphate fertilizer granules with starch-CMC-Na binder: improving granule mechanical and slow-release properties. *J Environ Chem Eng.* **13**: 119547.
- Cheng J, Liao Z, Hu S C, Geng Z C, Zhu M Q, Xu W Z. 2022. Synthesis of an environmentally friendly binding material using pyrolysis byproducts and modified starch binder for slow-release fertilizers. *Sci Total Environ.* **819**: 153146.
- Cheng Y, Wu M, Lu J, Zhang Y, Lu R, Li Y, Cai Y, Xiang H, Zhuang Z, Qiu Z, Yu B. 2024. Optimizing fabrication of coated fertilizers integrated with biochar for enhanced slow-release properties: Mechanisms and cost-effectiveness analysis. *Ind Crops Prod.* **222**: 120077.
- Edeh I G, Masek O, Füsseis F. 2023. 4D structural changes and pore network model of biomass during pyrolysis. *Sci Rep.* **13**: 22863.
- Enders A, Lehmann J. 2012. Comparison of wet-digestion and dry-ashing methods for total elemental analysis of biochar. *Commun Soil Sci Plant Anal.* **43**: 1042–1052.
- Fachini J, Figueiredo C C, Vale A T. 2022. Assessing potassium release in natural silica sand from novel K-enriched sewage sludge biochar fertilizers. *J Environ Manage.* **314**: 115080.
- Fang L, Li J, Donatello S, Cheeseman C R, Poon C S, Tsang D C W. 2020. Use of Mg/Ca modified biochars to take up phosphorus from acidextract of incinerated sewage sludge ash (ISSA) for fertilizer application. *J Clean Prod.* **244**: 118853.
- Freitas I F, Novais R F, Villani E M A, Novais S V. 2013. Phosphorus extracted by ion exchange resins and Mehlich-1 from Oxisols (Latosols) treated with different phosphorus rates and sources for varied soil-source contact periods. *Rev Bras Cienc Solo.* **37**: 667–677.

- Guo F, Wang C, Wang S, Zhao X, Li G, Sun Z. 2024. The native SOC increase in woodland and lawn soil amended with biochar surpassed greenhouse — A seven-year field trial. *Sci Total Environ.* **907**: 167924.
- Haider F U, Coulter J A, Cai L, Hussain S, Cheema S A, Wu J, Zhang R. 2022. An overview on biochar production, its implications, and mechanisms of biochar-induced amelioration of soil and plant characteristics. *Pedosphere.* **32**: 107-130.
- Hajari E, Snyman S J, Watt M P. 2015. Nitrogen use efficiency of sugarcane (*Saccharum* spp.) varieties under in vitro conditions with varied N supply. *Plant Cell Tiss Org Cult.* **122**: 21–29.
- Han J, Lee S, Hyun S, Kim M. 2025. Phosphate sorption mechanisms in biochar: Insights from depth profiling of porous structure across pH and pyrolysis conditions. *Bioresour Technol.* **418**: 131953.
- Hawkesford M J, Cakmak I, Coskun D, De Kok L J, Lambers H, Schjoerring J K, White P J. 2023. Functions of macronutrients. In: Rengel Z et al. (eds). *Marschner's Mineral Nutrition of Higher Plants*. 4th ed. Academic Press, London. pp. 201–281.
- Hidayat E, Samitsu S. 2026. Glucose-derived carbon coating on biochar from empty fruit bunches as slow-release P fertilizer. *Bioresour Technol.* **443**: 133859.
- Hou J, Yi G, Hao Y, Li L, Shen L, Zhang Q. 2024. The effect of combined application of biochar and phosphate fertilizers on phosphorus transformation in saline-alkali soil and its microbiological mechanism. *Sci Total Environ.* **951**: 175610.
- Idbella M, Baronti S, Giagnoni L, Renella G, Becagli M, Cardelli R, Maienza A, Vaccari F P, Bonanomi G. 2024. Long-term effects of biochar on soil chemistry, biochemistry, and microbiota: results from a 10-year field vineyard experiment. *Appl Soil Ecol.* **195**: 105217.
- Janes-Bassett V, Blackwell M S A, Blair G, Davies J, Haygarth P M, Mezeli M M, Stewart G. 2022. A meta-analysis of phosphatase activity in agricultural settings in response to phosphorus deficiency. *Soil Biol Biochem.* **165**: 108537.
- Jin J, Khan S, Eltohamy K M, He S, Liu C, Li F, Liang X. 2023. Biochar–coupled organic fertilizer reduced soil water-dispersible colloidal phosphorus contents in agricultural fields. *Chemosphere.* **333**: 138963.
- Joseph S, Cowie A L, Van Zwieten L, Bolan N, Budai A, Buss W, Cayuela M L, Graber E R, Ippolito J A, Kuzyakov Y, Luo Y, Ok Y S, Palansooriya K N, Shepherd J, Stephens S, Weng Z, Lehmann J. 2023b1. How biochar works, and when it doesn't: a review of mechanisms controlling soil and plant responses to biochar. *GCB Bioenergy.* **13**: 1731–1764.
- Khan M N, Huang J, Shah A, Hao X, Han T, Núñez-Delgado A, Hayatu N G, Ahmed I, Liu W, Singh A K, Zhu X, Zhang H. 2025. Impact of modified biochar on phosphorus fractionation and biochemical properties for different soils. *Environ Sci Eur.* **37**: 80.
- Khan Z, Yang X J, Fu Y, Joseph S, Khan M N, Khan M A, Alam I, Shen H. 2023. Engineered biochar improves nitrogen use efficiency via stabilizing soil water-stable macroaggregates and enhancing nitrogen transformation. *Biochar.* **5**: 52.
- Klasson K T. 2017. Biochar characterization and a method for estimating biochar quality from proximate analysis results. *Biomass Bioenergy.* **96**: 50–58.
- Lopes A A C, Sousa D M G, Reis Júnior F B, Mendes I C. 2015. Air-drying and long-term storage effects on β -glucosidase, acid phosphatase and arylsulfatase activities in a tropical Savannah Oxisol. *Appl Soil Ecol.* **93**: 68–77.
- Lopes E M G, Reis M M, Frazão L A, Terra L E M, Lopes E F, dos Santos M M, Fernandes L A. 2021. Biochar increases enzyme activity and total microbial quality of soil grown with sugarcane. *Environ Technol Innov.* **21**: 101270.
- Li Q, Zhang J, Ye J, Liu Y, Lin Y, Yi Z, Wang Y. 2024. Biochar affects organic carbon composition and stability in highly acidic tea plantation soil. *J Environ Manage.* **370**: 122803.

- Liu Q, Wu C, Wei L, Wang S, Deng Y, Ling W, Xiang W, Kuzyakov Y, Zhu Z, Ge T. 2024. Microbial mechanisms of organic matter mineralization induced by straw in biochar-amended paddy soil. *Biochar*. **6**: 18.
- Lu J, Li Y, Cai Y, Jiang P, Yu B. 2023. Co-incorporation of hydrotalcite and starch into biochar-based fertilizers for the synthesis of slow-release fertilizers with improved water retention. *Biochar*. **5**: 44.
- Lustosa Filho J F, Barbosa C F, Carneiro J S S, Melo L C A. 2019. Diffusion and phosphorus solubility of biochar-based fertilizer: Visualization, chemical assessment and availability to plants. *Soil Till Res*. **194**: 104298.
- Lustosa Filho J F, Carneiro J S S, Barbosa C F, Lima K P, Leite A A, Melo L C A. 2020. Aging of biochar-based fertilizers in soil: Effects on phosphorus pools and availability to *Urochloa brizantha* grass. *Sci Total Environ*. **709**: 136028.
- Marschner P, Rengel Z. 2023. Nutrient availability in soils. In: Rengel Z et al. (eds.) *Marschner's Mineral Nutrition of Plants*. 4th ed. Academic Press, London. pp. 499–522.
- Malavolta E, Vitti G C, Oliveira S A. 1997. Assessment of plant nutritional status: Principles and applications (in Portuguese). 2nd ed. Potafos, Piracicaba, SP.
- Mendes I C, Sousa D M G, Dantas O D, Lopes A A C, Reis Júnior F B, Oliveira M I, Chaer G M. 2021. Soil quality and grain yield: A win–win combination in clayey tropical oxisols. *Geoderma*. **388**: 114880.
- Mendes I C, Souza L M, Sousa D M G, Lopes A A C, Reis Júnior F B, Lacerda M P C, Malaquias J V. 2019. Critical limits for microbial indicators in tropical Oxisols at post-harvest: The FERTBIO soil sample concept. *Appl Soil Ecol*. **139**: 85–93.
- Moll R H, Kamprath E J, Jackson W A. 1982. Analysis and interpretation of factors which contribute to efficiency of nitrogen utilization. *Agron J*. **74**: 562–564.
- Muraro P C L, Gonzales R G P, Laniella M V, Gularte M C, Oviedo L R, Oliveira J S, Silva W L, Baldez R N L. 2026. Biochar from *Eucalyptus grandis*: Synthesis, green activation, characterization and adsorption of organic contaminants. *J Mol Liq*. **443**: 129174.
- Neumann G, Ludewig U. 2023. Rhizosphere chemistry influencing plant nutrition. In Rengel Z et al. (eds.) *Marschner's Mineral Nutrition of Plants*. 4th ed. Academic Press, London. pp. 545–585.
- Novais R F, Neves J C L, Barros N F. 1991. Experiments in controlled environment. In Oliveira A J et al. (eds.) *Research Methods in Soil Fertility* (in Portuguese). Embrapa-SEA, Brasília, DF. pp. 189–253.
- Novais R F, Smyth T J. 1999. *Phosphorus in Soil and Plant under Tropical Conditions* (in Portuguese). UFV, Viçosa, MG. 399 p.
- Otoni J P, Matoso S C G, Pérez X L O, Silva V B. 2024. Potential for agronomic and environmental use of biochars derived from different organic waste. *J Clean Prod*. **449**: 141826.
- Ouattara H A A, Niamke B F, Ahoke M E M F, N'Guessan J L L, Yao J C, Amusant N, Dumarcay S. 2024. Physicochemical characterization, chemical composition and antioxidant activities of pyroligneous acids from cocktails of wood and agricultural residues from Ivory Coast. *J Anal Appl Pyrol*. **181**: 106629.
- Pogorzelski D, Lustosa Filho J F, Matias P C, Santos W O, Vergütz L, Melo L C A. 2020. Biochar as composite of phosphate fertilizer: Characterization and agronomic effectiveness. *Sci Total Environ*. **743**: 140604.
- Quaggio J A, Mattos Jr D, Van Raij B. 2022. Phosphorus. In Cantarella H et al. (eds.) *Fertilization and Liming Recommendations for the State of São Paulo* (in Portuguese). Instituto Agrônomo, Campinas, SP. pp. 95–105.
- Rajkovich S, Enders A, Hanley K, Hyland C, Zimmerman AR, Lehmann J. 2012. Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil. *Biol Fertil Soils*. **48**: 271–284.

- Ribeiro A C, Guimarães P T, Alvarez V V H. 1999. Recommendations for the use of correctives and fertilizers in Minas Gerais (in Portuguese). CFSEMG, Viçosa, MG.
- Rocabrana P C, Domene X, Preece C, Peñuelas J. 2024. Relationship among soil biophysicochemical properties, agricultural practices and climate factors influencing soil phosphatase activity in agricultural land. *Agriculture*. **14**: 288.
- Sahoo S S, Vijay V K, Chandra R, Kumar H. 2021. Production and characterization of biochar produced from slow pyrolysis of pigeon pea stalk and bamboo. *Clean Eng Technol*. **3**: 100101.
- Salimi M, Channab B E, El Idrissi A, Zahouily M, Motamedi E. 2023. A comprehensive review on starch: structure, modification, and applications in slow/controlled-release fertilizers in agriculture. *Carbohydr Polym*. **322**: 121326.
- Santos S R, Lustosa Filho J F, Vergütz L, Melo L C A. 2019. Biochar association with phosphate fertilizer and its influence on phosphorus use efficiency by maize. *Agric Sci*. **43**: e025718.
- Santos Júnior J M, Colen F, Pegoraro R F, Heinrichs R, Frazão L A, Sampaio R A, Fernandes L A. 2024. Biochar pellets as soil conditioner on the growth of *Urochloa brizantha* BRS Paiaguás. *Rev Ciênc Agron*. **55**: e20238690.
- Santos Júnior J M, Colen F, Frazão L A, Pegoraro R F, Fernandes L A. 2025a. Granulated organomineral fertilizers from by-products of the agricultural and forestry sector. *Sci Agric*. **82**: e20240132.
- Santos Júnior J M, Fernandes L A, Colen F, Frazão L A, Pegoraro R F. 2025b. Biochar-based granular fertilizers with agro-industrial binders enhance enzymatic activity and nutrient cycling in tropical Oxisols. *Agronomy*. **15**: 9.
- Schettini B L S, Jacovine L A G, Torres C M M E, Carneiro A C O, Villanova P H, Rocha S J S S, Rufino M P M X, Silva L B, Castro R V O. 2022. Furnace-kiln system: How does the use of new technologies in charcoal production affect the carbon balance? *Ind. Crop. Prod*. **187**: 115330.
- Smith P. 2012. Soils and climate change. *Curr Opin Environ Sustain*. **4**: 539–544.
- Solanki P, Bhargava A, Chhipa H, Jain N, Panwar J. 2015. Nano-fertilizers and their smart delivery system. In: Rai M et al. (eds.) *Nanotechnologies in Food and Agriculture*. Springer International Publishing, Cham. pp. 81–101.
- Song K, Jiang S, Liu Z, Cai Y, Liu W, Bian R, Zhang X, Zheng J, Li L. 2024. Biochar improves soil organic carbon sequestration potential in the topsoil and subsoil of a paddy field. *Curr Res Environ Sustain*. **8**: 100267.
- Suo F, Fu H, Liu J, Yin Z, Ma S, Dong L, Dong J, You X, Zhang L. 2025. Effect of individual and co-application of biochar and pyroligneous acid on corn seedling growth and microbial community of coastal soil. *Environ Technol Innov*. **40**: 104474.
- Tantriani, Purwanto B H, Cheng W, Tawaraya K. 2025. First-order lateral roots drive the highest rhizosphere acid phosphatase activity in soybean under phosphorus deficiency. *Rhizosphere*. **36**: 101166.
- Teixeira P C, Donagemma G K, Fontana A, Teixeira W G. 2017. *Manual of Soil Analysis Methods* (in Portuguese). 3rd ed. Embrapa Solos, Rio de Janeiro.
- Teng X, Huang D, Zhi Y, Li Y, Dong D, Wu X, Wang Y, Jiang Z, Huang H, Tang Y, Liu D, Xu W. 2025. Effects of biochar on soil properties as well as available and TCLP-extractable Cu contents: a global meta-analysis. *Sci Rep*. **15**: 32853.
- Van Raij B, Quaggio J A, Silva N M. 1986. Extraction of phosphorus, potassium, calcium and magnesium from soils by an ion-exchange resin procedure. *Commun Soil Sci Plant Anal*. **17**: 547–566.
- Van Raij B. 2019. *Soil Fertility and Nutrient Management* (in Portuguese). 2nd ed. NPCT, Piracicaba, SP.

- Vega C F P, Mota M F C, Lopes E M G, Santos Júnior J M, Colen F, Frazão L A, Pegoraro R F, Parra-Serrano L J, Napoli A, Fernandes L A. 2025. Biochar from eucalyptus waste improves the chemical and biological properties of an Inceptisol and sugarcane yield over time under tropical conditions. *Pedosphere*. doi: 10.1016/j.pedsph.2025.08.002.
- Vilas-Boas A C M, Tarelho L A C, Marques C C, Moura J M O, Santos M C, Paradela F, Nunes M I, Silvestre A J D. 2025. Improving bio-oil fractions through fractional condensation of pyrolysis vapors from *Eucalyptus globulus* biomass residues in a prototype auger reactor. *J Anal Appl Pyrol*. **192**: 107329.
- Wang C, Chen W, Yang L, Wei R, Ni J, Yang Y. 2019. Insights into the roles of the morphological carbon structure and ash in the sorption of aromatic compounds to wood-derived biochars. *Sci. Total Environ*. **693**: 133455.
- Wang Q, Yuan J, Yang X, Han X, Lan Y, Cao D, Sun Q, Cui X, Meng J, Chen W. 2022. Responses of soil respiration and C sequestration efficiency to biochar amendment in maize field of Northeast China. *Soil Tillage Res*. **223**: 105442.
- Wang Y, Uemoto M, Ueki Y, Yoshiie R, Naruse I. 2025a. Effects of inherent ash particles on the powdered biochar structure evolution in H₂O and CO₂ gasification. *J Energy Inst*. **119**: 101941.
- Wang N, Wang J, Liu P, Yin R, Han Q, Yu W, Tuo Y, Wang S. 2025b. Optimizing biochar-based slow-release fertilizers (BSRFs): Comprehensive impacts of binder types, pyrolysis temperatures, and nutrient formulations on mechanical strength and nutrient release dynamics. *Ind Crops Prod*. **232**: 121277.
- Wymore A W. 1993. Model-Based Systems Engineering: An Introduction to the Mathematical Theory of Discrete Systems and to the Tricategory Theory of Systems Design. CRC Press, Boca Raton, FL.
- Yan B, Duan M, Wang R, Li J, Wei F, Chen J, Wang J, Wu Y, Wang G. 2022. Planted forests intensified soil microbial metabolic nitrogen and phosphorus limitation on the Loess Plateau, China. *Catena*. **211**: 105982.
- Yang H, Zhang S, Hu J, Huang J, Ao Z, Wang X, Li Z, Liao X. 2024. Effects of biochar produced from distiller grains on agronomic performances of sorghum (*Sorghum bicolor* L.) and greenhouse gas emissions from soil. *Pedosphere*. **34**: 951-959.
- Yuan Y, Kong Q, Zheng Y, Zheng H, Liu Y, Cheng Y, Zhang X, Li Z, You X, Li Y. 2022. Co-application of biochar and pyroligneous acid improved peanut production and nutritional quality in a coastal soil. *Environ Technol Innov*. **28**: 102886.
- Xu T, Du M, Yan Y, Singh S. 2025. Wood-derived biochar for sustainable water remediation: insights into modification techniques, adsorption performance, techno-economic aspects, and future outlook. *J Mol Struct*. **1346**: 143141.

APÊNDICE B

Supplementary Material

Unlocking residual phosphorus in tropical soils: The role of agro-industrial binders in biochar-based granular fertilizers efficiency and soil health

TABLE S1

Chemical and textural properties^a of soil used in plant study.

pH (H ₂ O)	5.40
K (mg kg ⁻¹)	12.60
P (mg kg ⁻¹)	1.50
Ca ²⁺ (cmol _c kg ⁻¹)	0.31
Mg ²⁺ (cmol _c kg ⁻¹)	0.14
Al ³⁺ (cmol _c kg ⁻¹)	0.50
H+Al (cmol _c kg ⁻¹)	1.55
SB (cmol _c kg ⁻¹)	0.48
t (cmol _c kg ⁻¹)	0.98
CEC (cmol _c kg ⁻¹)	2.03
V (%)	23.73
m (%)	50.90
SOC (g kg ⁻¹)	1.00
P-Rem (mg kg ⁻¹)	36.50
Clay (g kg ⁻¹)	120
Silt (g kg ⁻¹)	100
Sand (g kg ⁻¹)	780

^aP and K: extracted by Mehlich-1 solution; Ca²⁺, Mg²⁺, and Al³⁺: extracted by 1 mol L⁻¹ KCl; H+Al: extracted by 0.5 mol L⁻¹ calcium acetate at pH 7.0; SB: Sum of exchangeable bases; t: effective cation exchange capacity; CEC: Cation exchange capacity at pH 7.0; CEC: Cation exchange capacity at pH 7.0; V: Base saturation; m: Aluminum saturation; SOC: Soil organic carbon determined by the Walkley-Black wet oxidation method; P-rem: remaining phosphorus.

TABLE S2

Selected soil chemical properties after five cropping cycles of Paiaguás grass fertilized with biochar-based granular fertilizers (BBGFs).

Treatments	Soil parameters								
	pH	P _{Mehlich}	P _{Resin}	K ⁺	SOC	Ca ²⁺	Mg ²⁺	CEC	V
		mg dm ⁻³			g kg ⁻¹	cmol _c dm ⁻³			%
SP	5.88 A	50.20 A	32.50 A	84.90 A	5.20 A	2.03 A	0.78 ^{ns}	3.78 ^{ns}	80.15 ^{ns}
NP	6.04 B	29.10 B	14.30 B	75.70 ^{ns}	6.40 B	1.80 B	0.85 ^{ns}	3.63 ^{ns}	78.26 ^{ns}
B+NP	6.28 C	30.60 C	17.90 C	77.90 ^{ns}	7.50 C	2.08 C	0.82 ^{ns}	3.82 ^{ns}	81.15 ^{ns}
B	6.42 D	11.60 D	10.70 D	74.40 ^{ns}	7.30 D	2.17 ^{ns}	0.86 ^{ns}	3.87 ^{ns}	83.21 ^{ns}
BBGFs-CW									
75	6.52 a	36.50 d	15.30 eBC	72.60 abc	6.70 dB	2.15 aAC	0.72 a	3.83 a	79.88 a
100	6.32 deC	37.80 c	18.50 cdC	74.80 abc	6.60 deB	2.17 aAC	0.79 a	3.96 a	79.55 a
125	6.47 abD	40.40 c	23.20 b	78.30 ab	6.10 fB	2.15 aAC	0.74 a	3.80 a	81.32 a
150	6.28 efC	46.20 a	28.90 a	77.40 abc	6.30 efB	2.13 aAC	0.72 a	3.74 a	81.54 a
BBGFs-PE									
75	6.17 g	45.20 a	16.50 de	75.30 abc	7.30 cCD	2.16 aAC	0.70 a	3.82 a	79.86 a
100	6.33 deC	37.60 d	18.60 cdC	71.40 bc	7.40 bcCD	2.16 aAC	0.77 a	3.87 a	80.38 a
125	6.31 deC	36.70 d	20.10 bc	70.50 c	7.10 cCD	2.15 aAC	0.73 a	3.82 a	80.11 a
150	6.24 fC	37.60 d	20.60 bc	79.20 a	7.10 cCD	2.19 aAC	0.78 a	3.81 a	83.22 a
BBGFs-BO									
75	6.42 bD	40.60 c	15.60 eBC	74.40 abc	7.30 cCD	2.25 a	0.78 a	3.85 a	83.64 a
100	6.41 bcD	41.80 bc	14.70 efB	71.80 bc	7.70 bCD	2.17 aAC	0.72 a	3.73 a	82.33 a
125	6.34 de	41.20 bc	14.30 efB	77.40 abc	8.10 a	2.19 aAC	0.77 a	3.84 a	82.28 a
150	6.35 cd	42.70 b	12.80 fB	76.10 abc	8.30 a	2.19 aAC	0.77 a	3.79 a	83.36 a

SP: Soluble phosphate; NP: Natural phosphate; B+NP: physical mixture of biochar and NP; B: Biochar; BBGFs: Biochar-based granular fertilizers with cassava wastewater (CW), pyroligneous extract (PE), or bio-oil (BO) binders. P_{Mehlich}: Phosphorus extracted by Mehlich-1; P_{Resin}: Phosphorus extracted by ion-exchange resin; SOC: Soil organic carbon; CEC: Cation exchange capacity at pH 7.0; V: Base saturation. Means followed by the same lowercase letter in the column do not differ from each other by Tukey's test ($p < 0.05$). Uppercase letters indicate the comparison of BBGFs treatments against four specific references by Dunnett's test ($p < 0.05$), where A = SP; B = NP; C = B+NP; and D = B. The presence of a corresponding uppercase letter on a BBGF treatment mean indicates it does not differ from that specific reference treatment. ns: Indicates no significant difference between the reference treatment and any of the BBGF treatments.

TABLE S3

Stubble dry mass and root-to-shoot ratio of Paiaguás grass after five cropping cycles fertilized with biochar-based granular fertilizers (BBGFs).

Treatments	Stubble	Root-to-total shoot ratios
SP	7.28±0.14 A	0.21±0.01 A
NP	2.91±0.19 B	0.31±0.03 ^{ns}
B+NP	5.08±0.13 ^{ns}	0.39±0.02 C
B	4.89±0.03 ^{ns}	0.43±0.01 D
BBGFs-CW		
75	4.75±0.45 bc	0.36±0.05 aC
100	4.33±0.81 c	0.33±0.03 abC
125	4.43±0.22 bc	0.28±0.00 b
150	4.92±0.11 abc	0.28±0.03 b
BBGFs-PE		
75	4.37±0.41 abc	0.32±0.03 ab
100	4.95±0.37 abc	0.28±0.02 ab
125	5.60±0.13 a	0.27±0.01 b
150	5.50±0.33 ab	0.29±0.02 ab
BBGFs-BO		
75	4.78±0.48 abc	0.28±0.03 ab
100	5.12±0.73 abc	0.25±0.01 bA
125	4.92±0.31 abc	0.25±0.01 bA
150	4.62±0.37 abc	0.26±0.03 bA

SP: Soluble phosphate; NP: Natural phosphate; B+NP: Physical mixture of biochar and NP; B: Biochar; BBGFs: Biochar-based granular fertilizers with cassava wastewater (CW), pyroligneous extract (PE), or bio-oil (BO) binders. Means followed by the same lowercase letter in the column do not differ from each other by Tukey's test ($p < 0.05$). Uppercase letters indicate the comparison of BBGF treatments against four specific references by Dunnett's test ($p < 0.05$), where A = SP; B = NP; C = B+NP; and D = B. The presence of a corresponding uppercase letter on a BBGF treatment mean indicates it does not differ from that specific reference treatment. ns: Indicates no significant difference between the reference treatment and any of the BBGF treatments.

TABLE S4

P uptake by shoot per cropping cycle, roots, and stubble of Paiaguás grass fertilized with biochar-based granular fertilizers (BBGFs).

Treatments	1 st cycle	2 nd cycle	3 rd cycle	4 th cycle	5 th cycle	Root	Stubble
SP	6.56±0.19 A	7.69±0.11 A	7.10±0.24 A	4.99±0.36 A	7.10±0.22 A	15.58±0.83 A	16.74±0.33 A
NP	2.04±0.11 B	3.02±0.23 B	5.07±0.09 B	4.49±0.11 B	5.21±0.43 B	12.18±0.85 B	7.27±0.49 B
B+NP	4.51±0.03 C	6.38±0.19 C	5.52±0.17 C	7.30±0.14 C	6.51±0.24 C	23.68±1.34 C	10.68±0.27 C
B	3.80±0.13 D	5.72±0.09 D	6.47±0.09 D	4.97±0.17 D	6.11±0.30 D	23.56±0.28 D	11.73±0.07 D
BBGFs-CW							
75	0.73±0.09 ab	2.23±0.09 g	4.53±0.22 fB	6.18±0.15 g	6.36±0.22 gCD	17.08±2.61 abcA	9.98±0.94 cdefCD
100	0.62±0.10 ab	2.62±0.30 gB	4.27±0.13 f	7.27±0.10 cdefC	7.70±0.07 cde	15.29±1.24 bcdAB	7.79±1.45 fB
125	0.95±0.24 b	2.43±0.18 g	5.86±0.16 deC	6.59±0.30 efgC	8.04±0.15 c	14.87±0.52 bcdAB	9.30±0.46 defBC
150	1.07±0.17 a	4.43±0.25 e	7.08±0.25 abA	6.46±0.58 fg	7.80±0.40 cd	15.33±1.51 bcdA	11.32±0.25 bcdeCD
BBGFs-PE							
75	0.86±0.28 ab	3.62±0.19 f	6.32±0.39 cdeD	7.56±0.19 bcdC	7.37±0.14 defA	14.36±1.83 cdAB	10.93±1.03 bcdeCD
100	0.78±0.15 ab	4.62±0.17 de	6.41±0.39 bcdD	7.97±0.19 bcC	9.38±0.24 b	15.08±1.37 bcdAB	11.87±0.88 bcCD
125	0.70±0.08 ab	5.94±0.33 cCD	7.46±0.37 aA	8.20±0.67 b	10.12±0.15 a	18.27±0.99 abA	11.75±0.26 bcdCD
150	0.88±0.12 ab	6.58±0.09 abC	7.79±0.19 a	9.30±0.09 a	10.79±0.16 a	19.82±1.03 a	14.84±0.90 aA
BBGFs-BO							
75	0.75±0.07 ab	5.19±0.35 d	5.65±0.07 eBC	6.00±0.18 g	5.25±0.09 hB	13.86±1.76 cdAB	9.08±0.91 efBC
100	0.67±0.12 ab	5.08±0.15 d	6.66±0.21 bcAD	6.77±0.22 defgC	6.77±0.44 fgAC	13.14±1.06 dAB	12.80±1.83 abD
125	0.83±0.05 ab	7.13±0.11 a	6.54±0.46 bcdAD	7.45±0.26 bcdeC	7.10±0.24 efA	12.53±0.59 dAB	11.32±0.70 bcdeCD
150	0.88±0.16 ab	6.30±0.33 bcC	6.29±0.31 cdeD	5.99±0.25 g	6.33±0.08 gCD	14.54±1.29 bcdAB	10.16±0.82 cdefCD

SP: Soluble phosphate; NP: Natural phosphate; B+NP: Physical mixture of biochar and NP; B: Biochar; BBGFs: Biochar-based granular fertilizers with cassava wastewater (CW), pyroligneous extract (PE), or bio-oil (BO) binders. Means followed by the same lowercase letter in the column do not differ from each other by Tukey's test ($p < 0.05$). Uppercase letters indicate the comparison of BBGF treatments against four specific references by Dunnett's test ($p < 0.05$), where A = SP; B = NP; C = B+NP; and D = B. The presence of a corresponding uppercase letter on a BBGF treatment mean indicates it does not differ from that specific reference treatment. ns: Indicates no significant difference between the reference treatment and any of the BBGF treatments.

TABLE S5

Ca uptake by shoot per cropping cycle, roots, and stubble of Paiaguás grass fertilized with biochar-based granular fertilizers (BBGFs).

Treatments	1 st cycle	2 nd cycle	3 rd cycle	4 th cycle	5 th cycle	Root	Stubble
SP	15.07±0.45 A	20.70±0.30 A	21.56±0.72 A	18.80±1.37 A	24.85±0.79 A	37.82±2.00 A	32.74±0.64 A
NP	4.45±0.24 B	9.15±0.68 B	16.95±0.29 B	18.20±0.44 B	18.46±1.52 B	29.38±2.04 B	13.08±0.87 B
B+NP	12.60±0.07 C	18.46±0.54 C	17.83±0.54 C	24.57±0.46 C	21.39±0.78 C	61.97±3.52 C	21.35±0.55 C
B	12.82±0.45 D	19.19±0.33 D	19.89±0.29 D	19.87±0.69 D	18.34±0.89 D	63.75±0.75 D	21.01±0.12 D
BBGFs-CW							
75	1.98±0.24 a	7.77±0.33 eB	12.68±0.61 f	23.25±0.55 defgC	21.30±0.74 efC	40.32±6.17 abcA	22.32±2.11 bCD
100	1.66±0.28 a	7.28±0.82 e	12.05±0.37 f	25.91±0.37 bcdC	23.09±0.22 deAC	38.67±3.14 bcA	16.88±3.14 cB
125	2.14±0.54 a	6.44±0.48 e	16.85±0.45 eBC	24.81±1.14 bcdeC	25.31±0.49 cA	35.93±1.25 bcAB	18.61±0.91 bcCD
150	2.34±0.36 a	13.52±0.77 c	22.44±0.78 bA	26.54±2.37 abcC	25.25±1.31 cdA	39.49±3.89 abcA	20.18±0.45 bcCD
BBGFs-PE							
75	2.52±0.84 a	11.27±0.62 d	24.99±1.55 a	23.62±0.59 cdefC	22.10±0.40 efC	37.99±4.85 bcA	18.80±1.78 bcCD
100	1.95±0.37 a	13.29±0.48 c	21.78±1.32 bcAD	27.31±0.67 ab	29.69±0.78 a	39.12±3.54 abcA	22.26±1.66 bCD
125	1.86±0.20 a	18.89±1.06 bCD	23.46±1.17 abA	29.22±2.34 a	28.03±0.42 ab	43.44±2.34 abA	27.42±0.61 a
150	2.28±0.32 a	19.07±0.25 bCD	23.07±0.55 abA	29.46±0.29 a	27.26±0.40 bc	48.46±2.51 a	22.54±1.36 abCD
BBGFs-BO							
75	2.15±0.20 a	13.33±0.90 c	18.12±0.22 deBCD	20.28±0.61 gABD	20.75±0.36 fC	35.06±4.44 bcAB	19.60±1.97 bcCD
100	1.92±0.35 a	14.17±0.41 c	18.52±0.59 deBCD	20.60±0.66 fgABD	20.60±1.33 fC	33.86±2.73 cAB	22.53±3.22 abCD
125	2.01±0.12 a	21.65±0.35 aA	19.51±1.37 cdCD	22.65±0.80 efgC	20.45±0.69 fC	33.56±1.59 cAB	20.17±1.25 bcCD
150	2.37±0.44 a	18.30±0.97 bCD	22.48±1.10 bA	21.40±0.90 fgAD	20.42±0.25 fC	33.40±2.95 cAB	22.64±1.83 abCD

SP: Soluble phosphate; NP: Natural phosphate; B+NP: Physical mixture of biochar and NP; B: Biochar; BBGFs: Biochar-based granular fertilizers with cassava wastewater (CW), pyroligneous extract (PE), or bio-oil (BO) binders. Means followed by the same lowercase letter in the column do not differ from each other by Tukey's test ($p < 0.05$). Uppercase letters indicate the comparison of BBGF treatments against four specific references by Dunnett's test ($p < 0.05$), where A = SP; B = NP; C = B+NP; and D = B. The presence of a corresponding uppercase letter on a BBGF treatment mean indicates it does not differ from that specific reference treatment. ns: Indicates no significant difference between the reference treatment and any of the BBGF treatments.

TABLE S6

Mg uptake by shoot per cropping cycle, roots, and stubble of Paiaguás grass fertilized with biochar-based granular fertilizers (BBGFs).

Treatments	1 st cycle	2 nd cycle	3 rd cycle	4 th cycle	5 th cycle	Root	Stubble
SP	7.90±0.23 A	11.65±0.17 A	10.15±0.34 A	10.95±0.79 A	13.85±0.44 A	23.14±1.23 A	27.65±0.54 A
NP	2.77±0.15 B	5.52±0.41 B	9.91±0.17 B	9.93±0.24 B	10.65±0.88 B	18.28±1.27 B	10.17±0.68 B
B+NP	7.71±0.04 C	11.04±0.33 C	10.30±0.31 C	14.28±0.27 C	13.02±0.48 C	35.51±2.02 C	17.28±0.44 C
B	7.10±0.25 D	10.26±0.17 D	12.50±0.18 D	11.32±0.40 D	11.72±0.57 D	35.34±0.42 D	15.64±0.09 D
BBGFs-CW							
75	1.19±0.14 a	4.62±0.20 dB	8.57±0.41 e	11.48±0.27 eAD	11.62±0.40 fBD	26.56±4.06 abcA	16.15±1.52 bCD
100	1.07±0.18 a	4.62±0.52 dB	8.71±0.27 e	12.32±0.18 deAD	16.35±0.16 c	24.73±2.01 abcA	16.45±3.06 bCD
125	1.37±0.35 a	4.56±0.34 d	11.07±0.29 cdAC	13.19±0.61 cdeC	14.91±0.29 dA	21.06±0.74 cAB	15.06±0.74 bCD
150	1.46±0.23 a	7.64±0.44 b	12.82±0.45 bD	16.14±1.44 b	17.82±0.93 b	24.16±2.38 abcA	16.74±0.37 abCD
BBGFs-PE							
75	1.54±0.51 a	5.97±0.32 cB	10.54±0.65 dABC	14.49±0.37 bcC	11.97±0.22 fCD	23.63±3.02 bcA	17.06±1.61 abCD
100	1.21±0.23 a	7.71±0.28 b	11.37±0.69 cdCD	15.55±0.38 bC	19.07±0.50 ab	24.51±2.22 abcA	15.33±1.14 bCD
125	1.18±0.13 a	11.76±0.66 aAC	15.12±0.76 a	15.32±1.23 bC	19.47±0.29 a	27.65±1.49 abA	20.71±0.46 a
150	1.24±0.17 a	11.86±0.16 aAC	15.14±0.36 a	18.61±0.18 a	19.66±0.29 a	29.74±1.54 a	18.14±1.10 abCD
BBGFs-BO							
75	1.26±0.11 a	8.53±0.58 b	11.48±0.14 bcdD	11.71±0.35 deAD	13.66±0.23 deAC	23.24±2.94 bcA	16.25±1.64 bCD
100	1.08±0.19 a	8.20±0.24 b	11.93±0.38 bcD	12.66±0.41 deD	13.54±0.87 eAC	20.71±1.67 cAB	18.43±2.64 abCD
125	1.22±0.07 a	11.16±0.18 aACD	12.21±0.86 bcD	13.41±0.47 cdC	12.50±0.42 efCD	21.43±1.02 cAB	15.25±0.95 bCD
150	1.27±0.23 a	10.92±0.58 aACD	14.48±0.71 a	13.47±0.57 cdC	12.37±0.15 efCD	21.22±1.88 cAB	15.71±1.27 bCD

SP: Soluble phosphate; NP: Natural phosphate; B+NP: Physical mixture of biochar and NP; B: Biochar; BBGFs: Biochar-based granular fertilizers with cassava wastewater (CW), pyroligneous extract (PE), or bio-oil (BO) binders. Means followed by the same lowercase letter in the column do not differ from each other by Tukey's test ($p < 0.05$). Uppercase letters indicate the comparison of BBGF treatments against four specific references by Dunnett's test ($p < 0.05$), where A = SP; B = NP; C = B+NP; and D = B. The presence of a corresponding uppercase letter on a BBGF treatment mean indicates it does not differ from that specific reference treatment. ns: Indicates no significant difference between the reference treatment and any of the BBGF treatments.

TABLE S7

K uptake by shoot per cropping cycle, roots, and stubble of Paiaguás grass fertilized with biochar-based granular fertilizers (BBGFs).

Treatments	1 st cycle	2 nd cycle	3 rd cycle	4 th cycle	5 th cycle	Root	Stubble
SP	67.16±1.98 A	107.43±1.56 A	102.48±3.44 A	72.59±5.29 A	111.82±3.55 A	202.92±10.78 A	147.72±2.88 A
NP	24.27±1.29 B	43.42±3.25 B	75.14±1.31 B	86.02±2.07 B	71.95±5.94 B	153.01±10.63 B	61.62±4.12 B
B+NP	54.47±0.31 C	65.93±1.95 C	96.60±2.90 C	110.22±2.07 C	100.75±3.69 C	279.93±15.90 C	104.21±2.67 ^{ns}
B	58.80±2.07 D	80.58±1.37 D	99.99±1.48 D	86.11±3.01 D	85.57±4.15 D	286.21±3.38 D	92.36±0.54 D
BBGFs-CW							
75	9.39±1.13 a	34.63±1.49 e	82.07±3.96 dB	89.77±2.14 eBD	79.13±2.75 eBD	190.68±29.17 bcAB	102.13±9.64 abD
100	7.27±1.22 a	29.06±3.27 e	51.05±1.56 g	111.86±1.62 bcC	96.84±0.92 deC	203.50±16.52 abA	102.19±19.00 abD
125	10.07±2.55 a	29.42±2.20 e	62.86±1.67 f	111.47±5.12 bcC	109.20±2.10 bcA	188.33±6.58 bcAB	94.80±4.64 bD
150	11.23±1.74 a	56.67±3.24 c	93.84±3.28 cCD	116.57±10.40 bcC	112.88±5.84 bA	205.38±20.24 abA	101.42±2.27 abD
BBGFs-PE							
75	12.70±4.21 a	47.98±2.63 dB	103.58±6.41 abcACD	107.73±2.71 cdC	93.63±1.70 eC	202.01±25.79 abA	86.59±8.18 bD
100	9.66±1.86 a	59.35±2.13 c	95.73±5.83 bcACD	135.04±3.31 a	131.65±3.44 a	200.79±18.19 abA	105.36±7.85 abD
125	9.06±1.00 a	80.15±4.51 bD	104.94±5.25 abACD	125.07±10.02 ab	126.14±1.90 a	223.63±12.06 aA	103.54±2.31 abD
150	12.31±1.73 a	83.68±1.10 abD	111.57±2.66 a	120.95±1.18 bcC	115.97±1.68 bA	227.42±11.80 aA	96.19±5.83 bD
BBGFs-BO							
75	11.60±1.06 a	44.39±3.00 dB	74.46±0.90 deB	87.13±2.63 eBD	80.64±1.38 eD	163.88±20.76 cdB	101.81±10.25 abD
100	9.41±1.70 a	58.42±1.68 c	67.85±2.16 efB	95.07±3.05 deBD	91.83±5.93 eD	180.44±14.55 cdAB	123.39±17.65 a
125	9.27±0.55 a	91.00±1.46 a	61.68±4.35 f	89.99±3.18 eBD	103.38±3.47 cdC	166.58±7.92 cdAB	104.80±6.50 abD
150	10.45±1.94 a	80.53±4.27 bD	104.96±5.12 abACD	89.88±3.78 eBD	92.34±1.13 eD	158.38±14.01 dB	89.63±7.73 bD

SP: Soluble phosphate; NP: Natural phosphate; B+NP: Physical mixture of biochar and NP; B: Biochar; BBGFs: Biochar-based granular fertilizers with cassava wastewater (CW), pyroligneous extract (PE), or bio-oil (BO) binders. Means followed by the same lowercase letter in the column do not differ from each other by Tukey's test ($p < 0.05$). Uppercase letters indicate the comparison of BBGF treatments against four specific references by Dunnett's test ($p < 0.05$), where A = SP; B = NP; C = B+NP; and D = B. The presence of a corresponding uppercase letter on a BBGF treatment mean indicates it does not differ from that specific reference treatment. ns: Indicates no significant difference between the reference treatment and any of the BBGF treatments.

5 CONSIDERAÇÕES FINAIS

A abordagem sequencial adotada nesta tese, do desenvolvimento tecnológico dos grânulos à caracterização biológica do solo e à validação agrônômica em cultivos sucessivos, permitiu demonstrar que a granulação do biocarvão com fontes fosfatadas e aglutinantes agroindustriais constitui uma estratégia viável para superar simultaneamente os gargalos operacionais do biocarvão pulverizado e a baixa eficiência das fontes solúveis convencionais em solos tropicais. A integração dos resultados dos três estudos evidencia que os BBGFs não apenas eliminam os riscos de emissão de material particulado e as perdas por deriva eólica inerentes ao biocarvão em pó, mas também estabelecem um sistema de liberação contínua de P cuja eficiência agrônômica equipara-se, e em casos específicos supera, à de fontes solúveis.

O primeiro estudo revelou que a natureza do aglutinante modula de forma determinante as propriedades físico-mecânicas dos grânulos e, conseqüentemente, seu comportamento no solo. Os grânulos formulados com BO apresentaram maior resistência à compressão, maior densidade e elevado índice de resistência ao impacto, atributos desejáveis para o manuseio, o transporte e a aplicação mecanizada. O PE, por sua vez, conferiu aos grânulos maior índice de salinidade e menor pH, enquanto a CW resultou em maior afinidade pela água. Todos os BBGFs promoveram incrementos expressivos na produção de matéria seca de feijão comum em relação ao solo não fertilizado, com destaque para as formulações com PE, que propiciaram os maiores ganhos de biomassa radicular (755,17%). Esses resultados demonstram que a seleção criteriosa do aglutinante permite direcionar as propriedades dos grânulos conforme as exigências específicas de cada sistema de produção.

O segundo estudo aprofundou a compreensão das interações entre os BBGFs e a biologia do solo, ao demonstrar que todos os fertilizantes granulados estimularam significativamente a atividade das enzimas β -glicosidase, fosfatase ácida e arilsulfatase em relação aos controles. Os BBGFs formulados com BO na proporção de 150% mantiveram a atividade enzimática mais elevada e estável ao longo dos 40 dias de incubação, configurando a formulação mais efetiva para o aumento da saúde biológica do solo. Os BBGFs-PE maximizaram a fosfatase ácida aos 10 dias na proporção de 125%, porém apresentaram declínio subsequente e inibiram a arilsulfatase em proporções mais elevadas. Os BBGFs-CW destacaram-se no incremento do P disponível, alcançando valores de até 24,0 mg kg⁻¹. A redução generalizada da atividade enzimática observada aos 40 dias em todos os tratamentos reflete a transição de um efeito *priming* positivo, com mineralização acelerada impulsionada pelo carbono lábil dos aglutinantes, para um efeito *priming* negativo, em que predominam as formas recalcitrantes do carbono pirogênico e a estabilização da matéria orgânica do solo.

O terceiro estudo consolidou a validação agrônômica dos BBGFs ao demonstrar que as formulações com PE nas proporções de 125% e 150% alcançaram eficácia agrônômica relativa de 96,8% e 101,3%, respectivamente, equiparando-se ao KH₂PO₄ utilizado como referência de fonte solúvel de P. O resultado mais expressivo consistiu na superação da fonte solúvel de referência em 6,5% na absorção total de P acumulada ao longo dos cinco ciclos de cultivo de *Urochloa brizantha* BRS Paiaguás, com os BBGFs-PE a 150% alcançando 70,01 mg por vaso frente a 65,76 mg por vaso do tratamento com KH₂PO₄. Esse desempenho deveu-se ao perfil de liberação contínua e gradual dos BBGFs, em contraste com a solubilização imediata e a subsequente fixação do P proveniente da fonte solúvel. Enquanto o KH₂PO₄ proporcionou absorção de P aproximadamente sete vezes superior no primeiro ciclo, esse efeito declinou acentuadamente a partir do terceiro ciclo em razão da fixação pelos colóides do solo e do esgotamento do

P lábil. Os BBGFs-BO, embora tenham restringido a produção de biomassa nas proporções mais altas do aglutinante devido à hidrofobicidade dos grânulos, promoveram o maior Índice de Qualidade do Solo (SQI = 0,539), refletindo a superioridade dessa formulação no aumento da atividade enzimática e dos atributos químicos do solo. Todos os BBGFs elevaram o pH, o carbono orgânico e as bases trocáveis do solo em relação à fertilização mineral isolada, reafirmando os benefícios da matriz de biocarvão como condicionador de solos ácidos.

A síntese dos três estudos permite estabelecer que cada aglutinante ocupa um nicho funcional distinto na tecnologia de BBGFs. O PE, nas proporções de 125% e 150%, configurou-se como o aglutinante de melhor equilíbrio entre eficiência agrônômica e aumento da qualidade do solo, sendo capaz de substituir efetivamente fontes solúveis de P em Latossolos de textura franco-arenosa. O BO destacou-se como o aglutinante mais efetivo para a saúde biológica do solo e a estabilidade estrutural dos grânulos. A CW, embora tenha apresentado uma fase inicial de baixa liberação que limitou o desempenho agrônômico nos primeiros ciclos, demonstrou recuperação a partir do quarto ciclo, o que sugere potencial para aplicações em sistemas de cultivo de longo prazo ou em consórcio com fontes de rápida disponibilidade.

Do ponto de vista científico, esta pesquisa contribui para o avanço do conhecimento sobre a utilização de coprodutos da cadeia agroindustrial na formulação de fertilizantes de eficiência aprimorada, ampliando o entendimento das interações entre biocarvão, aglutinantes orgânicos bioativos e os componentes químicos e biológicos de solos tropicais intemperizados. Do ponto de vista prático, os BBGFs representam uma alternativa tecnológica com potencial para reduzir a dependência de fertilizantes fosfatados de alta solubilidade e importados, promover a valorização de resíduos agroindustriais abundantes no Brasil e contribuir simultaneamente para o sequestro de carbono e a melhoria da saúde de solos agricultáveis. Ressalta-se, contudo, a necessidade de estudos complementares em condições de campo e em horizontes temporais mais amplos, que avaliem a persistência dos efeitos observados sob variabilidade climática, diversidade edáfica e sistemas de manejo representativos da agricultura tropical, de modo a viabilizar recomendações técnicas robustas para a adoção dessa tecnologia em escala comercial.