



MARINA MARIÁ PEREIRA

**TRANSFORMING WASTE PHOSPHORUS INTO A
NUTRIENT-RICH SOURCE FOR A GREENER FUTURE**

**LAVRAS – MG
2026**

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Thesis submitted to the Universidade Federal de Lavras in fulfillment of the requirements of Agronomy/Plant Physiology Program for the degree of *Doctor Scientiae*.

Professor DSc. Eduardo Gusmão Pereira
Adviser

Professor DSc. Juliana Cristina Tristão
Co-adviser

Professor DSc. Adnane Beniaich
Co-adviser

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APROVADA em 18 de dezembro de 2025.
Professor DSc. Adnane Beniaich UM6P
Professor DSc. Elisa Monteze Bicalho UFV
Professor DSc. Hudson Wallace Pereira de Carvalho USP
Professor DSc. Vitor de Laia Nascimento UFLA

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 **EDUARDO GUSMAO PEREIRA**
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Verifique em <https://validar.iti.gov.br>

Professor DSc. Eduardo Gusmão Pereira
Adviser

Professor DSc. Juliana Cristina Tristão
Co-adviser

Professor DSc. Adnane Beniaich
Co-adviser

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RESUMO

A escassez e os elevados custos dos adubos minerais tradicionalmente utilizados têm direcionado a pesquisa científica para novas formas de obtenção de fertilizantes. Nesse contexto, compreender como as plantas respondem a fontes renováveis de nutrientes, bem como desenvolver estratégias eficazes para aplicação dessas tecnologias no campo é essencial para garantir a segurança alimentar e nutricional, ao mesmo tempo em que se reduzem os impactos ambientais associados ao manejo de fertilizantes. Esta tese foi estruturada em dois capítulos que abordam o desafio da demanda agrícola por fósforo (P) com a necessidade de reduzir a dependência de reservas não renováveis de rocha fosfática. No Capítulo I, o foco foi a síntese, caracterização e avaliação agronômica de materiais à base de cálcio e ferro (Ca/Fe) obtidos a partir de resíduos da mineração de ferro. O rejeito de mineração foi submetido a tratamento térmico para obtenção do material de referência (R900) e posteriormente modificado por impregnação com Ca, originando o material ReFert, caracterizado pelo início de formação de fases de ferrita de cálcio com elevada afinidade por fosfato. O ReFert apresentou capacidade de remoção de P substancialmente superior à de seu precursor sem Ca, confirmando a formação de domínios reativos Ca/Fe e seu potencial para a recuperação de P de meios aquosos. O material carregado com P (ReFertP) foi então avaliado por meio de técnicas de *priming* e revestimento de sementes de milho (*Zea mays* L.) em solo ácido, evidenciando que o P adsorvido pode ser gradualmente disponibilizado na rizosfera, sustentando a germinação, o crescimento inicial e o acúmulo de P em níveis comparáveis aos de fertilizantes solúveis convencionais. Esses resultados demonstraram que materiais recuperados podem ser estrategicamente posicionados na interface semente-solo, com uma nutrição inicial eficiente e a valorização de resíduos de Fe. No Capítulo II, a investigação concentrou-se no comportamento desses materiais em solos alcalinos, nos quais a fixação de P por Ca e carbonatos limita fortemente a eficiência dos fertilizantes. Um experimento em casa de vegetação com azevém (*Lolium multiflorum* Lam.) comparou quatro tratamentos para suprimento de P (controle, TSP, ReFert e ReFertP) ao longo de 126 dias. O ReFertP atuou como uma fonte de liberação lenta de P, promovendo o aumento gradual do P disponível na rizosfera, a manutenção da produção de biomassa e a elevada eficiência de uso do fósforo ao fim do experimento. De forma particularmente relevante, o ReFert aplicado sem adsorção prévia de P também desempenhou papel ativo na dinâmica do fósforo no solo, interagindo com os estoques nativos de P, adsorvendo fosfato da solução do solo e tornando-o progressivamente disponível às plantas por meio de processos na rizosfera. Em conjunto, os dois capítulos demonstram que

resíduos da mineração de ferro enriquecidos com Ca podem ser transformados em materiais multifuncionais, capazes de remover P de efluentes, reciclar esse nutriente para uso agrícola e regular sua disponibilidade em solos ácidos e alcalinos. Esses resultados reforçam o potencial do ReFert como uma interface funcional entre remoção, recuperação e reutilização de P, contribuindo para uma economia circular mais resiliente e sustentável.

Palavras-chave: Nutrição vegetal; Fluxo de nutrientes; Eficiência no uso de nutrientes; Fertilizante; Bioeconomia circular.

ABSTRACT

The resource constraints and rising costs of conventionally used mineral fertilizers have driven scientific research toward alternative pathways for fertilizer production. In this context, understanding how plants respond to renewable nutrient sources and also developing effective strategies for transferring these technologies to the field is essential to ensure food and nutritional security while reducing the environmental impacts associated with fertilizer management. This thesis was structured into two chapters addressing the challenge of meeting agricultural phosphorus (P) demand while reducing dependence on non-renewable phosphate rock reserves. In Chapter I, the focus was on the synthesis, characterization, and agronomic evaluation of calcium and iron-based (Ca/Fe) materials derived from Fe mining activity. The mining waste was heat-treated to produce a reference material, R900, and then modified by Ca impregnation, resulting in ReFert, in which the formation of Ca ferrite domains provides an affinity for phosphate. ReFert exhibited higher P removal capacity than its Ca-free precursor and highlighted its potential for P recovery from aqueous solution. The P-loaded material, ReFertP, was then evaluated using seed priming and coating techniques applied to maize (*Zea mays* L.) grown in acidic soil. These experiments demonstrated that the adsorbed P could be gradually released in the rhizosphere, sustaining germination, early plant growth, and P accumulation at levels comparable to those achieved with conventional soluble fertilizers. These results showed that recovered materials can be strategically positioned at the seed–soil interface, promoting efficient early P nutrition while simultaneously valorizing Fe-rich mining residues. In Chapter II, the investigation was focused on the behavior of these materials in alkaline soils, where P fixation by Ca and carbonates strongly limits fertilizer efficiency. A greenhouse pot experiment with ryegrass (*Lolium multiflorum* Lam.) compared four P supply treatments (control, triple superphosphate - TSP, ReFert, and ReFertP) for 126 days. ReFertP was a slow-release P source, promoting a gradual increase in rhizospheric P availability, sustaining biomass production, and resulting in high phosphorus use efficiency by the end of the experiment. ReFert actively influenced soil P dynamics by interacting with native soil P pools, adsorbing phosphate from the soil solution, and progressively making it available to plants through the rhizosphere. Together, these two chapters demonstrate that Ca-enriched Fe mining residues can be transformed into multifunctional materials would are capable of removing P from effluents, recycling this nutrient for agricultural use, and regulating its availability in both acidic and alkaline soils. These findings reinforce the potential of ReFert as

a functional interface between P removal, recovery, and reuse, contributing to a more resilient and sustainable circular nutrient economy.

Keywords: Plant nutrition; Nutrient flows; Nutrient use efficiency; Fertilizer; Circular bioeconomy.

INDICADORES DE IMPACTO

O presente trabalho teve como objetivo desenvolver e avaliar um material fertilizante inovador a partir de rejeitos de mineração ricos em ferro, modificados por impregnação com cálcio e tratamento térmico, visando sua aplicação como adsorvente e fonte gradual de fósforo (P) para sistemas agrícolas, contribuindo para a sustentabilidade do uso desse nutriente estratégico. Os resultados demonstraram impactos tecnológicos, ambientais, econômicos e sociais relevantes, tanto diretos quanto potenciais. Do ponto de vista tecnológico, o estudo validou uma rota de síntese de baixo custo para transformar resíduos minerais em um insumo agrônomo funcional, com elevada capacidade de adsorção de fosfato e liberação controlada de P em resposta a processos rizosféricos, alcançando desempenho agrônomo comparável ao do superfosfato triplo, com aumento da eficiência de uso de fósforo pelas plantas e manutenção da produção de biomassa. Ambientalmente, o reaproveitamento de rejeitos de mineração contribui para a redução de passivos ambientais, mitigando riscos associados ao acúmulo desses resíduos e diminuindo perdas de P para o ambiente, o que tem potencial para reduzir processos de eutrofização em corpos hídricos. Do ponto de vista econômico, a tecnologia apresenta potencial de redução da dependência de fertilizantes fosfatados importados, favorecendo a segurança alimentar e a soberania nacional em insumos agrícolas, especialmente para agricultores de regiões tropicais com solos de alta fixação de P, como o território brasileiro. Os impactos sociais se manifestam de forma potencial e indireta, ao favorecer sistemas produtivos mais eficientes e sustentáveis, com benefícios para agricultores, cadeias produtivas agrícolas e para a sociedade em geral, ao promover práticas alinhadas à economia circular e à transição para uma agricultura de baixo impacto ambiental. O trabalho possui caráter extensionista em potencial, uma vez que os resultados podem subsidiar parcerias futuras entre universidade, setor produtivo, cooperativas agrícolas e órgãos públicos, com impacto direto em produtores rurais e comunidades agrícolas, especialmente em regiões mineradoras e agrícolas. Os impactos do estudo se enquadram principalmente nas áreas temáticas de meio ambiente, tecnologia e produção, trabalho e educação, conforme a Política Nacional de Extensão, e estão alinhados aos Objetivos de Desenvolvimento Sustentável da ONU, em especial os ODS 2 (Fome Zero e Agricultura Sustentável), 9 (Indústria, Inovação e Infraestrutura), 12 (Consumo e Produção Responsáveis), 13 (Ação contra a Mudança Global do Clima) e 15 (Vida Terrestre), contribuindo para a Agenda 2030 por meio do desenvolvimento de tecnologias sustentáveis aplicadas à agricultura e à gestão responsável de recursos naturais.

IMPACT INDICATORS

The present study aimed to develop and evaluate an innovative fertilizer material derived from iron-rich mining residues, modified through calcium impregnation and thermal treatment, for use as a phosphorus (P) adsorbent and a gradual P source in agricultural systems, thereby contributing to the sustainable use of this strategic nutrient. The results demonstrated relevant technological, environmental, economic, and social impacts, both direct and potential. From a technological perspective, the study validated a low-cost synthesis route to transform mineral residues into a functional agronomic input, exhibiting high phosphate adsorption capacity and controlled P release in response to rhizosphere processes, achieving agronomic performance comparable to triple superphosphate, with increased phosphorus use efficiency by plants and sustained biomass production. Environmentally, the reuse of mining residues contributes to the reduction of environmental liabilities, mitigating risks associated with the accumulation of these wastes and decreasing P losses to the environment, which has the potential to reduce eutrophication processes in water bodies. From an economic standpoint, the technology shows potential to reduce dependence on imported phosphate fertilizers, strengthening food security and national sovereignty over agricultural inputs, particularly for farmers in tropical regions with soils characterized by high P fixation, such as those found in Brazil. Social impacts are manifested in a potential and indirect manner, as the technology favors more efficient and sustainable production systems, benefiting farmers, agricultural value chains, and society as a whole by promoting practices aligned with the circular economy and the transition to low-impact agriculture. The study presents potential extension activities, as its results may support future partnerships between universities, the productive sector, agricultural cooperatives, and public institutions, with direct impacts on rural producers and farming communities, especially in mining and agricultural regions. The impacts of this work are mainly classified within the thematic areas of environment, technology and production, work, and education, according to the Brazilian National Extension Policy, and are aligned with the United Nations Sustainable Development Goals, particularly SDGs 2 (Zero Hunger and Sustainable Agriculture), 9 (Industry, Innovation and Infrastructure), 12 (Responsible Consumption and Production), 13 (Climate Action), and 15 (Life on Land), contributing to the 2030 Agenda through the development of sustainable technologies applied to agriculture and responsible natural resource management.

SUMMARY

FIRST PART	13
General Introduction	13
References	14
CHAPTER I	18
FROM MINING WASTE TO FERTILIZER: CALCIUM-IRON OXIDES FOR PHOSPHORUS RECOVERY AND EARLY MAIZE NUTRITION	18
HIGHLIGHTS	19
ABSTRACT	19
1. Introduction	19
2. Materials and methods	22
2.1. Local	22
2.2. Adsorbent material synthesis	22
2.3. Characterization methods of adsorbent material	22
2.4. Adsorption capacity tests	23
2.5. Seed characterization, germination test, and priming methodology	24
2.6. Desorption tests, priming application, and seed coating	25
2.7. Seed coating	26
2.8. Measurements of gas exchange	26
2.9. Chlorophyll a fluorescence and chlorophyll measurements	27
2.10. Morphological and nutritional analysis	27
2.11. Statistical analysis and experimental design	28
3. Results	28
4. Discussion	39
5. Conclusions	41
References	42
Supplementary Data	46
CHAPTER II	55
TRANSFORMING IRON MINING BY-PRODUCTS INTO SOIL AMENDMENTS TO ENHANCE PHOSPHORUS AVAILABILITY IN ALKALINE SOILS	55
HIGHLIGHTS	56
ABSTRACT	56
1. Introduction	56
2. Materials and methods	58
2.1. Local	58

2.2. Adsorbent material synthesis	58
2.3. Phosphorus adsorption capacity test.....	59
2.4. Characterization methods for the adsorbent material	59
2.5. Pots experiments	60
2.5.1. Experimental design and treatments	60
2.5.2. Rhizosphere soil collection, pH, and P levels.....	61
2.5.3. Shoot morphological traits, growth rate, and P levels	62
2.5.4. Rhizosphere root morphological traits	62
2.6. Statistical Analysis and Data Visualization.....	63
3. Results	63
3.1. Adsorbent material characterization and adsorption capacity	63
3.2. Rhizosphere pH changes and final P levels.....	65
3.3. Rhizosphere and shoot morphological traits	66
3.4. Shoot growth rate.....	67
4. Discussion	69
5. Conclusions	71
References	72
Supplementary data	76
THIRD PART	81
Concluding remarks	81

FIRST PART

General Introduction

The supply of mineral fertilizers is one of the primary factors contributing to the increase in agricultural crop productivity. Many of these fertilizers are obtained from non-renewable sources through financially expensive extraction processes, resulting in significant environmental impacts. New technologies will likely increase the recovery of nutrients from different organic wastes within the food system in forms that allow safe recycling back into crop production, thus enabling a more circular nutrient economy (Dobermann et al., 2022). Recovering and using fertilizers from alternative sources is a promising path to increase sustainability in the food chain, minimizing the tradeoffs between productivity and environmental impact. Rethinking production processes and fertilizer use can decrease costs and increase independence in obtaining this resource.

Phosphorus (P) is a crucial nutrient that supports crop growth, soil biodiversity, ecological functioning, and global food production (Duncan et al., 2019; Oliverio et al., 2020; Wu et al., 2016). However, P is a finite, non-renewable resource, and its long-term availability has been the subject of continuous debate (McDowell; Haygarth, 2025). Global phosphate rock resources exceed 300 billion tons, while reserves were approximately 74 million tons in 2024, mainly concentrated in China, Morocco, the United States, and Russia (USGS, 2025b). According to the International Fertilizer Association, current extraction technologies and projected consumption rates would allow phosphate rock reserves to last roughly 350 years (IFA, 2023). Regardless of the apparent abundance of geological reserves, the projected increase in agricultural demand, reaching 51.8 million tons of P_2O_5 by 2028 (USGS, 2025b), shows the need for sustainable nutrient strategies.

At the same time, global P losses from agricultural runoff, leaching, and wastewater discharge contribute to eutrophication, promoting harmful algal blooms, oxygen depletion, and the degradation of aquatic ecosystems (Frazão et al., 2021; Smil, 2000). While P accumulates excessively in soils, 70% of global croplands now exhibit P surplus (Cordell et al., 2009), only a small fraction remains available to plants due to rapid adsorption and immobilization on soil mineral surfaces (Madison et al., 2023; Shen et al., 2011; Vance et al., 2003).

Considering the environmental impacts of excessive P inputs and the mineral fertilizer consumption, recycling P from waste streams has become a central strategy in the transition to a circular nutrient economy. Mining industries generate large quantities of waste. Steelmaking

alone produces 200 to 400 kg of Fe-rich by-products per ton of steel (World Steel Association, 2020). These materials, rich in Fe oxides, have high potential for valorization due to their strong sorption capacities and reactive surface chemistry (Matei et al., 2022; Cundy et al., 2008). Recent studies demonstrate that Ca and Fe adsorbents derived from mining and metallurgical by-products exhibit high P adsorption capacity and can efficiently remove P from wastewater (Araújo et al., 2024; Karasa et al., 2024; Kasprzyk et al., 2021; Bacelo et al., 2020). Integrating P recovery, removal, and reuse not only mitigates eutrophication but also reduces dependence on non-renewable phosphate rock, reinforcing global sustainability goals. Once recovered, these materials can potentially function as slow-release fertilizers, synchronizing P release with plant demand and minimizing fixation losses (Dobermann et al., 2022; Poole et al., 2021). In this context, converting Fe-rich mining waste into value-added P fertilizers aligns with the principles of circular bioeconomy and may offer a promising pathway to expand nutrient recovery, reduce environmental degradation, and optimize fertilizer use efficiency in agriculture.

Considering these global challenges and the opportunities posed by circular nutrient strategies, this thesis was structured into two complementary chapters that collectively address the potential of modified Fe-rich mining residues as sustainable P sources. Chapter I focuses on the synthesis, characterization, and P-adsorption performance of Ca/Fe-based materials derived from mining waste, aiming to transform mining by-products into value-added sorbents. Examine the agronomic behavior of these recovered P materials when applied to seeds via priming techniques, assessing their desorption dynamics and capacity to support P uptake and early plant growth in acidic soils. Chapter II examines the agronomic behavior of these recovered P materials when applied to alkaline soils, assessing their desorption dynamics, effects on rhizosphere processes, and their capacity to support P uptake, plant growth, and fertilizer use efficiency. Together, these chapters contribute to the development, evaluation, and validation of circular bioeconomy strategies for recovering P from waste streams and converting mining residues into slow-release, high-efficiency P fertilizers capable of improving nutrient management while decreasing environmental impacts.

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SECOND PART

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CHAPTER I

FROM MINING WASTE TO FERTILIZER: CALCIUM-IRON OXIDES FOR PHOSPHORUS RECOVERY AND EARLY MAIZE NUTRITION

Marina Mariá Pereira, Departamento de Biologia, Instituto de Ciências Naturais, Universidade Federal de Lavras (UFLA), 37200-900, Lavras, MG, Brasil.

<https://orcid.org/0000-0002-6959-0155>.

Matheus Henrique Pimentel Araújo, Instituto de Ciências Exatas e Tecnológicas, Universidade Federal de Viçosa – *Campus Florestal* (UFV), Florestal, Minas Gerais 35690-000, Brasil. <https://orcid.org/0000-0002-5081-4016>.

Elisa Monteze Bicalho, Instituto de Ciências Biológicas e da Saúde, Universidade Federal de Viçosa – *Campus Florestal* (UFV), Florestal, Minas Gerais 35690-000, Brasil.

<https://orcid.org/0000-0003-1746-0663>.

Juliana Cristina Tristão, Instituto de Ciências Exatas e Tecnológicas, Universidade Federal de Viçosa – *Campus Florestal* (UFV), Florestal, Minas Gerais 35690-000, Brasil.

<https://orcid.org/0000-0001-5226-8381>.

Eduardo Gusmão Pereira, Instituto de Ciências Biológicas e da Saúde, Universidade Federal de Viçosa – *Campus Florestal* (UFV), Florestal, Minas Gerais 35690-000, Brasil.

Corresponding author: egpereira@ufv.br. <https://orcid.org/0000-0001-5660-2949>.

HIGHLIGHTS

- Ca/Fe oxides derived from iron mining waste can reclaim P from aqueous solution.
- ReFertP release P during seed germination and enhance early maize root development.
- ReFertP has potential as a sustainable alternative P source within a circular bioeconomy.

ABSTRACT

Phosphorus (P) is an essential nutrient, but it has finite resources and reserves, and its losses from agricultural, industrial, and domestic sources worsen eutrophication, threatening aquatic ecosystems. Recovering P from wastewater is crucial for environmental protection and for extending global P reserves within a circular bioeconomy. Iron mining waste, rich in Fe oxides, presents an opportunity for valorization as an adsorbent in P recovery, while in agriculture, improving P-use efficiency, particularly through seed priming or coating, has been fundamental for early plant development. This study synthesized calcium–iron (Ca/Fe) oxides (named ReFert) from mining waste, producing a material capable of removing P from aqueous solution and subsequently functioning as an alternative fertilizer for maize (*Zea mays* L.). Material characterization by SEM–EDS, XRD, Mössbauer spectroscopy, confirmed significant structural and mineralogical transformations, including the formation of Ca ferrite, which markedly enhanced P adsorption capacity from 3 to $\sim 31 \text{ mg g}^{-1}$ across a wide pH range. Desorption assays showed that osmopriming with the P-enriched material (ReFertP) accelerated germination and increased root growth, indicating improved early nutrient access. In greenhouse trials, all P-fertilized plants outperformed the unfertilized control. Although single superphosphate applied to the soil produced the greatest biomass and higher photosynthetic performance. ReFertP matched or exceeded single superphosphate in shoot P concentration when applied directly to the soil. Overall, ReFertP efficiently adsorbed and supplied P, demonstrating its potential as a sustainable alternative fertilizer that integrates wastewater remediation with agricultural productivity, thereby promoting circular bioeconomy strategies by converting iron mining waste into value-added inputs.

Keywords: Calcium/Iron Oxide; Circular Economy, Iron Mining Waste; Phosphorus Recovery.

1. Introduction

Phosphorus (P) is one of the most important nutrients that sustains soil biodiversity, ecological processes, and human life on Earth (Oliverio et al., 2020; Duncan et al., 2019; Wu et al., 2016). However, this is a finite, non-renewable resource, and a target of continuous debate

regarding the extent of global phosphate rock reserves (McDowell; Haygarth, 2025). The International Fertilizer Association predicted that there are mineable and processable phosphate rock deposits to supply approximately 350 years of phosphate at projected usage rates and with current technology (IFA, 2023). Contradictorily, excessive P leakage from industrial, agricultural, and household sources contributes significantly to undesirable changes in the ecology of water bodies, disturbing the balance of plant and fish species, as well as other aquatic organisms (McDowell; Haygarth, 2024). The process by which water supplies become enriched with nutrients is known as eutrophication, often leading to excessive growth of harmful algae and invasive aquatic plants, causing severe ecological imbalances (Frazão et al., 2021; Ajmal et al., 2018). Therefore, decreasing P flow through soil management and alternative fertilizer sources is essential to protect the environment and maintain food production.

Recycling P from wastewater using a mining waste/byproduct material is an important strategy to extend the lifespan of phosphorus resources and reserves, and at the same time, attenuate environmental pollution. During mining activities, large volumes of soil and rock are displaced to recover valuable minerals, generating a range of 5 to 14 billion tons of tailings (Schoenberger, 2016). Among these mining activities is the exploitation of iron ore deposits. According to the 2025 Mineral Commodity Summaries, global crude iron ore reserves total approximately 200 billion tons, with the largest reserves distributed across Australia, Brazil, Russia, and China (USGS, 2025a). According to the World Steel Association (2020), various by-products are generated, including sludge, dust, and scale, which represent, on average, 200 kg from scrap-based steelmaking and 400 kg from iron ore-based steelmaking per ton of steel. From a circular economy perspective, in which reuse and regeneration contribute to decreasing the consumption of natural resources, the waste/by-products generated by the iron-mining industry hold substantial potential for valorization when converted into value-added materials for environmental remediation (Matei et al., 2022).

The environmental cycling of a wide range of important organic, inorganic, and radioactive contaminants is strongly influenced by iron (Fe) reactions, owing to its effects on contaminant mobility, sorption, and degradation as an electron donor and, in its various mineral forms, as a precipitant and sorbent substrate (Cundy et al., 2008). Effective P recovery methods from wastewater help mitigate eutrophication's environmental impacts and provide a sustainable solution for P reuse (Araújo et al., 2024; Bacelo et al., 2020). These methods include chemical precipitation, biological uptake, and advanced technologies such as enhanced biological P removal and struvite crystallization (Kataki et al., 2016). The reactions that control

the amounts of P in solution include dissolution–precipitation, adsorption–desorption, and the hydrolysis of organic matter (Haygarth et al., 2013; Hinsinger, 2001). Adsorption is a physicochemical process in which a molecule, the adsorbate, is adsorbed onto the solid surface of an adsorbent (Ali; Jain, 2005). Different studies have reported promising results in P removal from aqueous solutions using adsorbed waste/by-products material made of calcium oxides (Karasa et al., 2024; Kasprzyk et al., 2021; Bacelo et al., 2020). The implementation of these technologies can foster a circular bioeconomy in P use, reducing dependence on finite phosphate rock resources and contributing to environmental sustainability.

Increasing the lifespan of the world's P reserves lies in improving the nutrient use efficiency in agriculture, also recovering P from the environment, and making it available to plants. Once available to the plants, the efficient uptake and use of phosphorus fertilizers are the primary goals. However, several mechanisms influence P acquisition by plants during their initial growth, including root morphological attributes (Sun et al., 2021; Wen et al., 2019; Vance et al., 2003). Most of the phosphate fertilizer applied during crop sowing is adsorbed by the soil, so the direct supply of P to the seeds is efficient at preventing losses to the environment and optimizes its use (Sekiya; Yano, 2010). Applying fertilizers directly to seeds, either by coating them with adhesive polymers or by conditioning them as a priming technique, is common for micronutrients and pesticides, such as fungicides (Pedrini et al., 2017; Farooq et al., 2012), and can also be used for supplying fertilizers. The priming technique is a pre-sowing treatment that induces a physiological state that enables a more efficient seed germination process, with faster and synchronized germination and an improvement in the stand establishment (Lutts et al., 2016; Paparella et al., 2015). Normally based on seed imbibition, priming allows seeds to pass through the reversible stages of germination before radicle protrusion, once the seeds retain their desiccation tolerance and can be stored until final sowing.

Considering these aspects, this paper proposes a potential use for an iron-mining waste/by-product and introduces a possible new value-added fertilizer for society. In this study, we sought to remove P from an aqueous solution via an adsorption process onto a solid phase using calcium-iron (Ca/Fe) oxides synthesized from mining waste/by-product and directly used as a potential alternative fertilizer for maize (*Zea mays* L.), after material characterization. We expected that the germination and early growth stages of maize plants involve the interaction between root exudates and the adsorbed material, which promotes the desorption of phosphate from mining waste/by-product Ca/Fe oxides, enhancing phosphorus bioavailability in the rhizosphere, and supporting initial plant development. This study may provide a reference for

the practical application of synthesized alternative fertilizer made from Fe mining waste/by-product oxides in sustainable P removal and recovery, promoting plant initial development and nutrition.

2. Materials and methods

2.1. Local

The assays were performed at the laboratories and a greenhouse, at the Federal University of Viçosa, *Campus Florestal*, Minas Gerais, Brazil (19°53'22" S, 44°25'57" W, and 776 masl).

2.2. Adsorbent material synthesis

Mining waste mud from an iron ore by pellet-feed processing factory was used as an iron source to synthesize calcium oxides for phosphorus removal from aqueous solution. The raw material originates from the Germano industrial unit belonging to Samarco Mining Company in Mariana City, Minas Gerais, Brazil (20°22'41" S, 43°25'0" W, and 718 masl). The waste contains approximately 50% iron (Fe) oxides and 19% silica (SiO₂), with a density of 1.92 g cm⁻³ (Samarco Mining Company). The raw material was dried in an oven at 90 °C, finely ground using a mortar and pestle, and stored until the experiments began.

The synthesis of calcium oxide employed the wet impregnation method, following a proportion of 10% calcium, m/m (Ca/waste). Calcium nitrate tetrahydrate salt [Ca(NO₃)₂·4H₂O], purchased from *Êxodo Científica*[®], was used as a calcium source. The mass corresponding to the percentage of Ca was solubilized in 50 mL of deionized water under magnetic stirring. After complete solubilization of the salt, the dry waste was slowly added under stirring. The mixture was heated on a hotplate at 90 °C until completely dry. When magnetic stirring was no longer possible due to the formation of a lumpy sludge, the solid was kept in an oven at the same temperature before being stored in glass bottles. After drying, the solid was calcined at 900 °C for 1h, with a heating rate of 5 °C min⁻¹ in a Sanchis 1200 horizontal tubular furnace. The calcined materials were finely ground using a mortar and pestle, and this prepared adsorbent material was named ReFert, as a reference for the network project: ReFert – Promoting the Circular Bioeconomy from Residues to Fertilizers.

2.3. Characterization methods of adsorbent material

The synthesized materials were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Mössbauer spectroscopy to evaluate the influence of calcination

temperature on the formation of calcium ferrites, the basis for an alternative source of phosphate fertilizer. To characterize the surface of the synthesized materials, SEM images were provided using a FEG - Quanta 200 FEI scanning electron microscope. To analyze the compositional map of the materials, energy dispersive spectroscopy (EDS) was performed on the same device, with a 5 min analysis time per sample.

The synthesized materials were analyzed by XRD to determine the crystalline phases present. The diffractograms were obtained using the Shimadzu device, model: XRD-7000 X-RAY diffractometer, with continuous scanning copper tube radiation ($K_{\alpha 1} \lambda = 0.154 \text{ nm}$) and a scan range from 10° to 70° at 4° min^{-1} . The diffractograms were analyzed using the ProfEx program with the Crystallography Open Database (COD) database, and the diffractograms were plotted using the ORIGIN[®] program.

Using Mössbauer spectroscopy, the iron phases present in the samples were identified, and the hyperfine parameters were calculated. The Mössbauer spectra for ^{57}Fe were obtained at room temperature, with a $^{57}\text{Co}/\text{Rh}$ source, without constant acceleration. Hyperfine parameters and isometric deviations (IS) were calculated in the Normos program and calibrated according to Fe standards ($\alpha\text{-Fe}$). With continuous acceleration and ^{57}Co source in the Rhodium (Rh) matrix. In the measurements, sample holders with absorbers with around $10 \text{ mg of Fe cm}^{-2}$ were used.

2.4. Adsorption capacity tests

The adsorption tests were carried out in batches, in conical polypropylene tubes using 15 mg of material and 15 mL of phosphate solution at pH 6. The phosphate solution with an initial concentration (I_c) of $100 \text{ mg L}^{-1} \text{ KH}_2\text{PO}_4$ was prepared from a $1000 \text{ mg L}^{-1} \text{ KH}_2\text{PO}_4$ solution. The vials were kept under orbital shaking at 200 rpm for 24h at room temperature. Finally, the samples were centrifuged for 15 min at 3900 rpm and filtered through a $0.22 \mu\text{m}$ syringe filter. The equilibrium concentration (E_c) was determined by the ascorbic acid method described in Standard Methods for the Examination of Water and Wastewater (Clescerl et al., 1999), and readings were taken with λ of 880 nm in quartz cuvettes with an optical path of 1 cm. The phosphorus removal from aqueous solution per gram of sorbent was calculated using the equation $Q_e = [(C_0 - C_e) - M] \times V$, where C_0 is the initial concentration (mg L^{-1}) of phosphorus in the aqueous solution, C_e is phosphorus concentration in solution after adsorption, Q_e is phosphorus adsorbed per g of the sorbent (adsorption capacity), M is the mass (g) of the

sorbent, V is the volume of the aqueous solution (L) (Ajmal et al., 2018). From here, the P adsorbed material was named ReFertP.

2.5. Seed characterization, germination test, and priming methodology

Maize seeds (*Zea mays* L., cv. NS90) from *Nidera Sementes*[®] were used. Nidera NS90 is a cultivar for grain and silage production, with an early cycle, and recommended for cultivation in the central and southern regions of Brazil (www.niderasementes.com.br). These seeds were kept in Kraft packaging and stored in a refrigerator at ± 4 °C until the experiments began.

During all assays, the seeds were previously soaked in a 2.5% sodium hypochlorite (NaClO) solution (v/v) for 10 minutes and then triple-rinsed in deionized water. For orders of seed characterization, a germination test was carried out with five replications, each consisting of 25 seeds, arranged in transparent crystal polystyrene boxes (11.0 x 11.0 x 3.5 cm, gerboxes) on paper moistened with deionized water, and kept in a germination chamber, in a completely random design, with 25 °C (± 3 °C) temperature and 12h/12h photoperiod (Brasil, 2009). Seeds that had a protrusion of at least 2 mm from the embryonic axis were considered germinated. Germination counts were performed every 24 hours and were determined to be stable after four consecutive collections without changes. With this data, the germination percentage (G) was calculated (Maguire, 1962).

To determine the priming methodology, an imbibition curve assay was proposed, and water absorption by maize seeds was monitored in a completely random design, with five replications, each consisting of 20 seeds, placed in gerboxes, at room temperature (~ 25 °C ± 3 °C). The seeds from each repetition were previously weighed (initial weight), placed in gerboxes on a paper substrate, and moistened with deionized water. To monitor water absorption by the seeds, assessments were carried out every 1 h until rootlet protrusion occurred. The amount of water absorbed was calculated using the formula $WA = ((W_f - W_i) / W_i) \times 100$, where WA is the amount of water absorbed (%), W_i is the initial weight of the seeds (g), and W_f is the final weight in each time interval (g). The imbibition phases (Lutts *et al.*, 2016) were determined according to the time necessary for biomass stabilization, and the seed priming period was then determined. The seeds were placed under priming conditions for 12 hours, on an Ethik Technology shaking table, at 200 rpm.

2.6. Desorption tests, priming application, and seed coating

The influence of the germination process on the desorption of P present in ReFertP was investigated in a completely randomized experimental design test, with five replications, in a 2 x 3 x 4 factorial scheme, whose factors are the solution to humidify the seeds, deionized water and ReFertP solution, seed priming, non-priming (NP), hydropriming (HP), osmopriming (PP), and exposure times, 12h, 24h, 36h, and 48h, totaling 24 treatments and 120 experimental units. The water solutions were used to humidify the seeds with a 1mm layer at the bottom of the gerboxes, one consisting only of deionized water and the other obtained through a mixture of 15 mL of deionized water and 15 mg of ReFertP (1:1). The trials were set up with five replications, each replication consisting of 25 seeds, arranged directly on the surface of the germination box (gerbox) without filter paper, in a germination chamber, under temperature and photoperiod conditions determined by the RAS (Brasil, 2009). The seeds were packaged in Kraft paper and placed in an air-circulation oven until they reached a stable mass, after which they were weighed on a precision scale to obtain dry biomass data.

To evaluate the efficiency of ReFertP in supplying P during the initial establishment of maize seedlings, a second trial was performed in a completely randomized design, with 5 replications, in a 3 x 2 factorial scheme, with the factors being: seed priming (NP, HP, and PP) and humidifying solution (water or ReFertP), as previously described, totaling 6 treatments and 30 experimental units. The NP, HP, and PP seeds were placed in gerboxes, moistened with the two solutions, then transferred to the germination chamber under the conditions specified in the RAS (Brasil, 2009). After five days, fifteen seedlings from each replication were selected to measure the length of the roots and shoots, using a ruler graduated in cm. These seedlings were packaged in Kraft paper and taken to an air circulation oven until they reached a stable mass, when they were weighed on a precision scale, to obtain dry biomass data.

Priming conditioning and seed coating efficiency was verified in a trial performed in pots, in the greenhouse, with a randomized block design, factorial scheme (2 x 3) + 1, whose factors there are two sources of phosphate fertilizer (commercial fertilizer single superphosphate and ReFertP), applied in a concentration indicated for planting (Ribeiro *et al.*, 1999) and the management of phosphate fertilizer with 1) direct application to the soil, 2) priming, as previously described, and 3) coating the maize seeds with the aid of an adhesive polymer, plus the control, consisting of the seed without any conditioning and unamended and unfertilized soil. The soil was taken from the 0-20 cm layer from a field at the Federal University of Viçosa, *Campus Florestal*, with 63% clay, 20% silt, and 17% sand. The soil

samples were sieved at 2 mm. The chemical properties of the soil were determined: pH_{water} 5.7, P 3.6 mg dm⁻³, K 32 mg dm⁻³ (P e K - Mehlich-1), Ca^{2+} 3.21 cmol_c dm⁻³, Mg^{2+} 2.25 cmol_c dm⁻³, Al^{3+} 0 cmol_c dm⁻³ (Ca^{2+} , Mg^{2+} e Al^{3+} - KCl 1 mol L⁻¹), H+Al 2.64 cmol_c dm⁻³ (Calcium Acetate 0,5 mol L⁻¹ – pH 7,0). The 3 L pots were filled with a rock layer at the bottom, for water drainage, and filled to the top with soil. There will be thirty-five experimental units, arranged in 7 treatments. The seeds were sown in the pots, covered superficially with soil, and irrigated at 70% field capacity. Five days after emergence, thinning was carried out to leave only two plants per pot.

2.7. Seed coating

The seeds were covered with phosphate fertilizer sources (single superphosphate and ReFertP), at the concentration indicated for planting, according to (Ribeiro et al., 1999), to better adhesion to plant material, a commercial adhesive polymer, purchased from Likoseed Natural®, was used. For the ReFertP coating, the seeds were placed on filter paper, and their surfaces were sprayed with a solution (deionized water and polymer concentration according to the supplier's recommendation for maize seeds). The seeds sprayed with the polymer adhesive were immediately placed in a plastic container with a ReFertP and a commercial source of phosphate (single phosphate) and gently shaken to ensure adhesion on the seed surface. The seeds were air-dried at room temperature and protected from direct sunlight for sowing and evaluation.

2.8. Measurements of gas exchange

The maize plants in the greenhouse were evaluated at the V3 phenological stage, when the third leaf was fully expanded, and used to evaluate gas exchange analyses with an infrared gas analyzer [Infra Red Gas Analyzer (IRGA), Model Li-COR® 6400 XT, Lincoln, Nebraska, USA]. The net CO₂ assimilation measurements (A), stomatal conductance (g_s), transpiration (E), and intercellular CO₂ concentration (C_i) were evaluated in one plant per pot. The measurements were carried out during the morning, between 7 am and 11 am, and the light will be provided at a photosynthetic photon flux density (PPFD) of 1500 μmol m⁻² s⁻¹, with leaf area in (cm²), corrected according to the size of the leaf blade inside the chamber. The evaluations used a CO₂ control system (model 6400-01, Li-Cor Inc.), with a concentration of 400 μmol mol⁻¹, flow rate of 500 mmol s⁻¹, and block temperature of 28 °C.

2.9. Chlorophyll a fluorescence and chlorophyll measurements

The seedlings' shoots from each replication were collected, frozen in liquid nitrogen (N₂-liq), and stored in an ultra-freezer at -80 °C for quantification of photosynthetic pigments, using acetone (85% v/v) solution at 4 °C in the dark, using a spectrophotometer (Lichtenthaler, 1987). Chlorophyll *a* fluorescence was assessed using a portable fluorometer (FluorPen FP 100, Photon Systems Instruments, Brno, Czech Republic). Measurements were taken, and the variables described in Table 1S (Supplementary data) were calculated. Assessments of relative chlorophyll levels (total chlorophyll) were made using ClorofiLOG[®], a portable chlorophyll meter (Falker, Brazil), and obtained through the average of three measurements taken in the central portion of the leaf.

2.10. Morphological and nutritional analysis

After evaluating the photosynthetic variables, the evaluated plant was collected and separated into aerial parts (leaves and stems) and roots. The length of the shoot and root was measured using a graduated ruler (cm), and the stem diameter was measured with a digital caliper (mm). The number of leaves was counted, and the leaf area was measured using digital images and analyzed in ImageJ software (Schneider et al., 2012). Then, the plants were thoroughly cleaned in water and placed in a forced-air circulation oven until they reached a stable dry mass. Afterward, they were weighed on a precision digital scale. Soon after, the material was stored in a dry environment protected from the sun for nutritional analysis.

To determine the concentrations of P, Ca, and Fe by nitroperchloric digestion, 0.1 g of plant samples (seedlings and leaves) was reduced to particles smaller than 1 mm using a stainless-steel knife mill. Ten milliliters of a mixture of nitric acid (HNO₃) + perchloric acid (HClO₄) at a 4:1 ratio was added to this plant material inside a fume hood. The initial predigestion of the material was performed by adding HNO₃, and the mixture was left overnight for 12 h. The predigested material was moved to a digester block, and when it reached 95 °C, HClO₄ was added. Then, the temperature gradually increased until it reached 165 °C. When the extract reached a slightly yellowish crystalline color, the solution was removed from the digester block to cool, and then deionized water was added until the volume reached 25 mL (Malavolta et al., 1997). P was determined using the colorimetry method, according to Murphy and Riley (1962), and Fe and Ca were quantified by atomic absorption spectrometry (Malavolta et al., 1997).

2.11. Statistical analysis and experimental design

Statistical analyses were carried out using the R software (R Foundation for Statistical Computing, 2023). The normality and homogeneity of the data will be verified using the Shapiro-Wilk and Levene tests. If the normality of the data distribution was not proved, they were transformed with the most appropriate model. The data were subjected to ANOVA analysis of variance using the F test ($p < 0.05$). When the effects of the treatments are significant, the differences between the means were compared using the Tukey test ($p < 0.05$).

3. Results

3.1. Characterization of the adsorbent material

The sample R, corresponding to dry mining waste, presented an irregular surface, a complex morphology, and particles of varying sizes (Fig. 1 a). When the waste is calcined at 900°C for 1 hour, i.e., sample R900, the particle edges become more irregular (Fig. 1 b). ReFert samples were obtained when 10% Ca m/m is added to the surface of the material heat-treated at 900°C for 1h. In the ReFert sample, smaller particles were observed that were more rounded, had better-defined shapes, and appeared to be more strongly adhered to the surfaces of larger particles. Furthermore, the image shows a roughness on the surface of the sample (Fig. 1 c).

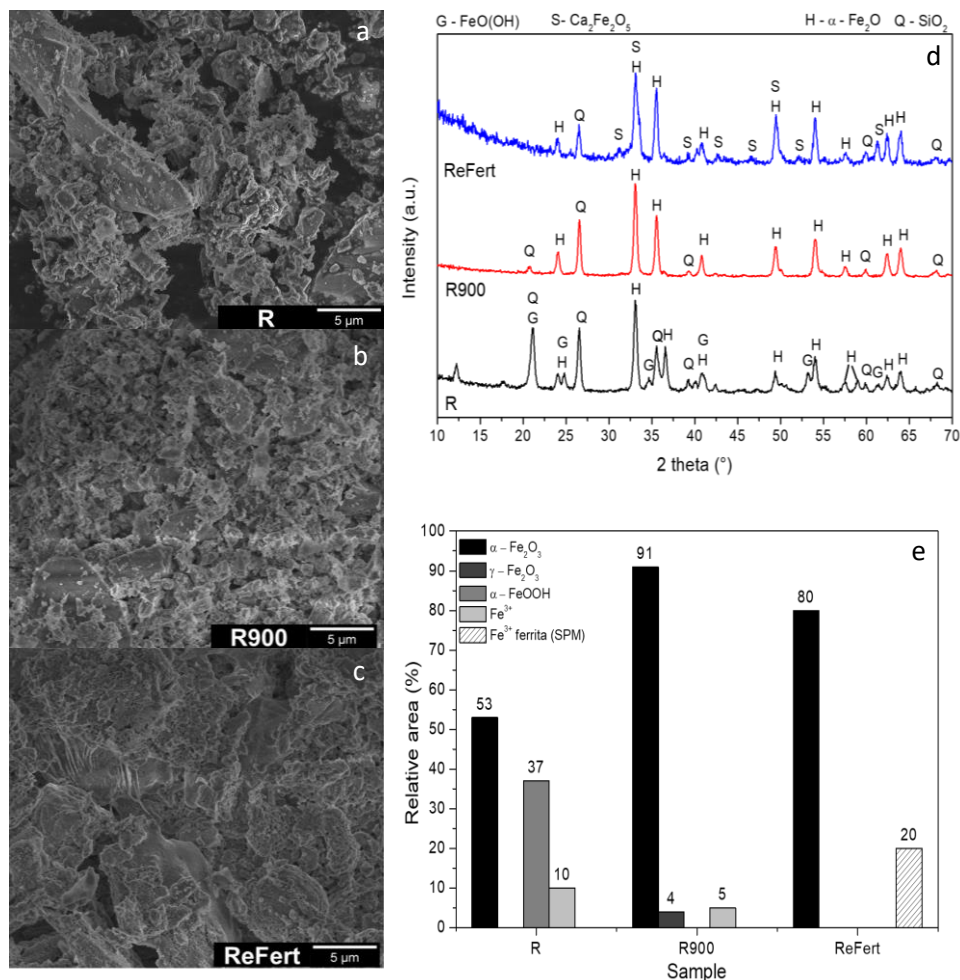


Figure 1 – SEM images at 10000x magnification for materials R, R900, and ReFert (a, b, c), XRD diffractograms obtained at room temperature for materials R, R900, and ReFert (d), Iron phase contents defined by the Mössbauer relative spectral area for materials R, R900, and ReFert (e).

The dry mining waste (sample R) presented diffraction peaks referring to the goethite phase (α -FeOOH – COD 040152898), which were observed at 2θ close to 24.71° ; 34.55° ; 36.51° ; 53.10° ; 58.99° ; 61.25° (Fig. 1 d). The silica phase (SiO_2 – COD 040084821) was observed with more prominent peaks at 2θ 26.58 and 34.57° . Peaks referring to hematite (α -Fe₂O₃ – COD 9002162) were also present at 2θ 21.15° ; 26.49° ; 40.73° ; 68.27° . After calcination, the sample R900 showed a diffractogram with finer and better-defined peaks (Fig. 1 d). The disappearance of peaks previously attributed to goethite (α -FeOOH – COD 040152898) was observed as an effect of heat treatment and loss of OH groups. Peaks referring to silica (COD 040084821) and hematite (COD 9002162) remained at the same 2θ values. The peaks attributed to the silica and hematite phases were observed, even after calcium addition in the ReFert material (Fig. 1 d). The diffractogram presented broader peaks, and new diffraction

peaks were observed, indicating the formation of a new crystalline phase. The calcium ferrite phase ($\text{Ca}_2\text{Fe}_2\text{O}_5$ – COD 9013469) can be identified with peaks at 2θ 39.2°; 42.4°; 52.1°; 61.2° and peaks at 2θ 33.05°; 40.83°, 54.03°, overlapping hematite peaks.

The hematite phase ($\alpha\text{-Fe}_2\text{O}_3$) with a relative area (RA) of 53%, goethite ($\alpha\text{-FeOOH}$) with RA of 37%, and Fe^{3+} dispersed with RA of 10% were observed, referring to dispersed iron particles present in the material (Fig. 1 e). The sample R900, which was calcined at 900 °C for 1 h, no longer shows the $\alpha\text{-FeOOH}$ phase; the material was mostly composed of hematite (RA 91%) and dispersed Fe^{3+} (RA 5%) (Fig. 1 e). In this sample, a new iron phase can be identified, maghemite ($\gamma\text{-Fe}_2\text{O}_3$) with RA of 4%. The ReFert adsorbent material was mostly composed of hematite (RA 80%); however, Fe^{3+} SPM, referring to calcium ferrite, can be observed with RA 20% (Fig. 1 e).

3.2. Adsorption capacity

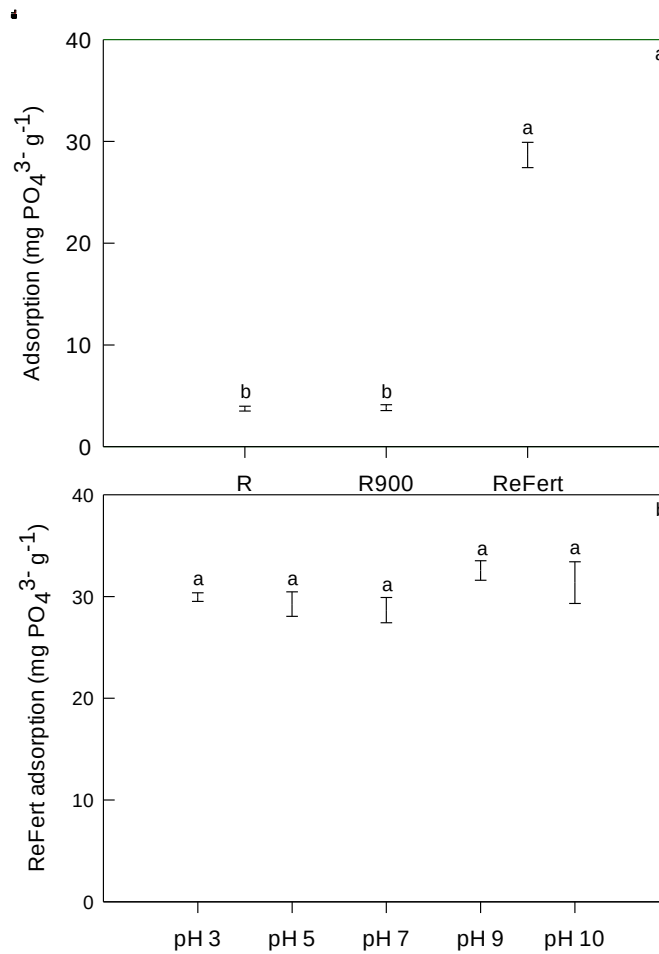


Figure 2 – Phosphate adsorption values (100 mg $\text{PO}_4^{3-} \text{L}^{-1}$ solution) for materials R, R900, and ReFert (a), ReFert phosphate adsorption values (100 mg $\text{PO}_4^{3-} \text{L}^{-1}$ solution) in different pH (3, 5, 7, 9, and 10) solutions (b).

The materials R and R900, composed of dry mining waste and calcined material, respectively, have an adsorption capacity of 3 mg g⁻¹ (Fig. 2 a). While ReFert material has a phosphate removal capacity close to 31 mg g⁻¹ (Fig. 2 a). After 24h, the results indicate that pH variation does not significantly alter the adsorption capacity of the material (Fig. 2 b).

3.3. Priming desorption strategy

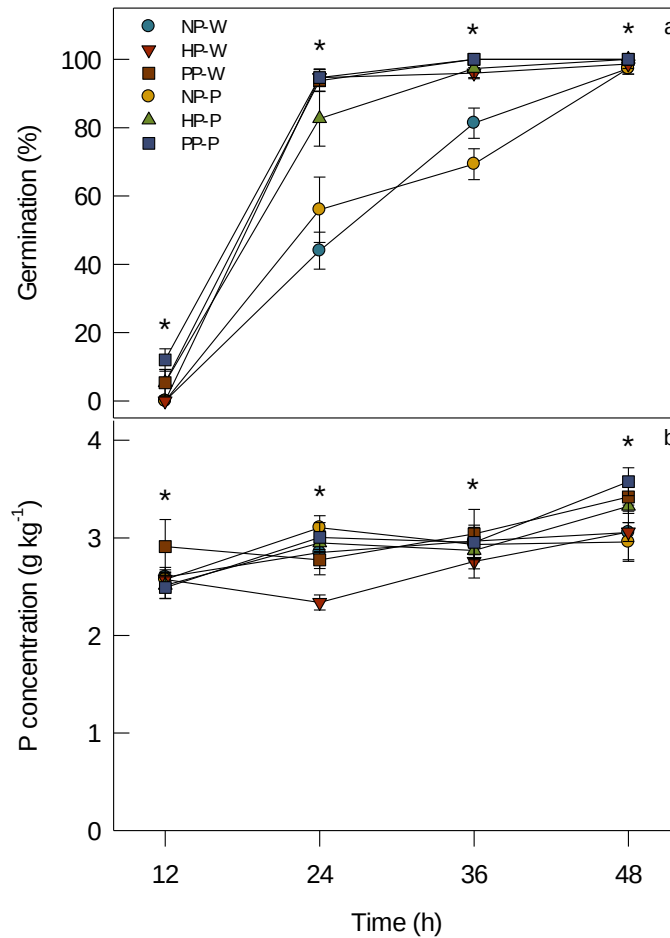


Figure 3 - Germination (%) and P concentration in maize (*Zea mays* L.) seeds over time. The treatments are in a completely randomized design, 2 x 3 x 4 factorial scheme, totaling 12 treatments, three seed conditioning, non-primed seeds (NP), hydroprimed seeds (HP), osmoprimed seeds with ReFertP (PP), two humidifying solutions, water (W) and solution with ReFertP 1:1 (P), and four-time evaluations 12 h, 24 h, 36 h and 48 h. The symbols represent 5 replications, and the bars represent standard errors for each treatment. * Indicate significant differences between treatments, according to Tukey's test ($p < 0.05$). Data on germination were transformed to $\arcsin \sqrt{(x)/100}$.

Germination and initial growth were investigated in maize seedlings by assays to verify the influence of the P source. The germination rate increases sharply between 12 to 24 hours for all treatments, reaching 100% at 36 hours for osmoprimed (PP) seeds, showing significant interaction between seed conditioning and germination time, since the non-primed seeds (NP) showed a lower germination rate over time concerning the other treatments (Fig. 3 a). Final germination was the same for all treatments, with 100, 100, and 98.7% for NP, PP, and hydroprimed (HP) seeds, respectively (Fig. 3 a).

The P concentrations range from 2.32 to 3.57 g kg⁻¹ across all treatments, showing no interaction (Fig. 3 b). A gradual increase in phosphorus concentration was observed across all treatments over time, starting at 12 h and reaching its peak at 48 hours, reflecting its role in supporting metabolic processes during germination. At 48 hours, the phosphorus environment showed maximum concentrations, reaching 2.93 g kg⁻¹ to NP seeds and 3.57 g kg⁻¹ to PP seeds.

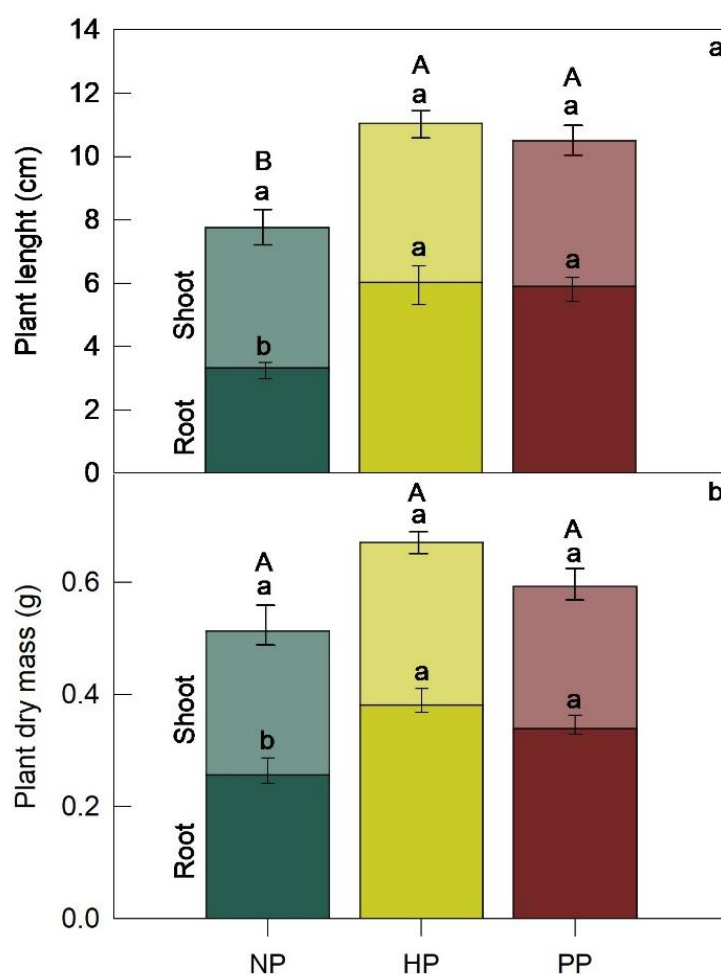


Figure 4 - Length of root and shoot (a), dry mass of root and shoot (b) of maize (*Zea mays* L.) seedlings at the end of 5 days. The treatments are characterized by three seed conditioning

methods: non-primed seeds (NP), hydroprimed seeds (HP), osmoprimed seeds with ReFertP (PP), germinated in gerboxes in germination chambers. The columns represent 5 replications, a compound of 10 seedlings, and the bars represent the standard errors of each treatment. Capital letters represent the plant's total length, with significant differences between treatments, and lowercase letters indicate significant differences between treatments, as determined by Tukey's test ($p < 0.05$). Data on the plant's total length were transformed to $1/\sqrt{x}$.

The total dry mass of maize seedlings, shoot dry mass, seed dry mass, and shoot length were the same for all seed conditioning treatments. However, seedlings whose seeds were submitted to priming (HP and PP) showed higher total length, root length, and root dry mass than non-primed (NP) seedlings (Fig. 4).

3.4. Seed coating desorption strategy

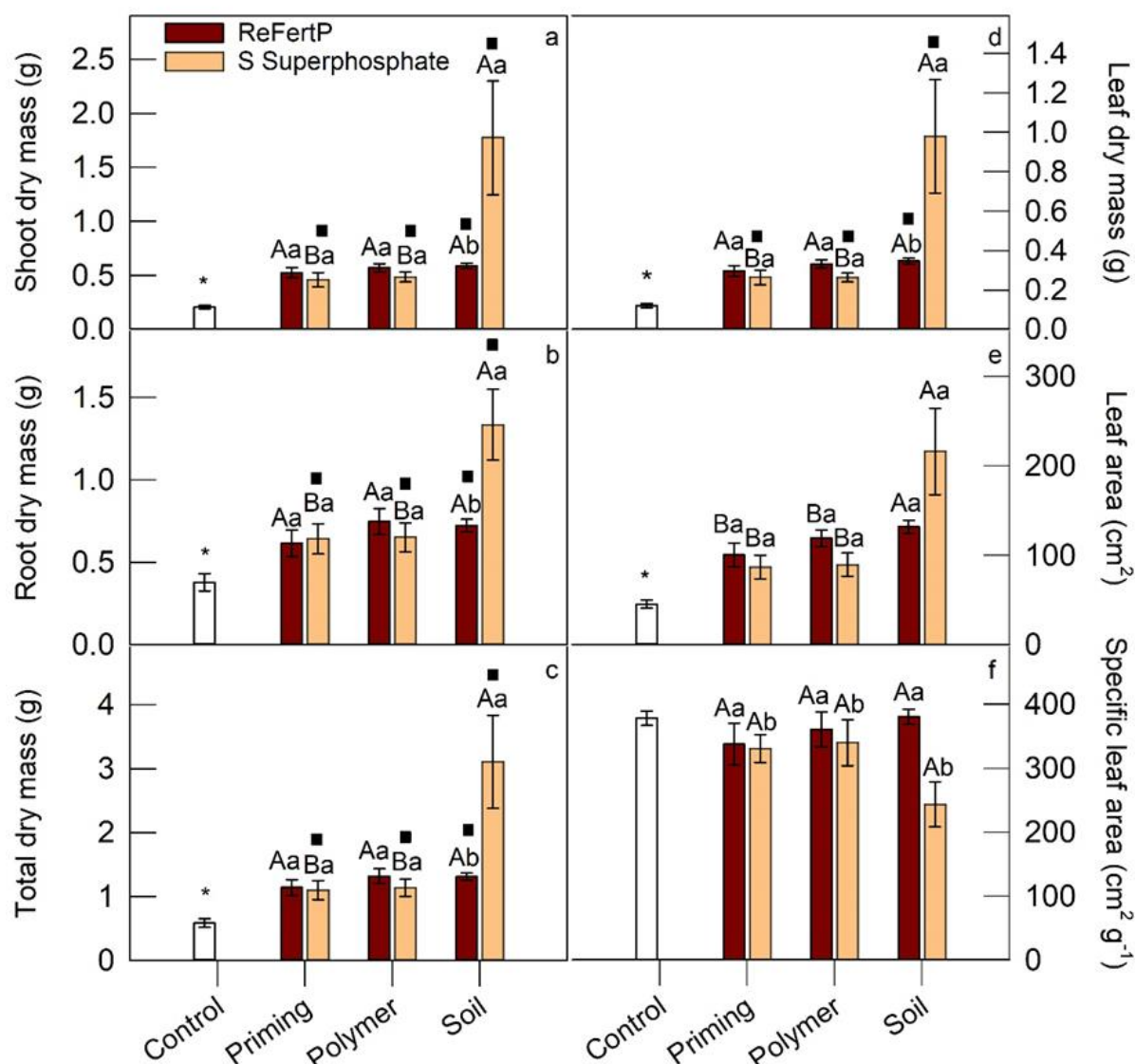


Figure 5 – Shoot (a), root (b), and total dry mass (c), leaf dry mass (d), leaf area (e), and specific leaf area (f) of maize plants (*Zea mays* L.) in V3. Treatments in a randomized block design, 3 x 2 + 1 factorial scheme, with three fertilizer supply methods (priming, polymer, and soil) and two sources of phosphorus (RefertP, and single superphosphate), and the control (without phosphate fertilizer). The columns represent 5 replications, and the bars represent the standard errors for each treatment. According to Tukey's test, capital letters indicate significant differences between fertilizer supply methods and lowercase letters indicate significant differences between phosphorus sources ($p < 0.05$). * Indicates interaction between Control and factors A x B. ■ Indicates interaction between factors A x B. Data on shoot dry mass (a), total dry mass (c), leaf dry mass (d), and leaf area (e) were transformed to $1/\sqrt{x}$.

At this point, we tried a different desorption strategy, when we prepared three seed phosphorus fertilizer supply forms (priming seed, polymer seed coating, and soil), with two phosphorus sources (ReFertP and single superphosphate), and the control (without phosphate fertilizer). The phosphorus fertilizer plants enhance plant growth compared to the control (Fig. 5). The dry mass yield was higher for the plants with phosphate fertilization using single superphosphate application directly to the soil (Fig. 5 a to d). The increase in leaf dry mass and area of single superphosphate soil plants suggests that this treatment improves leaf morphology for better photosynthetic performance (Fig. 5 e), resulting in the lowest specific leaf area too (Fig. 5 d to f).

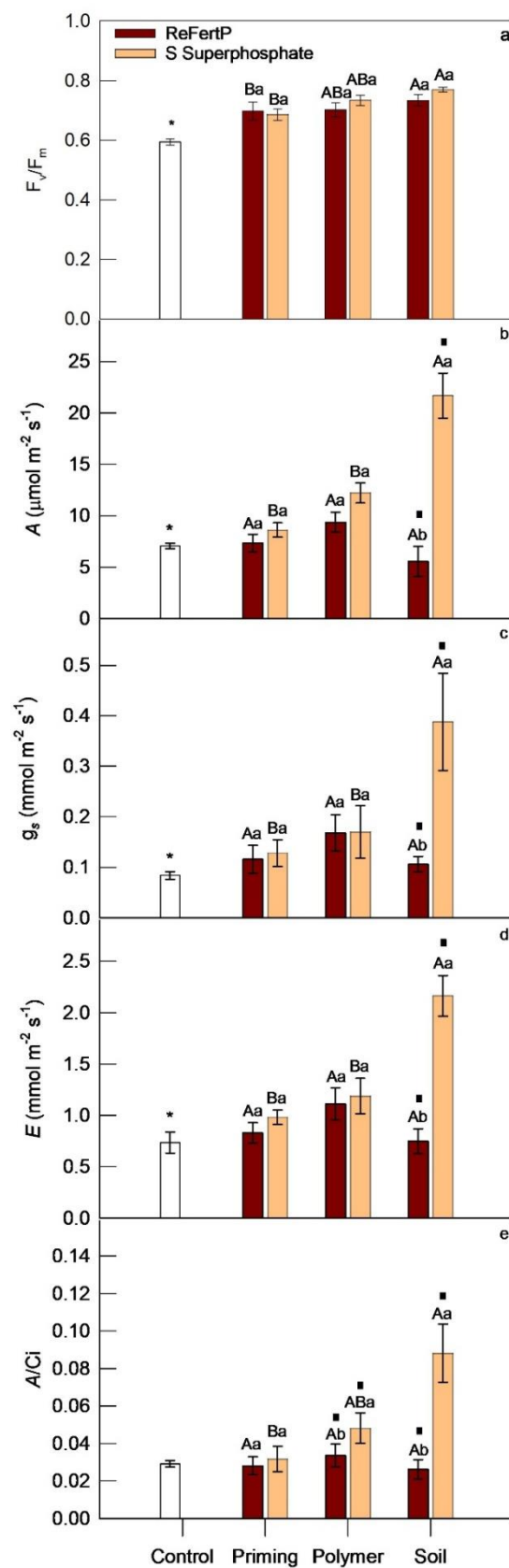


Figure 6 - Maximum quantum yield for PSII primary photochemistry - F_v/F_m (a), net photosynthetic rate – A (a), stomatal conductance (g_s), transpiration (E), and the ratio between A and internal CO_2 concentration (A/C_i) in leaves of maize plants (*Zea mays* L.) in V3. Treatments in a randomized block design, $3 \times 2 + 1$ factorial scheme, with three fertilizer supply methods (priming, polymer, and soil) and two sources of phosphorus (RefertP, and single superphosphate), and the control (without phosphate fertilizer). The columns represent 5 replications, and the bars represent the standard errors for each treatment. According to Tukey's test, capital letters indicate significant differences between fertilizer supply methods, and lowercase letters indicate significant differences between phosphorus sources ($p < 0.05$). * Indicates interaction between Control and factors A x B. ■ Indicates interaction between factors A x B. Data on F_v/F_m , g_s , and A/C_i were transformed to $1/\sqrt{(x)}$.

The low maximum PSII efficiency and the highest ΦD_0 showed by the control plants indicate possible stress due to phosphorus deficiency, since the values quantified for the phosphorus-fertilized plants were 0.83 for PSII, suggesting a better yield for these plants (Fig. S4 d; Fig. 6 a, b). Once again, for chlorophyll *a* fluorescence parameters the plants cultivated with P application directly in the soil stood out, followed by the plants that received the fertilizer via polymer and seeds conditioned by priming, no matter the P source (Fig. 6). However, when ReFertP was available via seed treatment, whether priming or polymer, it resulted in the same photosynthetic efficiency as plants fertilized with simple superphosphate, except for A/C_i (Fig. 6 e).

The P source form of application did not significantly affect the concentrations of iron 37(Fe) and calcium (Ca). However, an interaction in the case of P was observed (Fig. 7). The P concentration in plants fertilized with ReFertP promoted a superior or equivalent performance when compared to single superphosphate in all forms of application, especially when applied to the soil (Fig. 7 c).

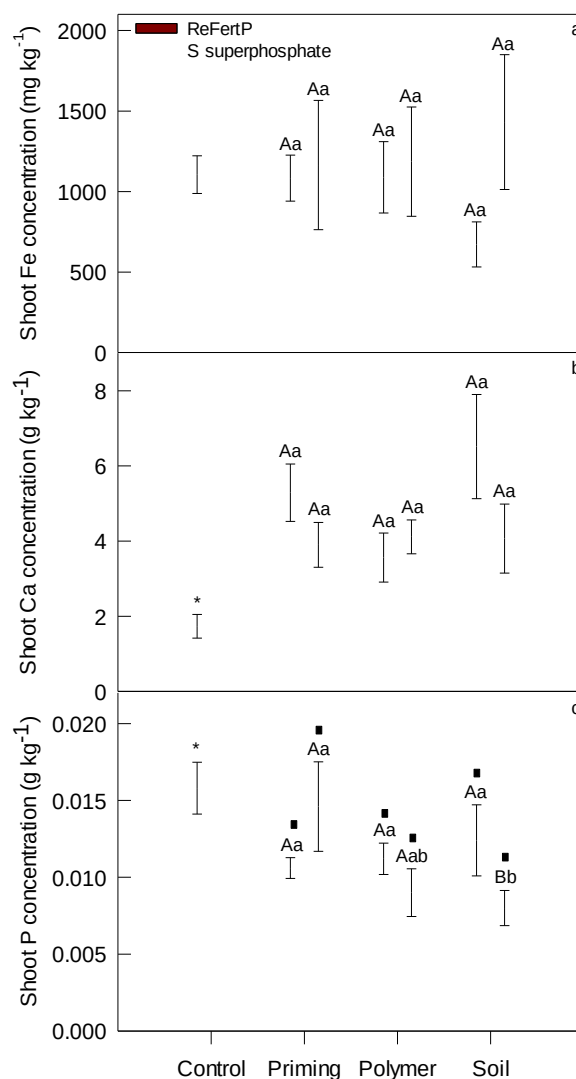


Figure 7 - The concentration of Fe (mg kg⁻¹), Ca (g kg⁻¹), and P (g kg⁻¹) in leaves of maize plants (*Zea mays* L.) in V3. Treatments in a randomized block design, 3 x 2 + 1 factorial scheme, with three forms of fertilizer application (priming, polymer, and soil) and two sources of phosphorus (RefertP and single superphosphate), and the control, without phosphate fertilizer. The columns represent 5 replications, and the bars represent the standard errors for each treatment. According to Tukey's test, capital letters indicate significant differences between fertilizer application methods, and lowercase letters indicate significant differences between phosphorus sources (p < 0.05). * Indicates the difference between Control and factors A x B. ■ Indicates interaction between factors A x B.

4. Discussion

The future of phosphorus (P) fertilizers lies in the possibility of recovering a significant proportion of the nutrient present in wastewater streams and returning these as fertilizers. We showed that the iron mining waste/by-products derived material can be used for P removal and can also be further be exploited as P-rich material for agricultural purposes, promoting a circular bioeconomy. We also demonstrated that the ease of operation and wide availability of the developed adsorbents made the adsorption process one of the most suitable for water treatment methods (Ali, 2012). This process promotes the sustainability of aquatic ecosystems and contributes to drinking water quality, which faces a severe challenge due to eutrophication of water bodies resulting from nutrient over-enrichment, such as P (McDowell; Haygarth, 2024).

The adsorbent chemical components, the size and shape of the adsorption sites, and the surface area interfere with the adsorption process (Wang et al., 2024; Wu et al., 2020). The greater irregularity of the edges of the waste mining material (R) upon heat treatment was possibly due to the loss of OH groups on the surface of the material and sintering processes occurring at high temperatures (Fig. 1 b). The calcination and calcium addition were efficient for calcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$) phase synthesis (Fig. 1 d). The calcium oxide material, ReFert, as indicated by XRD diffractograms and also by the small, rounded, and defined particles adhered to the surface of larger particles (Fig. 1 c and d). Mössbauer relative spectral area confirmed the results of the iron phases observed (Fig. 1 e). It indicated a relative area (RA) of 20% of Ca ferrites covering the adsorbent material, ReFert, with crystalline phases associated with phosphate removal.

The phosphate-removal capacity of the studied materials was confirmed by the adsorption tests. The adsorption capacity of the material was increased with the addition of Ca and heat treatment (Fig. 2 a). In addition to Ca, complementary EDS analysis and chemical mapping spectra showed that the elements iron (Fe), oxygen (O), silicon (Si), and aluminum (Al) were well distributed on the surface of the ReFert materials (Araújo et al., unpublished data). In addition to this study, iron oxide minerals, such as hematite (Fe_2O_3), goethite (FeOOH), and magnetite (Fe_3O_4), combined with alkaline metals such as Ca and Mg, have been utilized for phosphate adsorption in recent years (Araújo et al., 2024).

Other factors, such as pH, may change the adsorption capacity of the material and interfere with the P form. In solution, pH governs the phosphate dissociation equilibria in the solution, affects the strength of electrostatic attraction, and determines which phosphate species

are dominant at a certain pH (Nadagouda et al., 2024). In water, we can find different phosphate forms, especially orthophosphate (Wang et al., 2024). At pH 2.15, H_3PO_4 form is observed, H_2PO_4^- between pH 2.15 and 7.20, HPO_4^{2-} from pH 7.20 to 12, and PO_4^{3-} at pH values above 12 (Liu et al., 2018). The adsorbent material, ReFert, had the capacity to adsorb $31 \text{ mg PO}_4^{3-} \text{ g}^{-1}$ of $100 \text{ mg PO}_4^{3-} \text{ L}^{-1}$ solution at pH 6 (Fig. 2 b), an equal adsorption capacity of the different pH values, demonstrating that ReFert can be used to remove phosphate over a wide pH range. Iron oxides have a strong affinity for orthophosphate, which gives the adsorption process long-term stability. As a result, recovering orthophosphate is not easy and requires different strategies.

Although the plants take P in orthophosphate forms, H_2PO_4^- and HPO_4^{2-} , which occur in very low concentrations in the soil solution, the lower bioavailability is due to its adsorption or formation of complexes with metals such as Fe and Al, common in tropical soils and with high acidity (Haygarth et al., 2013; Syers et al., 2008; Essington, 2004). During germination and initial growth, root exudates of primary metabolites, such as sugars, organic acids, and amino acids (Sun et al., 2021), may contribute to accessing the P from the adsorbed material. Although all viable seeds had germinated within 24–48 hours (Fig. 3 a), the priming treatments affected the P content of the seedlings, particularly in those subjected to P-solution priming (Fig. 3 b). This initial measurement, 48 hours (Fig. 3 b), likely reflects the baseline phosphorus levels in the seeds before significant metabolic activity.

The priming technique is an effective tool, as it induces DNA repair processes and antioxidant system responses associated with pre-germination metabolism, reflecting on the homogeneity of germination and emergence, which also benefits the initial establishment of the plants in the field (Bhusal Thakur 2020). Despite the seedlings from the different treatments showing similar P concentrations after 5 days (approximately 4 g kg^{-1}), in all treatments (Fig. S1 c), the ReFertP-primed seedlings showed higher concentrations of Ca and Fe than the control and hydropriming seedlings (Fig. S1 a, b). These same seedlings also showed similar dry biomass (Fig. 4 b), but the total and root length of the seedlings from the priming seeds were longer (Fig. 4 a). Greater investment in roots may indicate a strategy to increase the efficiency of water and nutrient absorption, allowing the plants access to the nutrients in the environment. It is well-known that maize (*Zea mays* L.) and wheat (*Triticum aestivum* L.) plants showed greater investment in morphological changes of their roots during P deficiency in the soil, as compared to legumes such as broad bean (*Vicia faba*) (Lyu et al., 2016; Deng et al., 2014).

Although releasing phosphorus from Ca and Fe can be a slow process, it can form strong ionic interactions with these cations, constituting insoluble mineral-P complexes (Chen; Liao 2016). In addition to priming, adhesive polymers can optimize the plant's access to the nutrients. The adhesive polymers are applied through an aqueous solution to coat the seeds, without affecting germination, and to fix agrochemical products such as fertilizers in the plant material. In general, they have a high coverage rate and neutral pH, which increases their compatibility with different agrochemicals (Pedrini et al., 2017). This covering of seeds with fertilizers optimizes their availability, since diffusion is the main process by which P moves to the root surface (Syers et al., 2008). Despite the coverage with the polymer, all fertilized plants (i.e., except the control plants) showed similar root length (Fig. 2S b).

Phosphate fertilization is essential for plant growth and development, considering that non-fertilized control plants were not able to use the P present in the soil, showing lower productivity, especially in total dry biomass (Fig. 5 c). P fertilizer management lies in the knowledge of its solubility and its retention in the soil. Therefore, the input of phosphate fertilizers into the soil is important, but increasing P use efficiency is essential for agricultural productivity. The significant difference between single superphosphate and ReFertP at the soil treatment suggests that the former is more effective in promoting biomass accumulation under direct soil application (Fig. 5). A higher root biomass could indicate better nutrient and water uptake capabilities, particularly under soil fertilized with single superphosphate (Fig. 5 b).

Phosphorus plays a central role in photosynthesis through its requirement for phosphorylation and the exchange between the chloroplast and cytosol of triose phosphate (Dissanayaka et al., 2021). The supply of single superphosphate in the soil was effective in promoting photosynthetic activity, stomatal conductance, transpiration, and CO₂ use efficiency (Fig. 6). Furthermore, the material ReFertP, when applied directly to the soil, obtained lower performance, suggesting lower availability or efficiency in the P use for plants at this stage (Fig. 6 a). However, soluble P fertilizers could be inefficient because often only a small fraction is taken up in the year of application (Barrow et al., 2018).

5. Conclusions

The results of this study showed it was possible to synthesize the Ca/Fe oxide adsorbent material, ReFertP, from iron mining waste as a recyclable P-rich fertilizer. The ReFertP exhibited great phosphate adsorption capacity, maintaining efficiency across a wide pH range and confirming the formation of Ca–ferrite phases responsible for P removal. When applied as

an alternative P source, the adsorbed phosphorus released from ReFertP supported maize development during germination and early growth, achieving P concentrations comparable to those obtained with conventional fertilizers and, in some application modes, matching their physiological and morphological responses. Overall, this work advances circular bioeconomy strategies by transforming an abundant mining by-product into a value-added fertilizer, enabling P recovery, reducing dependence on finite phosphate rock reserves, and contributing to more sustainable nutrient management in agriculture.

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Supplementary Data

FROM MINING WASTE TO FERTILIZER: CALCIUM-IRON OXIDES FOR PHOSPHORUS RECOVERY AND EARLY MAIZE NUTRITION

Marina Mariá Pereira, Departamento de Biologia, Instituto de Ciências Naturais, Universidade Federal de Lavras (UFLA), 37200-900, Lavras, MG, Brasil.

<https://orcid.org/0000-0002-6959-0155>.

Matheus Henrique Pimentel Araújo, Instituto de Ciências Exatas e Tecnológicas, Universidade Federal de Viçosa – *Campus Florestal* (UFV), Florestal, Minas Gerais 35690-000, Brasil. <https://orcid.org/0000-0002-5081-4016>.

Elisa Monteze Bicalho, Instituto de Ciências Biológicas e da Saúde, Universidade Federal de Viçosa – *Campus Florestal* (UFV), Florestal, Minas Gerais 35690-000, Brasil.

<https://orcid.org/0000-0003-1746-0663>.

Juliana Cristina Tristão, Instituto de Ciências Exatas e Tecnológicas, Universidade Federal de Viçosa – *Campus Florestal* (UFV), Florestal, Minas Gerais 35690-000, Brasil.

<https://orcid.org/0000-0001-5226-8381>.

Eduardo Gusmão Pereira, Instituto de Ciências Biológicas e da Saúde, Universidade Federal de Viçosa – *Campus Florestal* (UFV), Florestal, Minas Gerais 35690-000, Brasil.

Corresponding author: egpereira@ufv.br. <https://orcid.org/0000-0001-5660-2949>.

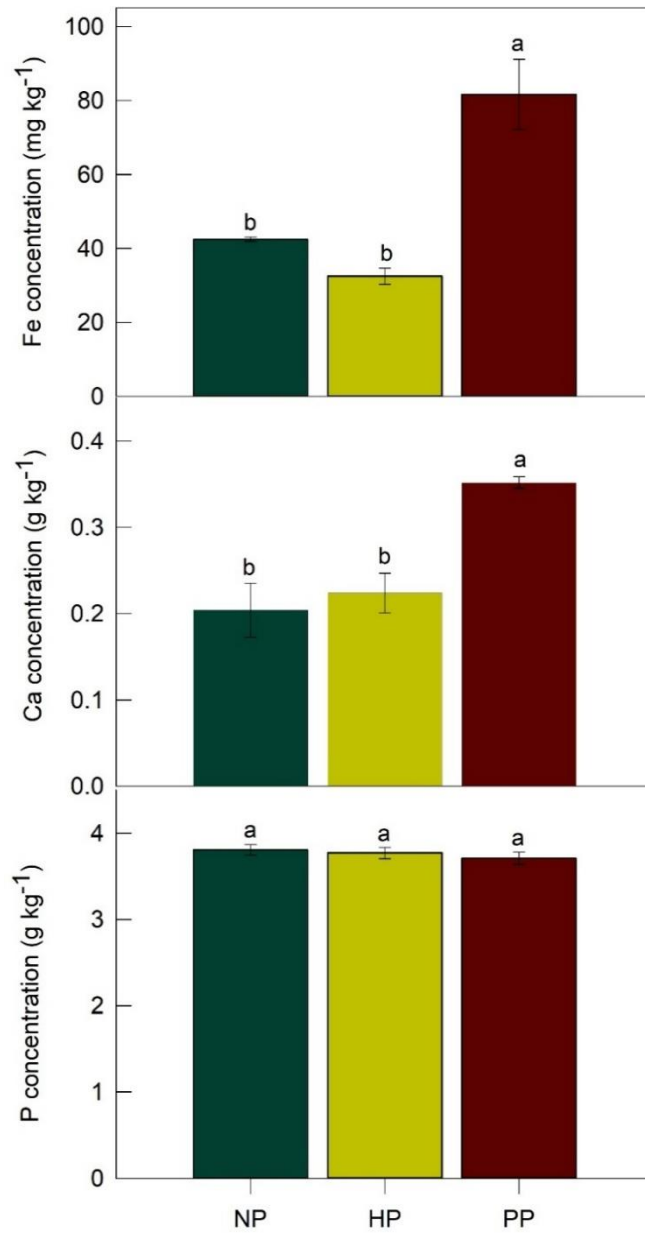


Figura S1. The concentration of Fe (mg kg⁻¹), Ca (g kg⁻¹), and P (g kg⁻¹) in maize (*Zea mays* L.) 5-day seedlings. The treatments are characterized by three seed conditioning methods: non-primed seeds (NP), hydroprimed seeds (HP), osmoprimed seeds with ReFertP (PP), germinated in gerboxes in germination chambers. The columns represent 5 replications, a compound of 10 seedlings, and the bars represent the standard errors of each treatment. Capital letters represent the plant's total length, with significant differences between treatments, and lowercase letters indicate significant differences between treatments, as determined by Tukey's test ($p < 0.05$).

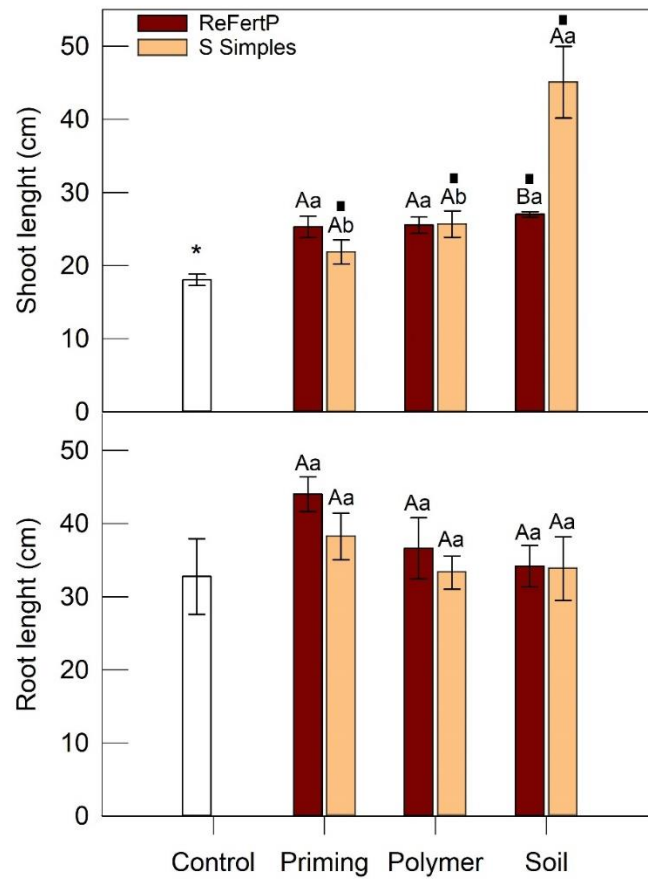


Figura S2. Shoot and root length (cm) of maize plants (*Zea mays* L.) in V3. Treatments in a randomized block design, 3 x 2 + 1 factorial scheme, with three fertilizer supply methods (priming, polymer, and soil) and two sources of phosphorus (RefertP, and single superphosphate), and the control (without phosphate fertilizer). The columns represent 5 replications, and the bars represent the standard errors for each treatment. According to Tukey's test, capital letters indicate significant differences between fertilizer supply methods, and lowercase letters indicate significant differences between phosphorus sources ($p < 0.05$). * Indicates interaction between Control and factors A x B. ■ Indicates interaction between factors A x B. Data on the plant's shoot and length were transformed $1/\sqrt{x}$.

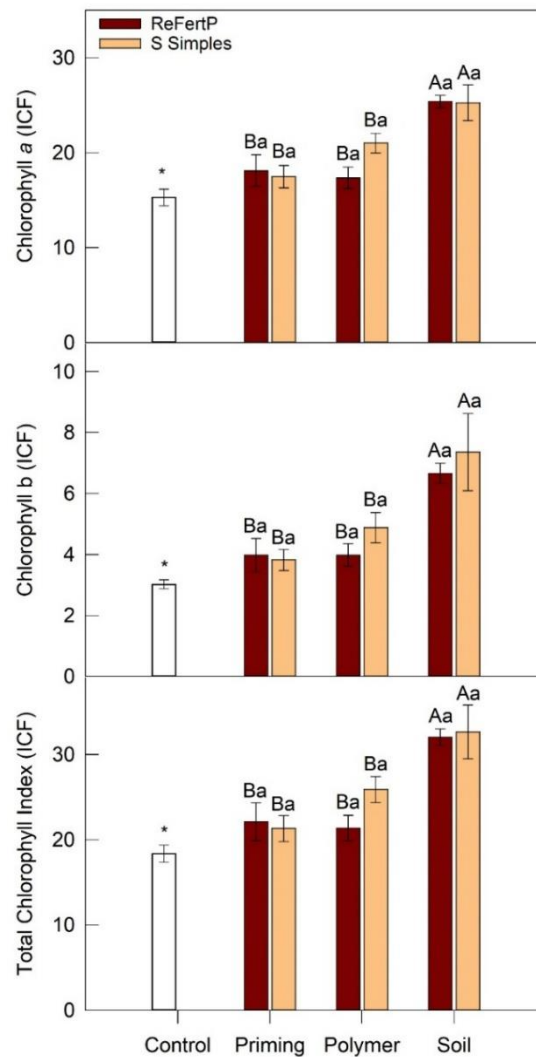


Figure S3. Chlorophyll *a*, Chlorophyll *b*, and Total Chlorophyll index in leaves of maize plants (*Zea mays* L.) in V3. Treatments in a randomized block design, 3 x 2 + 1 factorial scheme, with three fertilizer supply methods (priming, polymer, and soil) and two sources of phosphorus (RefertP, and single superphosphate), and the control (without phosphate fertilizer). The columns represent 5 replications, and the bars represent the standard errors for each treatment. According to Tukey's test, capital letters indicate significant differences between fertilizer supply methods, and lowercase letters indicate significant differences between phosphorus sources ($p < 0.05$). * Indicates interaction between Control and factors A x B. ■ Indicates interaction between factors A x B. ICF – Falker Chlorophyll Index.

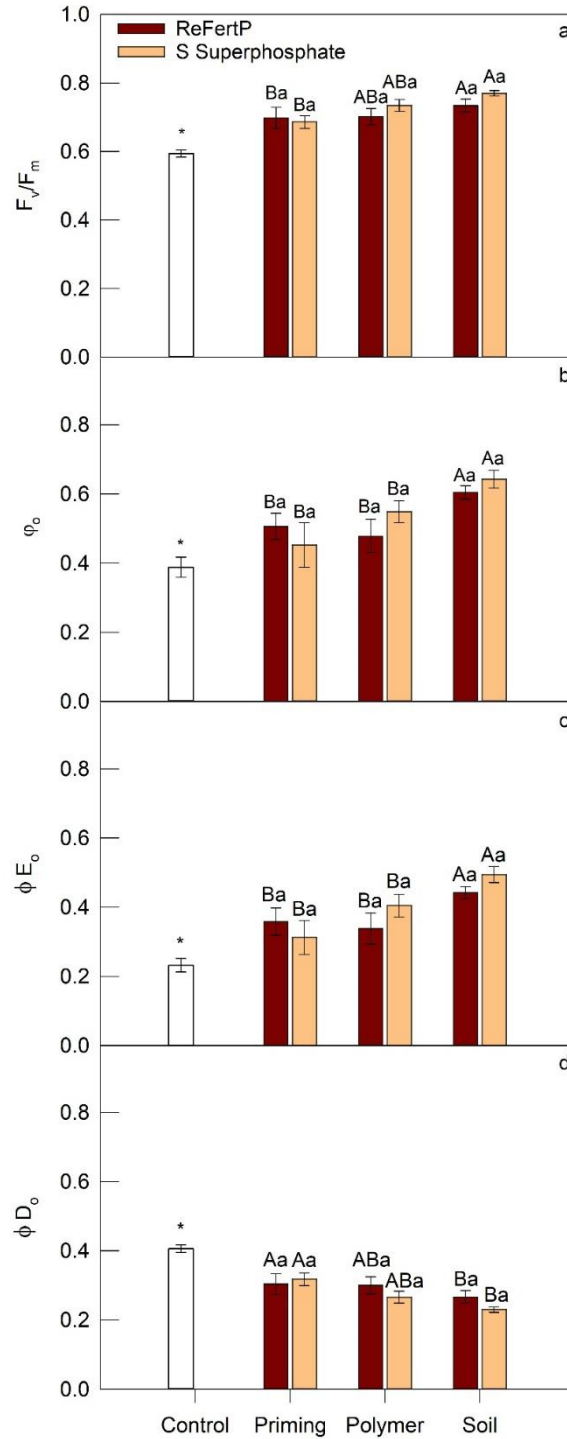


Figure S4. Energy flow absorbed per active RC unit (ABS/RC), excitation energy flow captured (reduced QA) per active RC unit at the beginning of the illumination of a dark-adapted sample (at $t = 0$) (TRo/RC), flow of electrons transferred per unit of active RC (at $t = 0$) (ETo/RC), total energy dissipated as heat, fluorescence and energy transfer to the PSI (in $t = 0$), per unit of active RC (DIO/RC) in leaves of maize plants (*Zea mays* L.) in V3. Treatments in a

randomized block design, $3 \times 2 + 1$ factorial scheme, with three fertilizer supply methods (priming, polymer, and soil) and two sources of phosphorus (RefertP, and single superphosphate), and the control (without phosphate fertilizer). The columns represent 5 replications, and the bars represent the standard errors for each treatment. According to Tukey's test, capital letters indicate significant differences between fertilizer supply methods, and lowercase letters indicate significant differences between phosphorus sources ($p < 0.05$). * Indicates interaction between Control and factors A x B. ■ Indicates interaction between factors A x B.

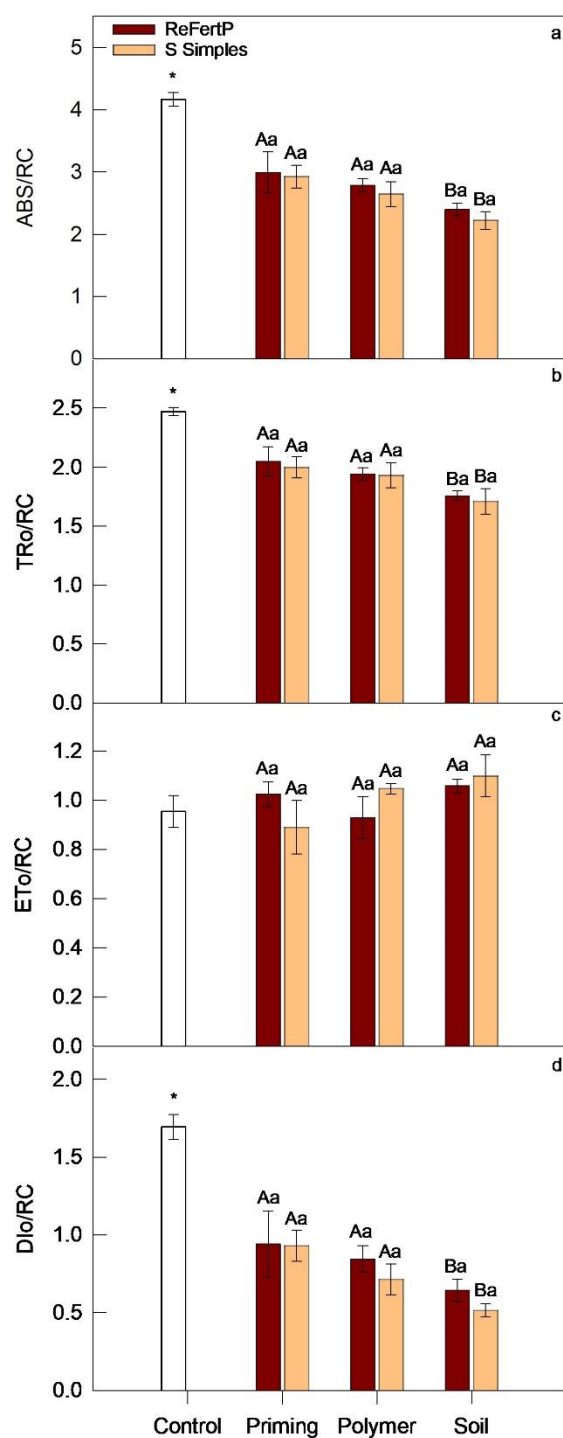


Figure S5. Maximum quantum yield for PSII primary photochemistry (F_v/F_m , a), probability of electron transport after reduction of QA^- (at $t = 0$) (Ψ_o , b), quantum efficiency for the transfer of electrons from QA^- to the electron transport chain (at $t = 0$) (ΦE_o , c), quantum efficiency for energy dissipation (at $t = 0$) (ΦD_o , d) in leaves of maize plants (*Zea mays* L.) in V3. Treatments in a randomized block design, $3 \times 2 + 1$ factorial scheme, with three fertilizer supplies' methods

(priming, polymer, and soil) and two sources of phosphorus (RefertP, and single superphosphate), and the control (without phosphate fertilizer). The columns represent 5 replications, and the bars represent the standard errors for each treatment. According to Tukey's test, capital letters indicate significant differences between fertilizer supply methods, and lowercase letters indicate significant differences between phosphorus sources ($p < 0.05$). * Indicates interaction between Control and factors A x B. Data on F_v/F_m (a) were transformed to $1/(x)$, and ΦD_o (d) were transformed to $1/\sqrt{(x)}$.

Table S1. Equations and definitions of the variables OJIP obtained from chlorophyll a fluorescence emission analyses (OJIP) according to (Strasser; Tsimilli-Michael; Srivastava, 2004).

Variables	Name and Description
$F_v/F_m = \Phi P_o = TR_o/ABS = [1 - (F_o/F_m)]$	Maximum quantum yield for PSII primary photochemistry
$\Psi_o = ET_o/TR_o = (1 - V_j)$	Probability of electron transport after reduction of Q_A^- (at $t = 0$)
$\Phi E_o = ET_o/ABS = [1 - (F_o/F_m)] * \psi_o = \Phi P_o * \Psi_o$	Quantum efficiency for the transfer of electrons from Q_A^- to the electron transport chain (at $t = 0$)
$\Phi D_o = 1 - \phi P_o = (F_o/F_m)$	Quantum efficiency for energy dissipation (at $t = 0$)
Specific energy flows	By active reaction centers (RCs) of PSII
ABS/RC	Energy flow absorbed per active RC unit
TR _o /RC	Excitation energy flow captured (reduced Q_A^-) per active RC unit at the beginning of the illumination of a dark-adapted sample (at $t = 0$)
ET _o /RC	Flow of electrons transferred per unit of active RC (at $t = 0$)
DI _o /RC	Total energy dissipated as heat, fluorescence, and energy transfer to the PSI (in $t = 0$), per unit of active RC

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Authors:	Marina Mariá Pereira Matheus Henrique Pimentel Araújo Kaoutar Benghzial Laura Melo Fernandes Moreira Adnane Beniaich Hudson Wallace Pereira de Carvalho Juliana Cristina Tristão Eduardo Gusmão Pereira
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CHAPTER II

TRANSFORMING IRON MINING BY-PRODUCTS INTO SOIL AMENDMENTS TO ENHANCE PHOSPHORUS AVAILABILITY IN ALKALINE SOILS

Marina Mariá Pereira, Departamento de Biologia, Instituto de Ciências Naturais, Universidade Federal de Lavras (UFLA), 37200-900, Lavras, MG, Brasil, <https://orcid.org/0000-0002-6959-0155>;

Matheus Henrique Pimentel Araújo, Instituto de Ciências Exatas e Tecnológicas, Universidade Federal de Viçosa – *Campus Florestal* (UFV), Florestal, Minas Gerais, 35690-000, Brasil, <https://orcid.org/0000-0002-5081-4016>;

Kaoutar Benghzial, Agricultural Innovation and Technology Transfer Center (AITTC), College of Agriculture and Environmental Sciences, Mohammed VI Polytechnic University (UM6P), Lot 660, Hay Moulay Rachid, Ben Guerir, 43150, Morocco, <https://orcid.org/0000-0001-8368-7554>;

Laura Melo Fernandes Moreira, Instituto de Ciências Exatas e Tecnológicas, Universidade Federal de Viçosa - *Campus Florestal* (UFV), Florestal, Minas Gerais, 35690-000, Brasil, <https://orcid.org/0009-0003-2962-6867>;

Adnane Beniaich, Agricultural Innovation and Technology Transfer Center (AITTC), College of Agriculture and Environmental Sciences, Mohammed VI Polytechnic University (UM6P), Lot 660, Hay Moulay Rachid, Ben Guerir, 43150, Morocco, <https://orcid.org/0000-0002-0381-0610>;

Hudson Wallace Pereira de Carvalho, Centro de Energia Nuclear na Agricultura (CENA), Universidade de São Paulo (USP), Piracicaba, São Paulo, 13416-000, Brasil, <https://orcid.org/0000-0003-0875-3261>;

Juliana Cristina Tristão, Ciências Exatas e Tecnológicas, Universidade Federal de Viçosa - *Campus Florestal* (UFV), Florestal, Minas Gerais, 35690-000, Brasil, <https://orcid.org/0000-0001-5226-8381>;

Eduardo Gusmão Pereira, Instituto de Ciências Biológicas e da Saúde, Universidade Federal de Viçosa - *Campus Florestal* (UFV), Florestal, Minas Gerais 35690-000, Brasil, <https://orcid.org/0000-0001-5660-2949>. Corresponding author: egpereira@ufv.br.

HIGHLIGHTS

- P adsorption capacity of ReFertP results from Ca/Fe structural synergy.
- P release of ReFert and ReFertP is gradual and strongly modulated by root activity.
- ReFertP gradual P release sustains initial plant growth.

ABSTRACT

Technological challenges associated with nutrient management reinforce the importance of strategies to support a circular P economy. This study aims to demonstrate that iron (Fe) mining by-products enriched with calcium (Ca) can be transformed into efficient P adsorbent materials and subsequently used as slow-release fertilizers in alkaline soils. Ca/Fe oxides adsorbent materials were synthesized from Fe mining residues by calcination and Ca impregnation, characterized using SEM–EDS and batch P-adsorption assays to obtain the P sorbed material, ReFertP. A greenhouse pot experiment was then conducted in alkaline soil using ryegrass (*Lolium multiflorum* Lam.) to compare four treatments: Control (without P source), triple superphosphate (TSP), ReFert (Ca/Fe oxide without P adsorption), and ReFertP (after P adsorption). Ryegrass plants were grown for 126 days and sampled across six harvests to assess biomass production, leaf traits, leaf P concentration, and P uptake. The synthesized material, ReFertP, exhibited higher P adsorption capacity than its Ca-free precursor, R900. TSP supplied immediately soluble P, resulting in biomass accumulation. We observed a slow release from ReFertP and ReFert interacting with and mobilizing native soil P. ReFert significantly enhanced plant P accumulation and biomass production (Fig. 3 and 4), even under low rhizospheric P availability (Fig. 2), demonstrating that the material can adsorb phosphate from the soil solution and gradually redistribute it through the rhizosphere. ReFert would be a multifunctional material capable of simultaneously acting as a P sink and a regulated P source, contributing to circular nutrient management by converting mining residues into value-added fertilizers.

Keywords: Alkaline Soils; Phosphorus Use Efficiency; Mining Waste Recycling; Phosphorous Adsorption; Slow-release Fertilizers.

1. Introduction

Phosphorus (P) is an essential nutrient for plant growth and development. Therefore, an adequate P supply is a crucial factor of plant quality and agricultural productivity. Ultimately, this P may lead to the eutrophication of lakes, rivers, and oceans, characterized by the uncontrolled proliferation of harmful algae and cyanobacteria, which deplete dissolved oxygen, impair light penetration, and ultimately cause the mortality of fish and other aquatic organisms

(McDowell; Haygarth, 2024; Smil, 2000). Even P fertilization in crop fields has far exceeded crop P use, leading to P excess in 70% of the world's cropland. However, only a small fraction of the soil P is available to plant roots in the soil solution, as it is quickly adsorbed and immobilized onto soil particle surfaces, thereby increasing costs instead of a proportional gain of productivity (Madison et al., 2023; Shen et al., 2011; Cordell et al., 2009; Vance et al., 2003).

Adsorption-desorption process is widely recognized as the primary mechanism regulating the retention and release of dissolved P on variably charged surface sites of soil constituents (Gérard, 2016). The P availability to plants is determined by: the spatial distribution and acquisition of P, which are influenced by root system architecture and mycorrhizal associations; and the bioavailability and uptake of P, which are regulated by chemical and biological interactions within the rhizosphere (Shen et al., 2011; Lambers et al., 2006). The rhizosphere processes, such as increased frequency and length of root hairs, root-induced changes in pH or redox potential, and root exudate release, play an essential role in nutrient acquisition (Lambers et al., 2006; Marschner, 1998). The use of innovative techniques, such as root traps or high-resolution imaging approaches, designed to capture and visualize root-soil interactions, has been increasingly used to unravel the mechanisms of P availability from emerging materials, thereby improving our knowledge of how plants access, mobilize, and ultimately acquire sorbed phosphorus (Li et al., 2024; Wang et al., 2016)

The maintenance of adequate P availability in the rhizosphere enhances the efficiency of root systems in mobilizing and acquiring P from the soil, as a result of the combined action of morphological and physiological adaptive strategies (Shen et al., 2011). Under acidic soil conditions, P released may be quickly immobilized on iron (Fe) and aluminum (Al) mineral surfaces or even be released (Gérard, 2016). Conversely, in calcareous soils, P availability and mobilization by plants are limited mainly by sorption and precipitation reactions, due to high calcium carbonate (CaCO_3) levels and high pHs (Qetrani et al., 2025). Plant P uptake and crop yield are influenced by the P source applied, as well as by the physicochemical properties of the soil. Nevertheless, there is a lack of how different P sources influence rhizosphere processes and, consequently, P utilization by plants in alkaline soils.

The emergence of P adsorbent materials, especially derived from iron mining waste, as a promising technology for recovering P from wastewater offers environmental remediation and resource recovery benefits (unpublished data from chapter 1). Converting these Fe-rich wastes into value-added sorbent materials aligns with the principles of reuse and regeneration, playing a crucial role in supporting a circular economy (Matei et al., 2022). Recent studies have

demonstrated that calcium (Ca) and Fe adsorbent materials derived from wastes/by-products showed high P adsorption capacity and can effectively remove P from aqueous systems (Araújo et al., 2024; Bacelo et al., 2020; Karasa et al., 2024; Kasprzyk et al., 2021). By integrating P removal, recovery, and reuse, such technologies decrease the reliance on non-renewable phosphate rock, mitigate environmental pollution, and contributing to the development of sustainable fertilizers, reinforcing the transition toward a circular and bio-based phosphorus economy.

This study examined the use of a P adsorption agent synthesized from mining waste material as a potential phosphate fertilizer when applied to alkaline soils. It is hypothesized that P adsorbed onto the alternative P-source from mining waste will be gradually desorbed in alkaline soil, following a controlled-release mechanism governed by the interactions with the soil ions in the rhizosphere of ryegrass plants (*Lolium multiflorum* Lam.). A gradual desorption is expected to sustain a moderate yet continuous increase in soil P availability, enhancing P acquisition and utilization efficiency by plants. Furthermore, the controlled release of P from the alternative source could promote higher P use efficiency in plants compared with soluble P fertilizer, as a result of lower fixation losses and synchronization between P release and plant demand.

2. Materials and methods

2.1. Local

The assays were performed at the laboratories and a greenhouse, at the Federal University of Viçosa (UFV), *Campus Florestal*, Minas Gerais, Brazil (19°53'22" S, 44°25'57" W, and 776 masl) and the Mohammed VI Polytechnic University (UM6P) in Ben Guerir city, Morocco (32°13'6" N, 7°52'43" W, and 449 masl).

2.2. Adsorbent material synthesis

Mining waste mud from an iron ore by pellet-feed processing factory was used as an iron source to synthesize calcium oxides for phosphorus removal from aqueous solution. Raw material originates from the Germano industrial unit belonging to Samarco Mining Company in Mariana City, Minas Gerais, Brazil (20°22'41" S, 43°25'0" W, and 718 masl). The waste contains approximately 50% iron (Fe) oxides and 19% silica (SiO₂), with a density of 1.92 g cm⁻³ (Samarco Mining Company). This raw material was dried in an oven at 90 °C, finely ground using a mortar and pestle, and calcined at 900 °C for 1h, with a heating rate of 5 °C min⁻¹.

¹ in a Nabertherm muffle furnace at UM6P. The calcined material was finely ground, and this prepared adsorbent material was named R900.

The calcium oxide synthesis was performed by the wet impregnation method, with a 10% calcium loading (Ca/waste, m/m) at the UFV laboratory. Calcium nitrate tetrahydrate salt [Ca(NO₃)₂·4H₂O], purchased from *Êxodo Científica*®, was used as a Ca source. The mass corresponding to the percentage of Ca was solubilized in deionized water under magnetic stirring in 50 mL of distilled water. After complete solubilization of the salt, slowly, and under stirring, the dry waste was added. The mixture was heated on a hot plate at 90 °C until completely dry. When magnetic stirring was no longer possible due to the formation of a lumpy sludge, the solid was kept in an oven at the same temperature before being stored in glass bottles. After drying, the solid was calcined at 900 °C for 1h, with a heating rate of 5 °C min⁻¹ in a Sanchis 1200 horizontal tubular furnace. The calcined materials were finely ground using a mortar and pestle, and this prepared adsorbent material was named ReFert as a reference for the research network ReFert: Promoting the Circular Bioeconomy from Residues to Fertilizers.

2.3. Phosphorus adsorption capacity test

The R900 and ReFert materials adsorbed phosphorus (P) in batches, using conical polypropylene tubes, using 50 mg of material and 50 mL of phosphate solution at pH 6. The phosphate solution with an initial concentration (I_c) of 100 mg L⁻¹ KH₂PO₄ was prepared from a 1000 mg L⁻¹ KH₂PO₄ solution. The vials were kept under orbital shaking at 200 rpm for 24h at room temperature (23 °C). Finally, the samples were centrifuged for 15 min at 3900 rpm and filtered through a 0.22 µm syringe filter. The equilibrium concentration (E_c) was determined using the ascorbic acid method described in Standard Methods for the Examination of Water and Wastewater. Readings were taken on a Thermo Scientific GENESYS spectrophotometer with a wavelength (λ) of 880 nm in quartz cuvettes with an optical path of 1 cm. The P removal from aqueous solution per gram of sorbent was calculated using the equation $Q_e = [(C_0 - C_e) - M] \times V$, where C₀ is the initial concentration (mg L⁻¹) of P in the aqueous solution, C_e is P concentration in solution after adsorption, Q_e is P adsorbed per g of the sorbent (adsorption capacity), M is the mass (g) of the sorbent, V is the volume of the aqueous solution (L) (Ajmal et al., 2018). Hereafter, the P adsorbed materials were named R900P and ReFertP.

2.4. Characterization methods for the adsorbent material

The P sorbent and sorbed materials, R900, R900P, ReFert, and ReFertP, were characterized by scanning electron microscopy (SEM) to evaluate the formation of calcium

ferrites and P adsorption. To characterize the surface of the synthesized materials, SEM images were provided using a TESCAN Integrated Mineral Analyzer (TIMA). To analyze the compositional map of the materials, energy-dispersive X-ray spectrometry (EDS) was performed on the same device, with an analysis time of 15 min on each sample.

Following the characterization and adsorption assays, the adsorbent material with the highest phosphate adsorption capacity was identified as the most promising candidate. To further evaluate its agronomic potential, this material was subsequently tested under greenhouse conditions.

2.5. Pots experiments

2.5.1. Experimental design and treatments

To investigate the potential agronomic performance of ReFert and ReFertP on P availability and ryegrass (*Lolium multiflorum* Lam.) growth in alkaline soils, a pot experiment was performed in a greenhouse at the experimental farm of UM6P, from November 2024 to April 2025. The region has a hot semi-arid climate (BSh), according to the Köppen-Greiger climate classification system, with hot and dry summers, while the winters are relatively mild and rainy (Kottek et al., 2006). The experiment used a randomized block design, with 4 phosphate fertilization conditions and 5 replications, totaling 20 experimental units.

The phosphate fertilization treatments were supplied through root traps, consisting of cylindrical perforated containers made by sectioning 10 mL plastic syringes (3 cm in length $\times$ 2 cm in diameter). The bottom of each cylindrical container was sealed with Parafilm[®] tape. At the same time, several perforations were made along the surface using a 60 W soldering iron, allowing the roots to grow through the openings and access the material inside. This design enabled controlled and direct contact between the roots and the phosphorus sources, while maintaining the physical integrity of the material within the soil.

Two different P sources were applied at 30 mg P kg⁻¹ (Hart et al., 2011), distributed among 4 root traps per pot, including ReFertP (phosphorus-adsorbed Ca waste mining oxides) and triple superphosphate (TSP), along with ReFert (Ca waste mining oxide, no P addition) and control (no P addition, C). Each root trap was filled with a soil layer and subsequently a layer of the corresponding treatment, continuing until it was full, except for the control treatment, which was filled only with soil, placed 2 cm below the surface of the pot, and covered with soil. TSP size was ground manually to a powder to remain at the same standard as the other P sources. During sowing and every 15 days until final harvesting, all the experimental units were

fertirrigated with a solution prepared using 20 mg kg⁻¹ nitrogen (N) as ammonium sulfate ((NH₄)₂SO₄), 10 µM boron (B) as boric acid (H₃BO₃), 0.2 µM copper (Cu), as copper sulfate (CuSO₄·5H₂O), 100 µM Fe as ammonium iron(II) sulfate ((NH₄)₂Fe(SO₄)₂·6H₂O), 2 µM manganese (Mn) as manganese sulfate (MnSO₄·H₂O), 0.05 µM molybdenum (Mo) as ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O), and zinc (Zn) as zinc sulfate (ZnSO₄·7H₂O) (Hart et al., 2011).

To fill the pots, the soil was taken from a homogeneous surface layer (0-20 cm) on the experimental farm field, classified as a calcisol (Mantel et al., 2023), with 21.9% clay, 33.3% silt, and 44.8% sand (ISO 17892-3, 2015). The soil samples were sieved (4 mm mesh). The 3 dm³ pots were filled with a rock layer at the bottom (0.3 kg), for water drainage, and filled to the top with the soil (2.1 kg). Soil pH_{water} was 7.13 (ISO10390, 2021), total P and Olsen's P contents of the soil were 2172.0 mg kg⁻¹ and 26.01 mg kg⁻¹, respectively (Olsen; Sommers, 1982; Olsen et al., 1954). Exchangeable cations, Ca, K, Mg, Na, average content, were 2.404 mg kg⁻¹, 194.4 mg kg⁻¹, 196.7 mg kg⁻¹, and 60.2 mg kg⁻¹, respectively; Cu, Mn, Fe, Zn, B, average content, were 0.6 mg kg⁻¹, 3.7 mg kg⁻¹, 2.1 mg kg⁻¹, 0.5 mg kg⁻¹, and 0.1 mg kg⁻¹, respectively; total N 0.1 %, and S, average content, 9.0 mg SO₃ 100 g⁻¹ (Bouray et al., 2024).

Seeds of ryegrass were obtained by the Agricultural Innovation and Technology Transfer Center of UM6P at the local market in Ben Guerir, Morocco. Previously to all assays, the seeds were soaked with sodium hypochlorite (NaClO) solution, 2.5% concentration (v/v), for 10 minutes and then triple-rinsed in deionized water. A seed germination test was previously carried out according to Brasil (2025), yielding a germination percentage of 90.6%.

The ryegrass seeds were sown in 3 dm³ pots filled with soil. All plants were grown under natural light in a greenhouse and irrigated with tap water to maintain 80% of the water-holding capacity, by weighing the pots every two days and adding the required amount of tap water as needed, until the end of the experiment.

2.5.2. Rhizosphere soil collection, pH, and P levels

At the end of the experiment, the root traps were carefully taken out of the pot, and the soil around the roots was gently shaken off, and this was designated as rhizospheric soil. After rhizospheric soil pH_{water} (ISO10390, 2021), total P, and Olsen's P contents of the rhizosphere soil were measured (Olsen; Sommers, 1982; Olsen et al., 1954).

2.5.3. Shoot morphological traits, growth rate, and P levels

Throughout the experiment, 6 cuts were made every three weeks, with the first cut being made 21 days after emergence. For each cut time, the shoot height was measured (cm), recording the length of the longest leaf. The leaf area (cm²) was calculated from a sample of 10 leaves using digital images and analyzed in Image J software (Schneider et al., 2012). Then, the shoots and leaves were subsequently put in Kraft bags and oven-dried at 65 °C (± 3 °C) until they reached a stable dry mass. Afterward, they were weighed on a precision digital scale to total dry biomass, and the specific leaf area (SLA) for each sample was calculated as the ratio of area over leaves' dry-mass (cm² g⁻¹) (Wright et al., 2004).

The absolute growth rate (AGR) was calculated using the equation: $AGR (g \text{ day}^{-1}) = (DW_2 - DW_1) / (t_2 - t_1)$; and the relative growth rate (RGR) was calculated using the equation: $RGR (g \text{ g}^{-1} \text{ day}^{-1}) = (\ln DW_2 - \ln DW_1) / (t_2 - t_1)$, where ln represents natural logarithm, DW₁ and DW₂ represent dry mass weight at times t₁ and t₂ (Hunt et al., 2002; Hunt, 1990). The NAR represents the plant dry mass increase per leaf area (LA) unit over a period of time. The NAR represented by the equation: $NAR (g \text{ m}^{-2} \text{ day}^{-1}) = (DW_2 - DW_1 / t_2 - t_1) \times (\ln LA_2 - \ln LA_1 / LA_2 - LA_1)$, where LA₁ and LA₂ represent leaf area at times t₁ and t₂ (Hunt et al., 2002; Hunt, 1990).

The shoot P concentrations were determined by nitric digestion; 0.5 g of plant samples (leaves) were reduced to particles smaller than 1 mm using a stainless-steel knife mill. Ten milliliters of a mixture of HNO₃ (65 %) were added to this plant material inside a fume hood. The material was moved to a digester block, and the temperature gradually increased until it reached 90 °C. After the solution was removed from the digester block to cool, and then deionized water was added until the volume reached 50 mL (Chtouki et al., 2022). The digestion solution was analyzed for total P content using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The P content was calculated from data on shoot biomass and P concentration.

The phosphorus use efficiency (PUE) can be divided into phosphorus acquisition efficiency, which is the ability to extract P, and internal phosphorus efficiency, which is the ability to convert the acquired P into biomass. According to Siddiqi and Glass (1981), $PUE (g^2 \text{ SDW mg P}^{-1}) = \text{shoot dry-mass} (g \text{ plant}^{-1}) / \text{shoot P concentration} (mg \text{ P g}^{-1})$.

2.5.4. Rhizosphere root morphological traits

At the end of the experiment, the root traps roots were thoroughly washed, subsequently put in Kraft paper and oven-dried at 65 °C (± 3 °C) until they reached a stable dry mass. The

root mass density (RMD, g cm^{-3}) was calculated based on the root traps volume, using the equation $\text{RMD} = \text{RM} / V$, where RM is the root mass (g), and V is the volume of the root traps (Yoshida, 1981).

2.6. Statistical Analysis and Data Visualization

Statistical analyses were carried out using the R software (R CORE TEAM, 2021). The normality and homogeneity of the data were verified using the Shapiro-Wilk and Levene tests. If the normality of the data distribution was not proved, they were transformed with the most appropriate model. The data were subjected to analysis of variance (ANOVA) using the F test ($p < 0.05$). When the effects of the treatments are significant, the differences between the means were compared using the Tukey test ($p < 0.05$).

3. Results

3.1. Adsorbent material characterization and adsorption capacity

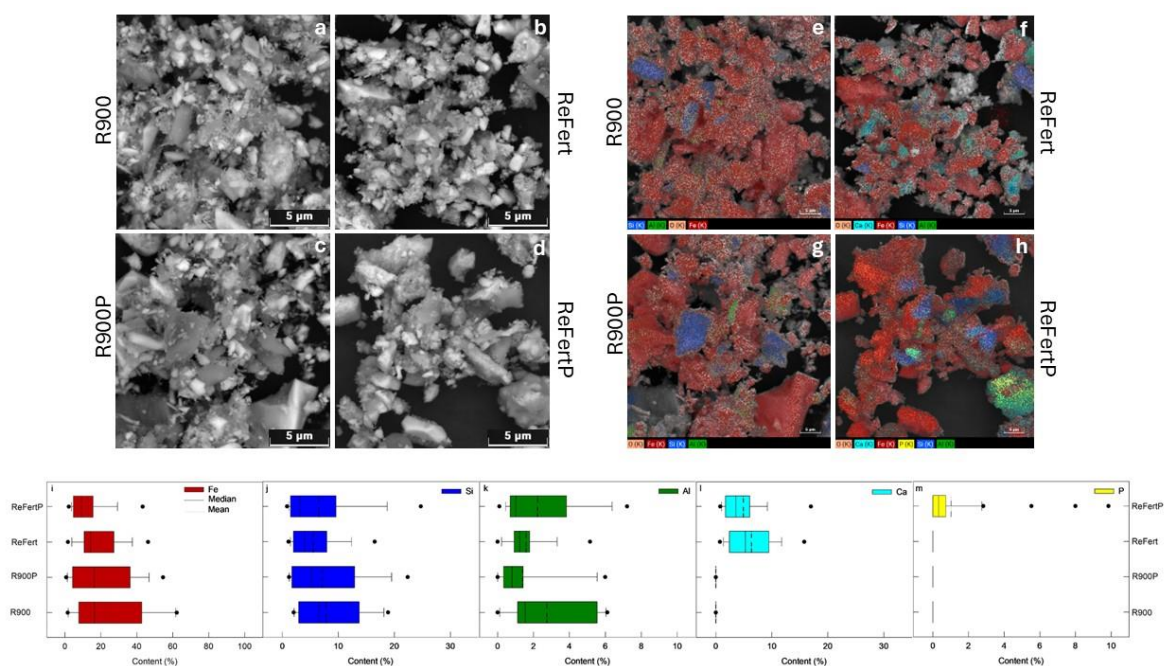


Figure 7 – SEM images (a, b, c, d), chemical mapping spectra (e, f, g, h), for chemical composition (i, j, k, l) for materials R900, R900P, ReFert, and ReFertP. Data are presented as box-plot charts; dots indicate 5th and 95th percentiles.

The R900 and R900P materials presented an irregular surface, with complex morphology (Fig. 1 a, c). After the calcium (Ca) oxide synthesis process, we observed better-defined shapes of the particles in ReFert and ReFertP (Fig. 1 b, d). The EDS and chemical

mapping spectra showed the elements aluminum (Al), iron (Fe), oxygen (O), and silicon (Si), in addition to Ca, well distributed on the surface of the materials (Fig. 1 e to h). Even though R900P had been subjected to the P adsorption process, no P was detected, and the atomic elemental composition showed similar average values (Fig. 1 i to m). P was detected in a few points, at the same region as Ca in the ReFertP sample, suggesting that Ca played a key role in P adsorption (Fig. 1 f, h), whilst the atomic elemental composition was similar in ReFert and ReFertP (Fig. 1 i to m). The phosphate removal capacity determined by 24 h adsorption tests detected 3.0 mg g⁻¹ in R900P, while ReFertP has a phosphate removal capacity close to 31 mg g⁻¹.

Based on the material characterization, which demonstrated that ReFert exhibited the highest phosphate removal capacity and the most favorable surface and chemical properties for phosphorus retention, this material was selected as the most promising P source and then referred to as ReFertP (Fig. 1 d, h).

3.2. Rhizosphere pH changes and final P levels

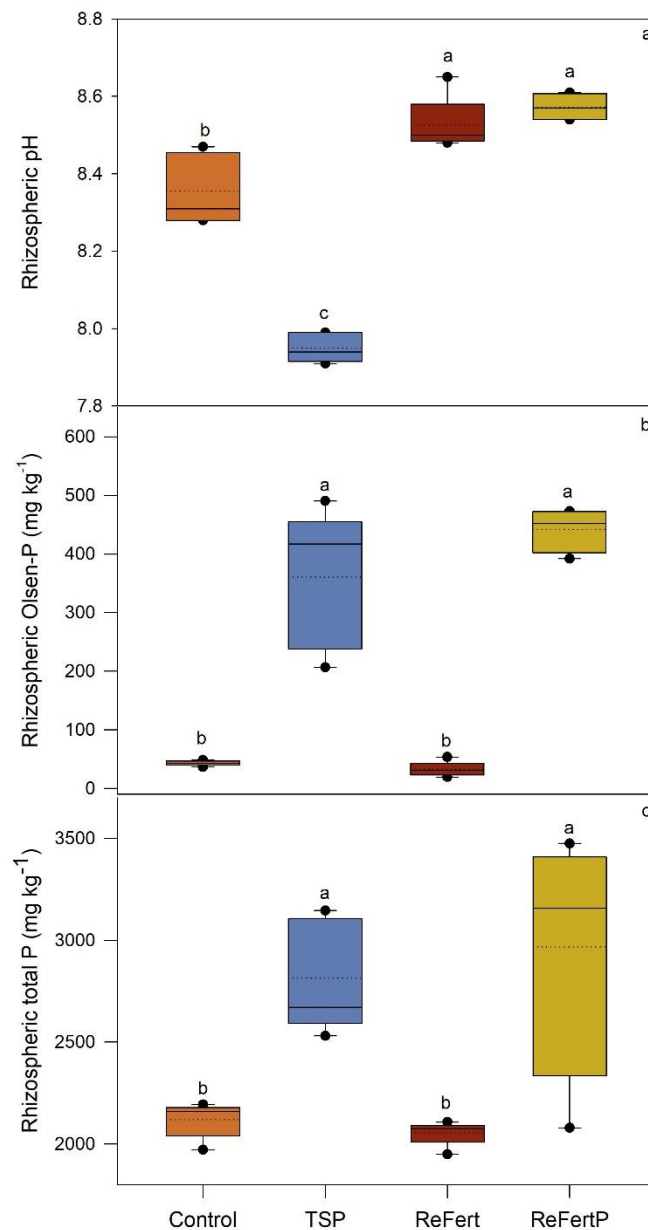


Figure 2 – Rhizospheric pH (a), Olsen-P (b), and total P (b) of ryegrass (*Lolium multiflorum* Lam.) 126 days after emergence. Treatments in a randomized block design, four phosphate fertilization treatments: control (no phosphate fertilizer, C), triple superphosphate fertilizer (TSP), waste mining oxides (ReFert), and phosphorus adsorbed calcium waste mining oxides (ReFertP). Each column represents 5 replications, each replicate consisted of 4 root traps per pot, and the bars represent standard errors for each treatment. Letters indicate a difference between the treatments, according to Tukey's test ($p < 0.05$). Data are presented as box-plot charts, with dots indicating the 5th and 95th percentiles.

The rhizospheric soil pH significantly decreased under the TSP (pH 7.96) compared to ReFert and ReFertP addition, followed by the control (Fig. 1 a). Following an application of 30 mg P kg⁻¹ from each source, a marked increase ($p < 0.05$) in rhizosphere Olsen-P and total P was observed in soils treated with ReFertP and TSP, 454.6 and 360.7 mg P kg⁻¹, 2977.5 and 2119.3 mg P kg⁻¹, respectively (Fig. 1 b, c).

3.3. Rhizosphere and shoot morphological traits

All the plants exhibited similar ($p < 0.05$) rhizosphere root dry mass and density inside the root traps (Fig. S1).

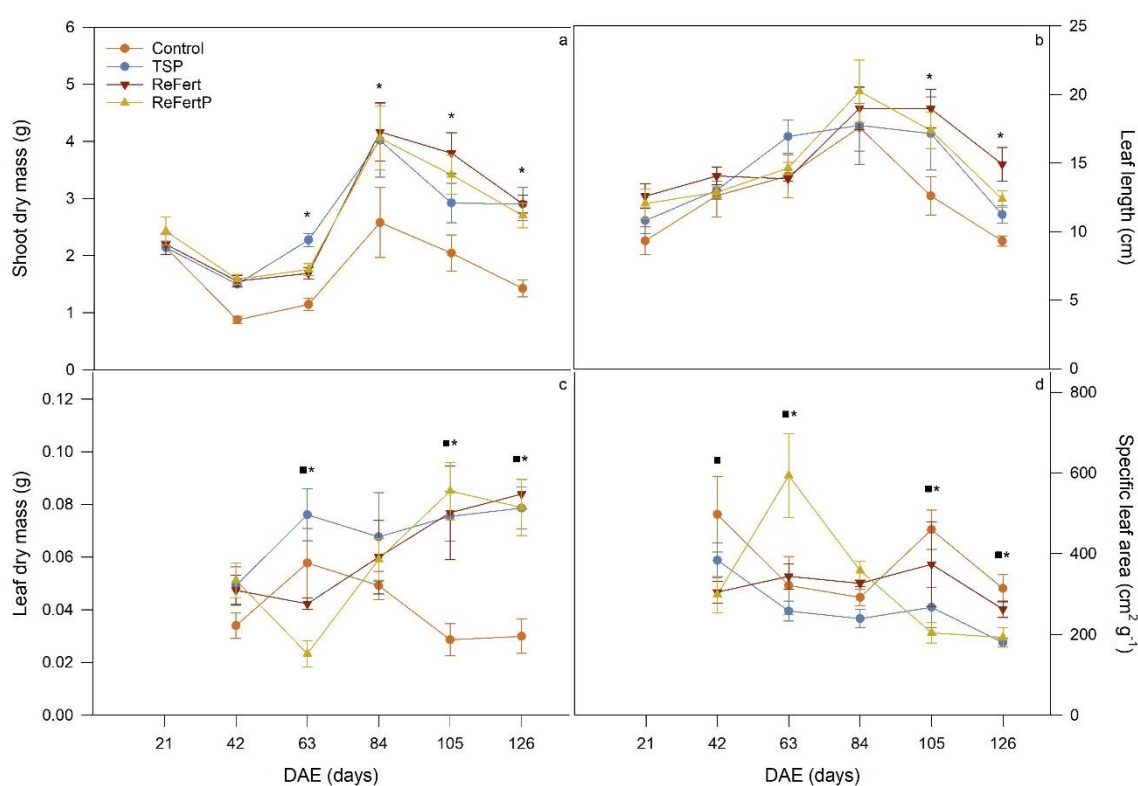


Figure 3 – Shoot dry mass (a), leaf dry mass (b), leaf length (c), and specific leaf area (d) of ryegrass (*Lolium multiflorum* Lam.) days after emergence (DAE). Treatments in a randomized block design, 4 x 6 factorial scheme, four phosphate fertilization conditions: control (no phosphate fertilizer, C), triple superphosphate fertilizer (TSP), waste mining oxides (ReFert), and phosphorus adsorbed calcium waste mining oxides (ReFertP); and pruning times: 21, 42, 63, 84, 105, and 126 days after emergence. The symbols represent 5 replications, and the bars represent standard errors for each treatment. * Indicate significant differences between treatments in the pruning time, ■ Indicates interaction between factors, according to Tukey's test ($p < 0.05$).

We just observed differences in leaf length (Fig. 3 b) and leaf area (Fig. S2) at the last two pruning, where Control plants showed the lowest ($p < 0.05$) values, and ReFert the highest ones ($p < 0.05$). Leaf dry mass (LDM) increased throughout the experimental period, with the highest ($p < 0.05$) values recorded from the 126 DAE. The exception was Control plants, which showed decreased LDM values from 63 DAE (Fig. 3 c). At the 63, 105, and 126 DAE, we noticed that an interaction ($p < 0.05$) occurred between the factors, pruning time and P sources (Fig. 3 c). The lowest LDM was observed in ReFertP at 63 DAE, and at 105 and 126 DAE in C plants (Fig. 3 c).

The highest value for specific leaf area (SLA) was shown for ReFertP at 63 DAE (Fig. 3 d). At the 42, 63, 105, and 126 DAE, we noticed that an interaction ($p < 0.05$) occurred between the factors, pruning time and P sources (Fig. 3 d). The highest SLA was observed in ReFertP plants at 63 DAE, and at 105 and 126 DAE in Control plants (Fig. 3 d).

3.4. Shoot growth rate

The plants showed increasing growth and net assimilation rates until reaching a maximum peak at 84 days, after which biomass accumulation began to decline (Fig. S3). At 63 DAE, it was noticed that higher ($p < 0.05$) absolute growth rate (AGR), relative growth rate (RGR), and net assimilation rate (NAR) in TSP plants, compared to the other treatments (Fig. S3). At 42 DAE ($p < 0.05$), Control plants exhibited lower RGR compared to the other treatments ($p < 0.05$) (Fig. 3S b).

The ReFert treatment promoted the highest ($p < 0.05$) P contents in plants from 84 to 126 DAE (Fig. 4 a). The highest ($p < 0.05$) P concentrations in the shoot were observed at 63 DAE in the Control, followed by the ReFert and TSP treatments, and then ReFertP (Fig. 4 b). At 126 DAE, the highest P concentrations were recorded in ReFert, followed by the control and TSP treatments, and then ReFertP (Fig. 4 b). Across all pruning, the TSP and ReFertP treatments showed the highest PUE ($p < 0.05$), especially at 126 DAE (Fig. 4 c). In contrast, the control treatment exhibited the lowest ($p < 0.05$) PUE values, with ReFert showing similar ($p < 0.05$) results at 126 DAE (Fig. 4 c).

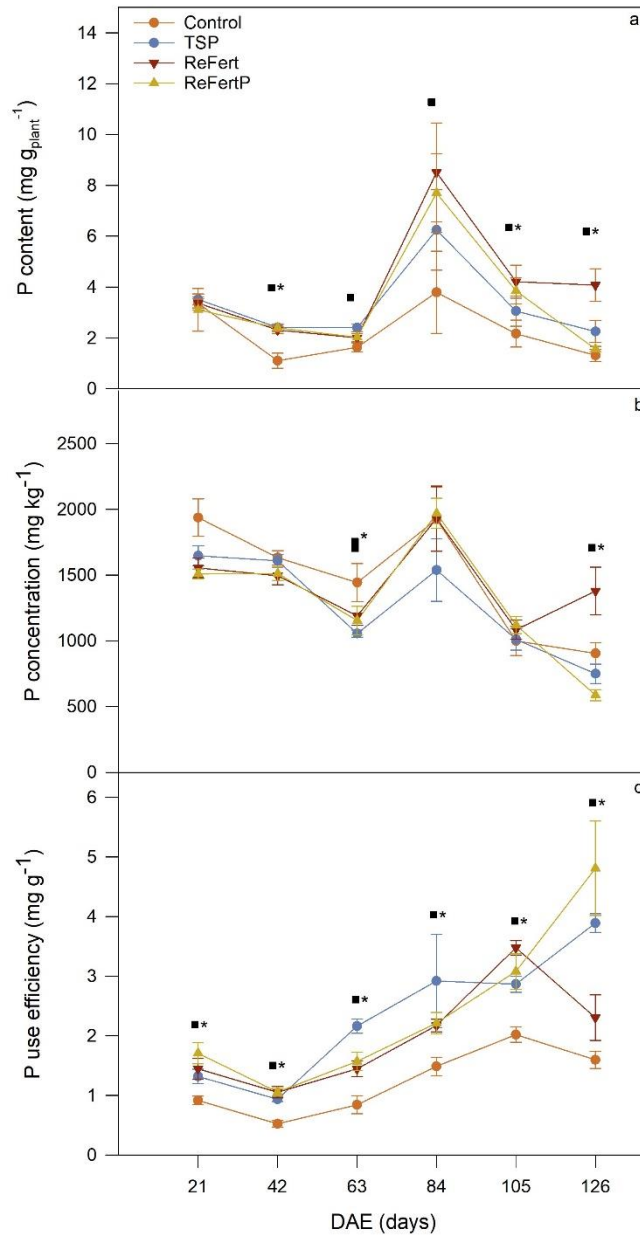


Figure 4 – Shoot phosphorus (P) content (a); P concentration (b), P use efficiency (c), and of ryegrass (*Lolium multiflorum* Lam.) days after emergence (DAE). Treatments in a randomized block design, 4 x 6 factorial scheme, four phosphate fertilization conditions: control (no phosphate fertilizer, C), triple superphosphate fertilizer (TSP), waste mining oxides (ReFert), and phosphorus adsorbed calcium waste mining oxides (ReFertP); and pruning times: 21, 42, 63, 84, 105, and 126 days after emergence. The symbols represent 5 replications, and the bars represent standard errors for each treatment. * Indicate significant differences between treatments in the pruning time, ■ Indicates interaction between factors, according to Tukey's test ($p < 0.05$). Data were transformed to $1/\sqrt{(x)}$.

4. Discussion

The present study demonstrated the potential of iron (Fe) mining by-products enriched with calcium (Ca) oxides (ReFert) as an effective phosphorus (P) adsorbent and a promising alternative P source for plants grown in alkaline soils. This work contributes to advancing sustainable fertilizer technologies and supports a bio-circular economy by transforming Fe-rich waste into a material capable of adsorbing P and subsequently releasing it gradually into the soil (Fig. 2). Promoting biomass gain in the early stages of ryegrass plants, similarly to triple superphosphate (TSP) supply (Fig. 3).

The adsorbent chemical components, the size and shape of the adsorption sites, and the surface area interfere with the adsorption process (Nadagouda et al., 2024; Wang et al., 2024; Wu et al., 2020). The defined shapes on the edges of particles in the calcinated waste mining material, R900 (Fig. 1 b), possibly is due to the removal of water, and consequently an increase in porosity and the material's enhanced surface (Nadagouda et al., 2024). On the contrary, the small, rounded, and defined particles adhered to the surface of larger particles present only in the calcium (Ca) iron (Fe) oxide material, ReFert (Fig. 1 b, d), suggest that calcination and Ca addition were efficient for the synthesis of calcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$), which was only spotted in a few areas (Fig. 1 d).

The formation of Ca/Fe oxide domains, as seen in SEM and EDS mapping, provided reactive Ca-associated sites that strongly bind phosphate (Fig. 1 h, l, m). Unlike R900P, where detectable P in the EDS maps was not observed, ReFertP showed P-rich areas associated with Ca (Fig. 1 g, h, m), indicating the role of Ca in enhancing phosphate adsorption affinity (Lee et al., 2022; Wang et al., 2018; Jiang et al., 2017; Lin et al., 2017). The phosphate removal capacity of 31 mg g^{-1} observed for ReFertP indicates that waste-derived Ca/Fe oxides can achieve technologically relevant performance. Ca promotes P retention through the formation of Ca/P precipitates or surface-bound Ca/phosphate complexes, such as hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), identified as a dominant sorption product in Ca-modified biochar (Wang et al., 2018). Forming ternary complexes, in which phosphate bridges Ca and metal oxides (Zr-P-Ca structures), adsorbed phosphate (Lin et al., 2017). Ultimately, Ca-rich adsorbents exhibited higher surface areas and porosity, with great selectivity for phosphate (Jiang et al., 2017). These mechanisms may explain why ReFertP (ReFert adsorbed material) showed higher P adsorption than R900 (no Ca-enriched material).

Alkaline or calcareous soils are characterized by elevated CaCO_3 contents and pH, as well as a strong capacity to immobilize P. P is predominantly removed from this soil solution through Ca^{2+} induced precipitation, which leads to the formation of low-solubility mineral phases such as hydroxyapatite, as well as by Al, Fe, manganese (Mn) oxides, and CaCO_3 adsorption (Tunesi et al., 1999). Secondary P minerals, such as aluminum (Al), Ca, and Fe phosphates, exhibit varying dissolution rates depending on the particle size and the soil pH. The solubility of Fe and Al phosphates increases with increasing soil pH, while Ca phosphate decreases, except in soil pH above 8 (Hinsinger, 2001). Under these conditions, soluble fertilizers such as TSP dissolve rapidly (Fig. 2b), but the precipitation of Ca/P phases can substantially reduce their long-term availability. The highest early shoot dry mass induced by TSP is consistent with its immediate solubility and rapid P supply (Fig. 3 a).

ReFertP was also made available to the ryegrass plants (Fig. 2 b), which may occur slowly, mainly through the gradual dissolution of Ca/P phases, and be governed not by rapid dissolution but by interactions with rhizosphere processes, including localized root-induced acidification, exudation, and ion exchange (Yan et al., 2018; Fageria, 2009; Lambers et al., 2006). ReFertP supported moderate initial growth but maintained a stable rate throughout the experiment, resulting in biomass values comparable to TSP until the last harvest (Fig. 3 a and c). Interestingly, plants fertilized with ReFert also showed biomass accumulation similar to that of the TSP and ReFertP treatments (Fig. 3 a, c). The low mobility and limited P availability were reported in recent studies of highly heterogeneous calcareous soils (Bouray et al., 2024). While the TSP application resulted in lower rhizosphere pH, indicative of immediate dissolution and acidifying effects, ReFertP maintained a higher pH, which may gradually release P as plant-induced acidification progressed (Fig. 2 a). The rhizosphere is the place where dynamic interactions between plants, soil, and microorganisms take place. Therefore, the nutrient availability is significantly affected by physical, chemical, and biological changes that occur in this critical zone (Fageria; Stone, 2006).

Even though rhizosphere dry mass and root density did not differ statistically among treatments (Fig. S1), the shifts in root distribution patterns are consistent with how plants modulate root system architecture in response to localized P availability (Madison et al., 2023). Local P enrichment is known to stimulate root proliferation, enhancing lateral root development and nutrient foraging (Richardson et al., 2009; Vance et al., 2003). This helps explain why TSP and ReFert tended to promote slightly denser rooting in the immediate rhizosphere, while ReFertP maintained a more homogeneous distribution.

The progressive and sustained response to ReFertP indicates that the material effectively supports plant growth (Fig. S3). The specific leaf area (SLA) would reflect a nutrient limitation condition, thinner leaves with greater area per unit mass, thereby reducing structural costs and optimizing light capture (Dissanayaka et al., 2021; Wright et al., 2004). The increase in SLA observed in ReFertP at 63 days after emergence (DAE), as well as the high SLA values found in the control at later stages, showed that under P deficiency, plants prioritize the allocation of internal P to essential metabolic processes, such as ATP-dependent reactions, membrane synthesis, and photosynthesis, thereby decreasing investment in structurally dense leaf tissue (Madison et al., 2023).

ReFertP and TSP enhanced plant P acquisition compared with the control at different rate (Fig. 4). At later stages, ReFertP supported high P use efficiency (PUE), equaling or even exceeding TSP by 126 DAE (Fig. 4 c). High PUE reflects the plant's capacity to convert absorbed P into biomass effectively, such that efficiency emerges when P release is synchronized with plant demand and when fixation losses to soil minerals are minimized (Hidaka; Kitayama, 2013). Slow-release P sources achieve this by hydrolyzing gradually, thereby maintaining bioavailable P while reducing precipitation with Ca^{2+} in alkaline soils (Qetrani et al., 2025; Chtouki et al., 2022). High PUE is close to enhanced internal recycling of foliar P and preferential allocation to metabolic P pools, mechanisms observed in species adapted to low-P environments (Hidaka; Kitayama, 2013). ReFertP plants showed efficient use of P despite the deficiency through the maintenance of the biomass production and the diluted P concentrations observed (Fig. 4 a and c). The high P content observed in ReFert plants at 105 and 126 DAE suggested a late mobilization of preexisting and sorbed P forms, demonstrating that Ca/P bounded can be progressively accessed through rhizosphere processes such as acidification and organic anion release (Qetrani et al., 2025).

5. Conclusions

These findings demonstrated that iron (Fe) mining by-products enriched with calcium (Ca) can be successfully transformed into an efficient phosphorus (P) adsorbent and a promising slow-release P source for crops grown in alkaline soils. The synthesized material, ReFertP, exhibited high phosphate adsorption capacity due to the formation of Ca/Fe oxide domains and effectively released P in response to root-driven rhizosphere processes. When applied to soil, ReFertP increased plant-available P, sustained biomass production, and enhanced phosphorus use efficiency, performing comparably to triple superphosphate (TSP) while delivering a more gradual and synchronized nutrient supply. In addition, ReFert also demonstrated the capacity

to interact with native soil P pools. The Ca/Fe oxide domains present in ReFert provide reactive surfaces capable of adsorbing phosphate from the soil solution, temporarily immobilizing P that would otherwise be rapidly precipitated or fixed in alkaline environments. This adsorbed P can subsequently be remobilized and supplied to plants through rhizosphere-driven processes. Thus, ReFert functions not only as a slow-release P source but also as a dynamic P buffer, moderating soil P availability. Converting Fe-rich mining residues into functional fertilizers integrates P removal, recovery, and reuse into a single technological pathway, and contributes directly to circular nutrient management, reducing dependence on non-renewable phosphate rock.

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Supplementary data

TRANSFORMING IRON MINING RESIDUES INTO SOIL AMENDMENTS TO ENHANCE PHOSPHORUS AVAILABILITY IN ALKALINE SOILS

Marina Mariá Pereira, Departamento de Biologia, Instituto de Ciências Naturais, Universidade Federal de Lavras (UFLA), 37200-900, Lavras, MG, Brasil, <https://orcid.org/0000-0002-6959-0155>;

Matheus Henrique Pimentel Araújo, Instituto de Ciências Exatas e Tecnológicas, Universidade Federal de Viçosa – *Campus Florestal* (UFV), Florestal, Minas Gerais, 35690-000, Brasil, <https://orcid.org/0000-0002-5081-4016>;

Kaoutar Benghzial, Agricultural Innovation and Technology Transfer Center (AITTC), College of Agriculture and Environmental Sciences, Mohammed VI Polytechnic University (UM6P), Lot 660, Hay Moulay Rachid, Ben Guerir, 43150, Morocco, <https://orcid.org/0000-0001-8368-7554>;

Laura Melo Fernandes Moreira, Instituto de Ciências Exatas e Tecnológicas, Universidade Federal de Viçosa - *Campus Florestal* (UFV), Florestal, Minas Gerais, 35690-000, Brasil, <https://orcid.org/0009-0003-2962-6867>;

Adnane Beniaich, Agricultural Innovation and Technology Transfer Center (AITTC), College of Agriculture and Environmental Sciences, Mohammed VI Polytechnic University (UM6P), Lot 660, Hay Moulay Rachid, Ben Guerir, 43150, Morocco, <https://orcid.org/0000-0002-0381-0610>;

Hudson Wallace Pereira de Carvalho, Centro de Energia Nuclear na Agricultura (CENA), Universidade de São Paulo (USP), Piracicaba, São Paulo, 13416-000, Brasil, <https://orcid.org/0000-0003-0875-3261>;

Juliana Cristina Tristão, Ciências Exatas e Tecnológicas, Universidade Federal de Viçosa - *Campus Florestal* (UFV), Florestal, Minas Gerais, 35690-000, Brasil, <https://orcid.org/0000-0001-5226-8381>;

Eduardo Gusmão Pereira, Instituto de Ciências Biológicas e da Saúde, Universidade Federal de Viçosa - *Campus Florestal* (UFV), Florestal, Minas Gerais 35690-000, Brasil, <https://orcid.org/0000-0001-5660-2949>. Corresponding author: egpereira@ufv.br.

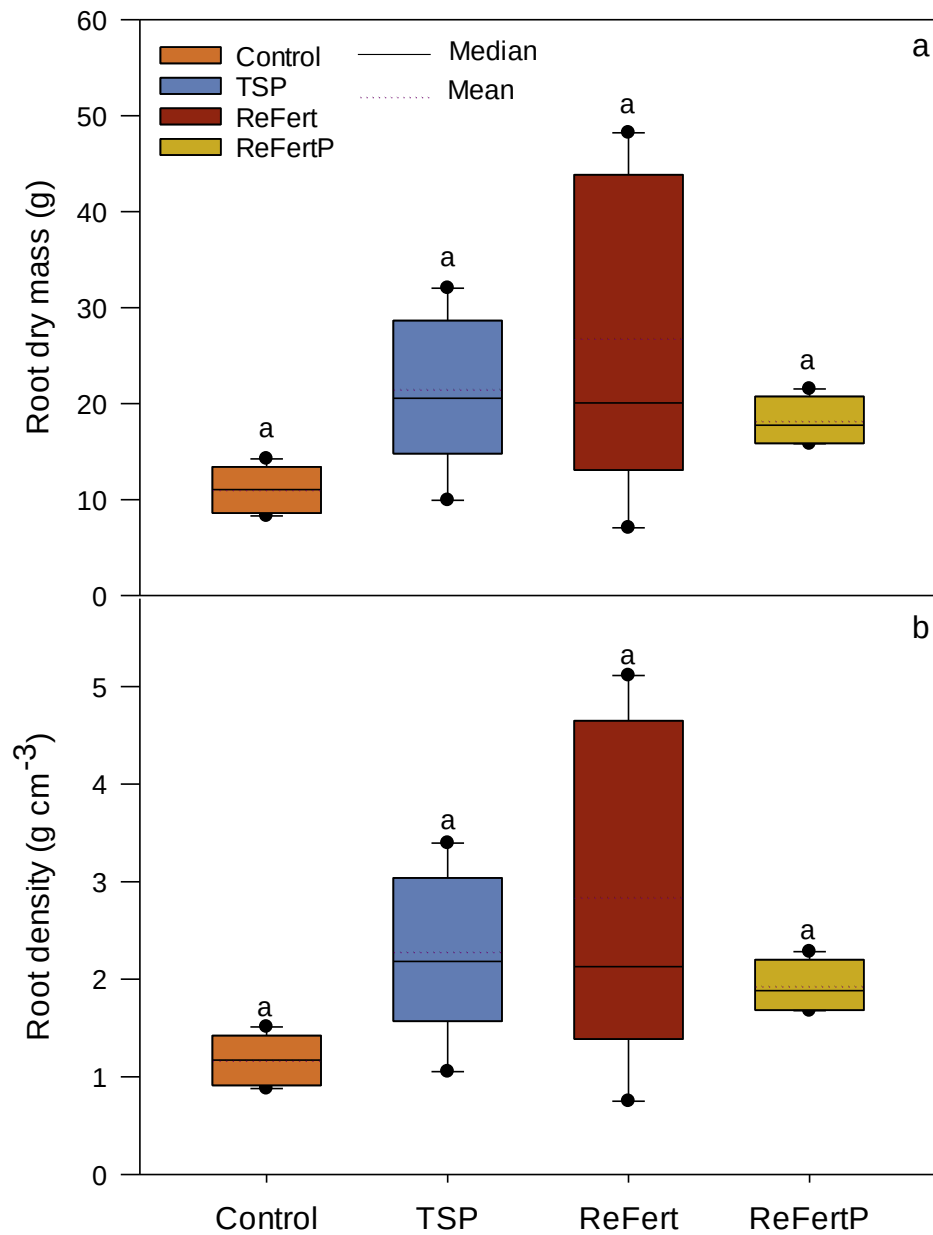


Figure S1 – Root dry mass (a) and root density (b) in root traps (rhizospheric area) of ryegrass (*Lolium multiflorum* Lam.) 126 days after emergence. Treatments in a randomized block design, four phosphate fertilization treatments: control (no phosphate fertilizer, C), triple superphosphate fertilizer (TSP), waste mining oxides (ReFert), and phosphorus adsorbed calcium waste mining oxides (ReFertP). Each column represents 5 replications, each replicate consisted of 4 root traps per pot, and the bars represent standard errors for each treatment. Letters indicate a difference between the treatments, according to Tukey's test ($p < 0.05$). Data are presented as box-plot charts, with dots indicating the 5th and 95th percentiles.

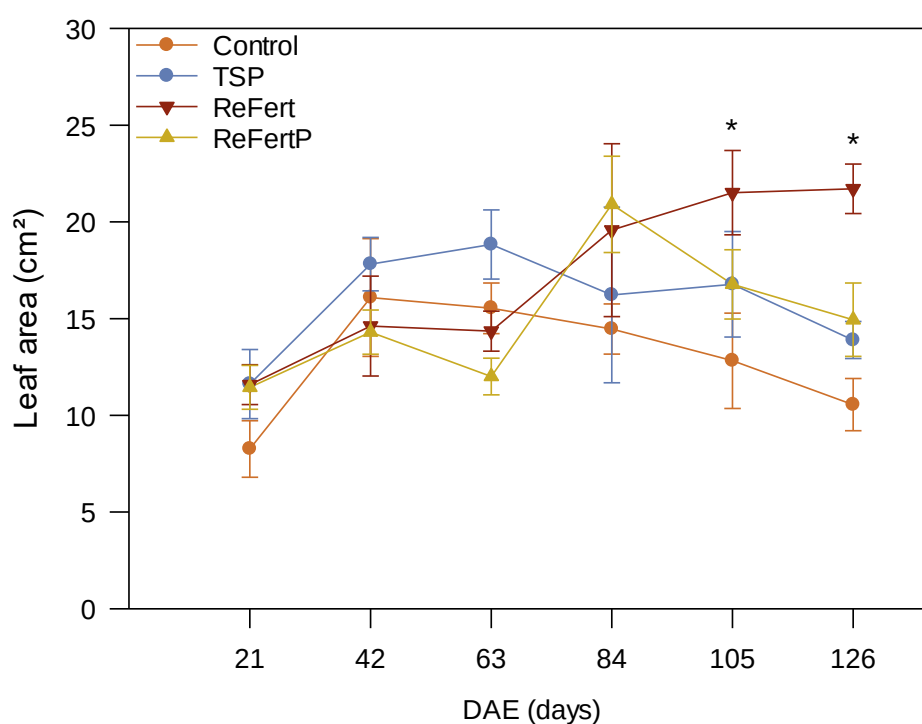


Figure S2 – Leaf area of ryegrass (*Lolium multiflorum* Lam.) days after emergence (DAE). Treatments in a randomized block design, 4 x 6 factorial scheme, four phosphate fertilization conditions: control (no phosphate fertilizer, C), triple superphosphate fertilizer (TSP), waste mining oxides (ReFert), and phosphorus adsorbed calcium waste mining oxides (ReFertP); and pruning times: 21, 42, 63, 84, 105, and 126 days after emergence. The symbols represent 5 replications, and the bars represent standard errors for each treatment. * Indicate significant differences between treatments in the pruning time, according to Tukey's test ($p < 0.05$).

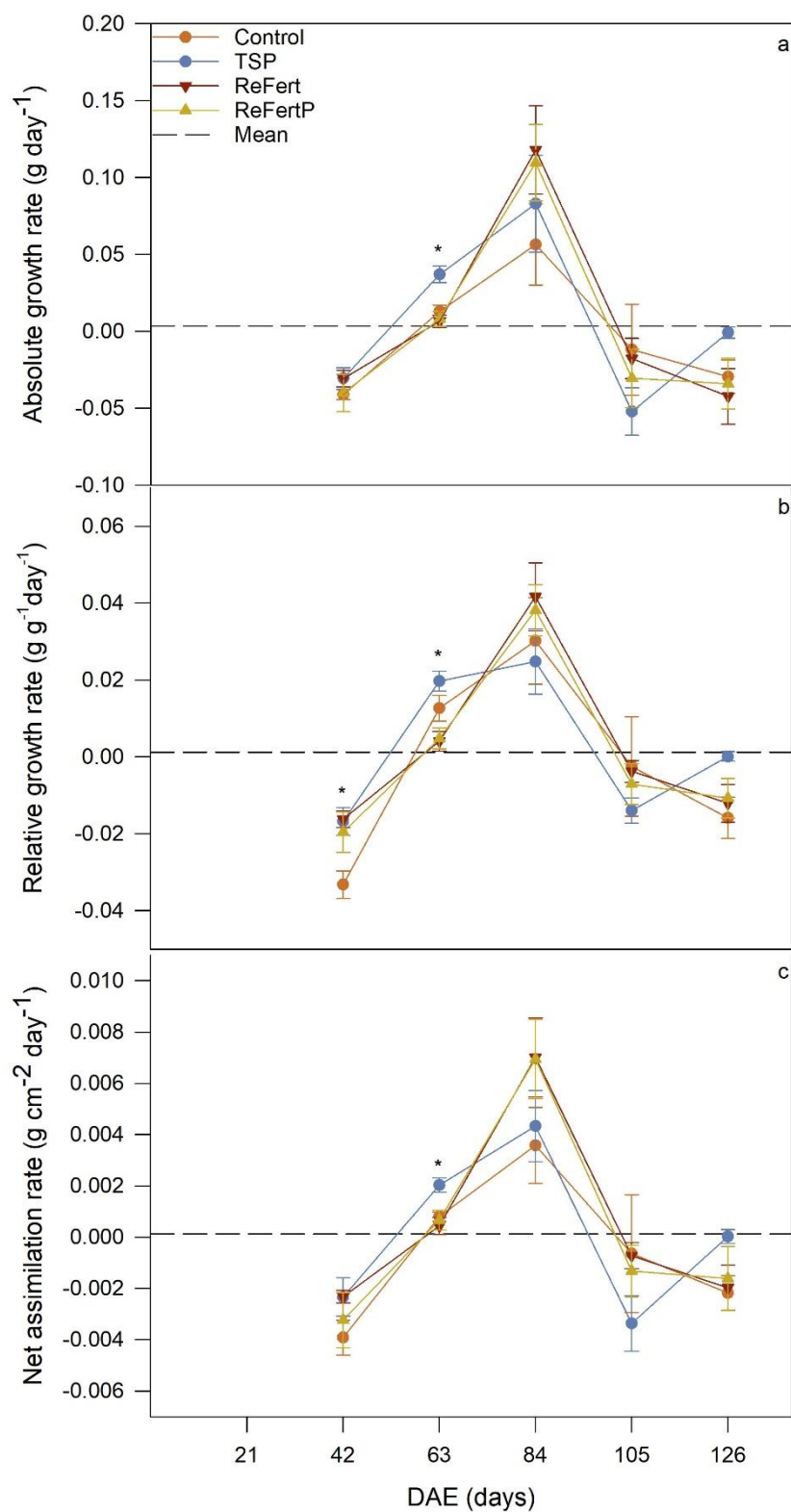


Figure S3 – Absolute growth rate (a), relative growth rate (b), and net assimilation rate (c) of ryegrass (*Lolium multiflorum* Lam.) shoot, days after emergence (DAE). Treatments in a randomized block design, 4 x 6 factorial scheme, four phosphate fertilization conditions: control (no phosphate fertilizer, C), triple superphosphate fertilizer (TSP), waste mining oxides

(ReFert), and phosphorus adsorbed calcium waste mining oxides (ReFertP); and pruning times: 21, 42, 63, 84, 105, and 126 days after emergence. The symbols represent 5 replications, and the bars represent standard errors for each treatment. Net assimilation rate data were obtained using 10 leaves per experimental unit. * Indicate significant differences between treatments in the pruning time, ■ Indicates interaction between factors, according to Tukey's test ($p < 0.05$).

THIRD PART

Concluding remarks

This thesis demonstrates that iron (Fe) mining by-products enriched with calcium (Ca) can be successfully transformed into multifunctional materials that address key challenges in phosphorus (P) management, from pollution control to sustainable fertilization. By integrating P removal, recovery, and agronomic reuse into a single technological pathway, the work advances circular nutrient and bioeconomy strategies while contributing to reduced dependence on finite phosphate rock resources.

We confirmed that Ca/Fe oxide materials synthesized from Fe-rich mining residues possess high and stable phosphate adsorption capacity across a wide pH range. Probably, the formation of Ca ferrite spotted domains increased surface reactivity and promoted strong phosphate binding, enabling efficient P recovery from aqueous solutions. These results reinforce the potential of mining by-products as value-added adsorbents for mitigating P losses to water bodies and controlling eutrophication, while generating P-enriched materials suitable for agricultural reuse.

Beyond P recovery, through seed priming and soil application, the P adsorbed material, ReFertP, provided a supply of P, supporting seed germination, early growth, and biomass production at levels comparable to conventional soluble fertilizers. The slow-release behavior of ReFertP may minimize rapid P fixation and promote high P use efficiency. ReFert, even without prior P adsorption, actively interacts with native soil P pools. The Ca/Fe oxide domains present in the material adsorb phosphate from the soil solution and subsequently remobilize it in response to the rhizosphere. This mechanism allowed plants fertilized with ReFert to accumulate P and biomass comparable to those receiving ReFertP and triple superphosphate, even under low-P and alkaline soil conditions. This result demonstrates that ReFert functions not only as a slow-release fertilizer, but also as a dynamic P buffer capable of enhancing the bioavailability of soil-derived P.

The findings of this thesis establish ReFert, Ca/Fe-based materials, as versatile tools for sustainable P management, capable of operating across contrasting soil pH conditions and fertilization strategies. By transforming abundant Fe-rich mining residues into effective P sorbents and agronomically functional P buffers, this study advances a circular approach to the P cycle, mitigating P losses to the environment and enhancing fertilizer use efficiency in

agriculture. These results open new perspectives for integrating waste valorization with resilient and resource-efficient nutrient management systems.