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PROGRAMA DE PÓS–GRADUAÇÃO EM AGRONOMIA

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TESE DE DOUTORADO SUBMETIDA AO PROGRAMA DE PÓS-GRADUAÇÃO EM AGRONOMIA, COMO PARTE DOS REQUESITOS NECESSÁRIOS À OBTENÇÃO DO GRAU DE DOUTOR (A) EM AGRONOMIA.

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FICHA CATALOGRÁFICA

Fachini, Jóisman

"NOVO FERTILIZANTE À BASE DE BIOCHAR DE LODO DE ESGOTO ENRIQUECIDO COM POTÁSSIO: CARACTERIZAÇÃO, LIBERAÇÃO DE K E POTENCIAL AGRONÔMICO"

Orientação: Cícero Célio de Figueiredo, Brasília, 2022. 116 p.: il.

Tese (Doutorado em Agronomia) – Universidade de Brasília, Faculdade de Agronomia e Medicina Veterinária, 2022.

1. Biochar de lodo de esgoto. 2. Fertilizante de liberação lenta. 3. Lixiviação. 4. Potencial agronômico.

I. Figueiredo, C.C. de. II. Drº

REFERÊNCIA BIBLIOGRÁFICA

FACHINI, J. **Novo fertilizante à base de biochar de lodo de esgoto enriquecido com potássio: caracterização, liberação de K e potencial agronômico.** Faculdade de Agronomia e Medicina Veterinária, Universidade de Brasília, 2022; 116 p. Tese de Doutorado em Agronomia.

CESSÃO DE DIREITOS

Nome do autor: JÓISMAN FACHINI

Título da Tese de Doutorado: Novo fertilizante à base de biochar de lodo de esgoto enriquecido com potássio: caracterização, liberação de K e potencial agronômico.

Grau: Doutora. **Ano**: 2022.

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AGRADECIMENTOS

Agradeço, em primeiro lugar, a Deus que me concedeu a vida. E em especial pela força e coragem durante toda essa longa caminhada.

A minha preciosa família que sempre acreditou que eu seria capaz. Em especial, aos meus pais Jocimar Fachini e Marilei Fachini e a minha irmã Juliana Fachini.

Ao meu marido, Guilherme Bertuol que desde o início dessa jornada me deu apoio e vibrou comigo em todos os momentos.

Ao meu incrível orientador, Dr. Cícero Célio de Figueiredo, por acreditar em mim e me dar esta grande oportunidade. Por me ensinar maravilhas e sempre estar disposto a me receber e me orientar para o caminho da certeza. Meu muito obrigada por me ensinar, me orientar e fazer meus olhos brilharem para este mundo de pesquisas e descobertas.

A toda a equipe do Laboratório de Estudo da Matéria Orgânica do Solo, em especial: ao Alysson Silva de Araújo, Jhon Kenedy, Ana Cláudia Servulo e Priscila Reis, que participaram de forma direta e indireta na execução deste trabalho, me ajudando nas atividades práticas, me dando conselhos e me motivando a seguir em frente.

À Companhia de Saneamento Ambiental do Distrito Federal (CAESB), especialmente à Engenheira Leiliane Saraiva Oliveira, pela disponibilidade do lodo de esgoto usado na produção do biochar de lodo de esgoto utilizado no desenvolvimento deste trabalho e por todas as informações indispensáveis para a realização deste trabalho.

À Embrapa Hortaliças, em especial ao pesquisador Dr. Juscimar da Silva, pela disponibilidade de espaço e apoio para montar o experimento em casa de vegetação, bem como as atividades práticas realizadas durante a condução do experimento.

Por fim, a todos que me apoiaram e acreditaram na minha vitória.

RESUMO

O tratamento térmico do lodo de esgoto (LE), por pirólise, gera um produto sólido, rico em carbono, denominado biochar, com potencial para ser usado como fertilizante. A baixa concentração de potássio (K) no LE é responsável pelo baixo teor deste nutriente no biochar de lodo de esgoto (BLE), não sendo suficiente para o adequado fornecimento de K para diversas culturas. Neste contexto, o enriquecimento do BLE com fontes de K é uma importante alternativa para tornar este produto um fertilizante mais completo para as plantas e viabilizar sua utilização na agricultura. O desenvolvimento de novos fertilizantes exige uma completa avaliação que envolve caracterização das matérias primas e dos produtos obtidos, dinâmica de liberação de nutrientes e avaliação agronômica. Ainda são escassos os trabalhos de enriquecimento do BLE com fontes potássicas a partir de diferentes tecnologias como granulação e peletização. Sendo assim, este estudo teve como objetivo principal produzir, caracterizar e avaliar a dinâmica de liberação de K e o potencial agronômico de um fertilizante de BLE enriquecido com K utilizando distintas tecnologias de enriquecimento. Diferentes fertilizantes de BLE enriquecidos com fontes de K foram produzidos utilizando três tecnologias de enriquecimento: granulação, peletização e mistura física na forma de pó. O presente trabalho é composto por três capítulos. O primeiro estudo abrangeu a produção e a caracterização química, física, morfológica e mineralógica dos fertilizantes enriquecidos. No segundo estudo, os fertilizantes obtidos foram avaliados quanto à dinâmica de liberação e lixiviação de K em experimentos de incubação. Por fim, com as informações obtidas nos dois primeiros estudos, foi avaliado o desempenho agronômico dos fertilizantes enriquecidos na produção de rabanete em casa de vegetação. De forma geral, verificou-se que as características físico-químicas, morfológicas e mineralógicas dos fertilizantes de BLE enriquecidos com K dependem das características químicas e da quantidade das matérias primas utilizadas, além da tecnologia de enriquecimento empregada. O enriquecimento do BLE com K retarda a liberação de K em até 77% comparados ao fertilizante mineral KCl, funcionando, portanto, como um fertilizante de liberação lenta. A dinâmica de liberação de K foi afetada pela tecnologia de enriquecimento e pela forma física dos fertilizantes. Na forma de pellets, os novos fertilizantes apresentaram a mais lenta liberação de K. Quando enriquecido com K, o BLE apresenta potencial semelhante ou superior ao KCl mineral no desenvolvimento da cultura, fornecimento de nutrientes para planta e para o solo, além de contribuir para um maior valor do conteúdo relativo da clorofila (índice SPAD) na cultura do rabanete.

Palavras-chave: Biochar de lodo de esgoto, fertilizante à base de biochar, fertilizante de liberação lenta, potencial agronômico.

ABSTRACT

The thermal treatment of sewage sludge (SS), by pyrolysis, generates a solid product, rich in carbon, called biochar, with the potential to be used as a fertilizer. The low concentration of potassium (K) in the SS is responsible for the low content of this nutrient in the sewage sludge biochar (SSB), not being sufficient for the adequate supply of K for several crops. In this context, the enrichment of SSB with K sources is an important alternative to make this product a more complete fertilizer for plants and enable its use in agriculture. The development of new fertilizers requires a complete evaluation that involves the characterization of raw materials and products obtained, dynamics of nutrient release and agronomic evaluation. There are still few works on SSB enrichment with K sources from different technologies such as granulation and pelletizing. Therefore, this study aimed to produce, characterize and evaluate the dynamics of K release and the agronomic potential of a K-enriched SSB fertilizer using different enrichment technologies. Different SSB fertilizers enriched with K sources were produced using three enrichment technologies: granulation, pelleting and physical mixing in powder form. This work consists of three chapters. The first study covered the production and chemical, physical, morphological and mineralogical characterization of enriched fertilizers. In the second study, the fertilizers obtained were evaluated regarding the dynamics of K release and leaching in incubation experiments. Finally, with the information obtained in the first two studies, the agronomic performance of enriched fertilizers in the production of radish in a greenhouse was evaluated. In general, it was found that the physical-chemical, morphological and mineralogical characteristics of K-enriched SSB fertilizers depend on the chemical characteristics and quantity of raw materials used, in addition to the enrichment technology employed. The enrichment of SSB with K delays the release of K, with a reduction of up to 77% compared to mineral fertilizer KCl, thus functioning as a slow-release fertilizer. The K release dynamics was affected by the enrichment technology and the physical form of the fertilizers. In the form of pellets, the new fertilizers showed the slowest release of K. When enriched with K, SSB has a similar or superior potential to mineral KCl in the development of the crop, supplying nutrients to the plant and to the soil, in addition to contributing to a higher value of the relative chlorophyll content (SPAD index) in the radish crop.

Keywords: Sewage sludge biochar, biochar-based fertilizer, slow-release fertilizer, agronomic potential.

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SUPPLEMENTAL MATERIAL

LIST OF ABBREVIATIONS

AAPFCO - Association of American Plant Food Control Officials
AD – Apparent density
Al – Aluminum
$Al(OH)_3$ – Gibbsite
$AlPO_4$ – Variscite
Al_2O_3 – Aluminum oxide
B – Boron
BBF – Biochar-based fertilizer
BET - Brunauer, Emmett and Teller
BLE – Biochar de lodo de esgoto
C – Carbon
Ca – Calcium
$CaCl_2$ – Calcium chloride
$CaCO_3$ –Calcite
$CaMg(CO_3)_2$ – Dolomite
CEC - Cation exchange capacity
CEN – European Committee for Standardisation
Cd – Cadmus
Cl - Chlorine
Co – Cobalt
CONAMA - National Environment Council
Cr – Chrome
CTC – capacidade de troca catiônica
Cu – Copper
DM – Dry mass
EDX - Energy dispersive X-ray spectrometry
FA - Fulvic acid
FC – Fixed carbon
Fe – Iron
FM – Fresh mass
H – Hydrogen
HA - Humic acid
HM - Heavy metals
HU – Humin
H_2SO_4 – Sulfuric acid
IBI – International Biochar Initiative
ICDD - International Center Diffraction Data
IUPAC - International Union of Pure and Applied Chemistry
K – Potassium
K-sap - K concentrations in the sap of radish plants
KCl – Potassium chloride
K_2O – Potassium oxide
K_2SO_4 – Potassium sulfate
LE – Lodo de esgoto
Mg – Magnesium
Mn – Manganese

Mo – Molybdenum
PMV – Micropore volume
N – Nitrogen
Ni – Níckel
O – Oxygen
OC – Organic carbon
OM – Organic matter
P - Phosphorus
Pb – Lead
P_2O_5 – Phosphorus pentoxide
PD – Particle density
PV – Pore volume
RE - Enrichment factor
S – Sulfur
SA - Specific surface area
SB - Sum of bases
SEM - Scanning electron microscopy images
Si – Silicon
SiO_2 - Quartz
SS - Sewage sludge
SSB - Sewage sludge biochar
TC – Total carbon
TN - Total nitrogen
USEPA – United States Environmental Protection Agency
V - Base saturation
XRD - X-ray diffraction spectra
Zn – Zinc

Sumário

1. INTRODUÇÃO

A expansão da atividade agrícola é acompanhada pela ampliação do uso de fertilizantes minerais solúveis. A produção nacional não acompanhou o crescimento acelerado da demanda por fertilizantes, tornando o Brasil fortemente dependente das importações de fertilizantes nos últimos anos (Conab, 2020). Apenas nos primeiros meses de 2022 (janeiro a abril) foi observado um acréscimo de 14,8% nas importações de fertilizantes comparado ao mesmo período no ano de 2021 (Conab, 2022). Cerca de 97% do potássio (K) usado na agricultura brasileira tem origem no exterior (AMA Brasil, 2020). Além disso, no geral, os solos brasileiros são naturalmente pobres em formas disponíveis de K (Bernardi et al., 2002) e apresentam predominantemente baixa capacidade de troca catiônica aumentando, assim, as perdas de K via lixiviação e reduzindo a eficiência de uso de fertilizantes potássicos (Cheng et al., 2017).

Além de aumentar a demanda por alimentos, outra consequência que o intenso crescimento populacional ocasionou nos últimos anos foi o aumento do volume de lodo de esgoto (LE) produzido. O LE apresenta potencial para ser usado na agricultura como fertilizante ou condicionador do solo, entre outras funções (Kirchmann et al., 2016; Alvarenga et al., 2016). No entanto, no Brasil a legislação sobre o uso agrícola de LE, Resolução CONAMA 498 (Brasil, 2020), tem limitado seu uso na agricultura a poucas situações. Isso tem como consequência o acúmulo de grandes volumes de LE em aterros, sem perspectiva de uso, gerando uma grande preocupação para governos e sociedade. O tratamento térmico por pirólise tem se destacado como uma opção para a reciclagem do LE, transformando-o num fertilizante, livre de organismos patogênicos e rico em carbono (C) e nutrientes como nitrogênio (N), fósforo (P), cálcio (Ca) e zinco (Zn) (Paz-Ferreiro et al., 2018). O produto sólido final desse processo é denominado biochar de LE (BLE). Pesquisas recentes têm demonstrado que o BLE apresenta alto potencial para fornecer nutrientes para o solo e aumentar a absorção de nutrientes pelas plantas, resultando em altos rendimentos das culturas estudadas (Sousa & Figueiredo, 2016; Yuan et al., 2016; Faria et al., 2018; Fachini et al., 2021a).

O BLE é enquadrado no grupo dos biochars que apresentam as mais altas concentrações dos principais nutrientes de plantas, em especial o P (Yue et al., 2017). De maneira geral, a etapa final do tratamento de esgotos promove a precipitação de N e P, tornando o LE concentrado nesses nutrientes. Por outro lado, o LE é considerado uma matéria prima com baixa concentração de K. Durante o tratamento do esgoto, o K é levado com a água na forma de sais solúveis, não sendo incorporado na parte sólida do LE sendo eliminado juntamente com o efluente líquido (Kirchmann et al., 2016; Figueiredo et al., 2018). Como consequência da baixa concentração de K no LE, o teor deste nutriente encontrado nos BLE não tem sido suficiente para o adequado fornecimento para diversas culturas (Sousa & Figueiredo, 2016; Fachini et al., 2021a). O K é o nutriente que mais frequentemente limita o crescimento e rendimento das plantas (Jin et al., 2011) por ser um cátion presente em inúmeros processos fisiológicos das plantas, atuando como ativador em vários sistemas enzimáticos (Hasanuzzaman et al., 2018). Sendo assim, a aplicação do BLE na sua matriz original não fornece em quantidades suficientes o K para as plantas, o que torna necessário a sua complementação com adubação mineral para o fornecimento de K (Faria et al., 2018).

Biochars enriquecidos com fontes minerais e/ou orgânicas para a produção de fertilizante à base de biochar (BBF) vem sendo pesquisado por diversos autores com o objetivo de equilibrar e viabilizar o fornecimento de nutrientes às plantas (Darby et al., 2016; Farrar et al., 2018; Puga et al., 2020; Carneiro et al., 2021). Além disso, os BBFs são considerados produtos com baixa taxa de aplicação e alta eficiência quando utilizados como fertilizante (Joseph et al., 2013). Diversos estudos com diferentes BBFs apontam que o enriquecimento do biochar com fertilizantes minerais apresenta o potencial de melhorar a eficiência no uso de nutrientes e aumentar a produtividade das culturas com baixa dose de aplicação (Melo et al., 2022) aumentando sua viabilidade econômica comparado a altas doses de aplicação de biochar puro. Além disso, a superfície dos biochars é caracterizada principalmente por grupos funcionais com potencial de gerar cargas negativas, contribuindo para uma maior sorção de cátions, como o K (Mukherjee et al., 2011). Dessa forma o enriquecimento do BLE com fontes minerais de K pode dar origem à um fertilizante de liberação lenta de K, solucionando o baixo fornecimento desse nutriente proveniente da aplicação de BLE puro e minimizando as perdas de K de fontes altamente solúveis

Os estudos com BBFs são recentes. Por isso, há uma grande variação nas metodologias empregadas para a obtenção do fertilizante final (Sim et al., 2020). Em uma meta-análise com 40 artigos publicados recentemente, foram observados somente o enriquecimento do biochar com N, P, NP ou NPK (Melo et al., 2022). Há carência de estudos que avaliem efeitos do enriquecimento de biochars somente com K, principalmente sob as tecnologias de granulação e peletização. Além disso, os processos de granulação e de peletização do biochar têm sido usados como alternativa para minimizar os riscos de poeiras e, consequentemente, minimizando possíveis problemas respiratórios causados pela aplicação de biochar em forma de pó (Vincevica-Gaile et al., 2019). De acordo com Bowden-Green & Briens (2016) o processo de granulação é considerado uma das inovações mais significativas para aplicar o biochar ao solo como um fertilizante sólido, resultando em produtos com maior resistência e qualidade. Neste contexto, reforça a necessidade de estudo do efeito do BLE enriquecido com K. O que tornaria possível a obtenção de um produto completo para fornecimento equilibrado de nutrientes às plantas e tecnologias para facilitar a aplicação de biochars em condições de campo. O objetivo deste trabalho foi desenvolver um BBF, tendo o BLE como matriz orgânica, enriquecido com K e avaliar o efeito da granulação e peletização sob as características físico-químicas, morfológicas e mineralógicas dos novos fertilizantes. Além disso, buscou-se avaliar a dinâmica de liberação de K e o efeito dos BBFs na fertilidade do solo, nutrição, fisiologia e no conteúdo relativo da clorofila (índice SPAD) da cultura do rabanete. Busca-se com este trabalho contribuir para a redução da dependência externa de fertilizantes, desenvolver mais uma alternativa de fertilizante sustentável para agricultura e a reciclagem do LE.

2. REVISÃO DE LITERATURA

2.1. Biochar

O biochar é um material sólido, rico em C, resultante do tratamento térmico por pirólise (Shin et al., 2019). Vários estudos com biochars derivados de diferentes matérias primas relatam aumentos do pH, CTC, teor de matéria orgânica e disponibilidade de nutrientes após a sua aplicação ao solo (Yuan et al., 2016; Alvarenga et al., 2016; Kleemann et al., 2017; Figueiredo et al., 2021; Chagas et al 2022). Também são verificados aumentos na produtividade das culturas devido a maior absorção de nutrientes pelas plantas após aplicação de biochar (Gwenzi et al., 2016; Jin et al., 2016; Souza & Figueiredo, 2016; Faria et al., 2018; Chagas et al, 2021; Fachini et al., 2021a).

O biochar apresenta a capacidade de reter nutrientes, melhorando a disponibilidade desses nutrientes para as plantas (Lehmann et al., 2011). A capacidade de adsorção do biochar é dependente das suas características físico-químicas, como a área superficial específica, volume de poros, grupos funcionais e CTC (Wang & Wang, 2019). Uma vez o biochar aplicado ao solo, os nutrientes solúveis em sua composição serão usados para atender as demandas nutricionais das plantas em curto prazo, já as formas mais estáveis presentes no biochar, permanecerão no solo por longos períodos, podendo ser decomposto, para fornecer e manter a fertilidade do solo no longo prazo (Liu et al., 2019). No entanto, a quantidade de nutrientes fornecidos e disponibilizados depende da concentração do nutriente no biochar e varia de acordo com a matéria prima utilizada para a sua produção (El-Naggar et al., 2019; Najafi-Ghiri et al., 2020).

Aumento da matéria orgânica do solo é outro benefício do uso de biochars já muito relatado. Demisie et al. (2014) encontraram um aumento significativo nos teores de carbono orgânico total, carbono da biomassa microbiana e da fração leve do carbono orgânico no solo com o aumento das doses aplicadas de biochar. No trabalho de Yue et al. (2017) foi verificado aumento dos teores de carbono orgânico do solo em aproximadamente 3 vezes, após a aplicação de 1% BLE no solo. Tian et al. (2016) encontram aumento de diversas frações de C no solo com a aplicação de biochar de madeira, como carbono orgânico particulado, carbono orgânico dissolvido e um aumento de 49% do carbono orgânico total. Uma meta-analise realizada com 196 artigos incluindo diversos tipos de biochars confirma o potencial do biochar em acumular C no solo, aumentando, em média, 64% o teor de carbono total além de aumentar as frações mais lábeis de C (Chagas et al., 2022).

O grande número de estudos com caracterização do biochar confirmam sua excelente característica físico-química que pode melhorar a retenção de nutrientes do solo, a capacidade de retenção de água, além de aumentar o sequestro de C (Liu et al., 2019). No entanto as altas taxas de aplicação de biochar podem ser uma barreira para difundir seu uso em larga escala na agricultura, pois sua viabilidade econômica quando aplicado em altas doses ainda é incerta (Melo et al., 2022). Sendo assim, uma alternativa que vem ganhando interesse é a produção de BBF. De acordo com Joseph et al. (2013) BBF é uma tecnologia mais econômica devido sua maior eficiência agronômica, além da possibilidade de ser aplicado em baixas taxas.

2.2. Biochar de Lodo de Esgoto

Quando aplicado ao solo além do fornecimento de matéria orgânica, macro e micronutrientes, o LE pode reduzir ou até mesmo eliminar a utilização de corretivos e fertilizantes minerais, principalmente aqueles que são fontes de N e P, sendo estes os nutrientes encontrados em maior concentração no LE (Kirchmann et al., 2016; Figueiredo et al., 2018). Por outro lado, o LE apresenta concentração baixa de K quando comparados aos demais resíduos orgânicos, apresentando uma faixa de 0,08 – 0,7%, com uma média 0,2% de K na matéria seca (Yuan et al., 2015; Gwenzi et al., 2016; Nakao et al., 2016; Kleemann et al., 2017; Figueiredo et al., 2018). Tontti et al. (2016) afirmam que o enriquecimento de LE, e seus produtos derivados, com fontes potássicas pode suprir a falta de K em suas composições podendo atingir até mesmo rendimentos similares aos obtidos com fertilizantes minerais comerciais NPK. No entanto, devido às limitações estabelecidas pela Resolução do Conselho Nacional do Meio Ambiente (CONAMA) nº 498 (Brasil, 2020), a maior parte do LE produzido é armazenado em pátios de secagem, sem uma solução definitiva, gerando problemas ambientais. Considerando-se as limitações apresentadas, torna-se necessário a busca por meios alternativos para que o uso do LE para fins agrícolas não seja negligenciado. Uma dessas alternativas é a transformação do LE por meio da pirólise em BLE.

Dependendo das condições de pirólise, o BLE pode apresentar até 6% de P em sua composição (Figueiredo et al., 2018) pois aproximadamente 98,5% do P presente no LE é mantido no BLE final (Yuan et al., 2016), dando à pirólise grande potencial para transformar o LE em um produto com alto fornecimento de P para o solo (Mackay et al., 2017; Figueiredo et al., 2021). No trabalho de Faria et al. (2018) com BLE aplicado ao solo combinado ou não com NPK, os resultados mais promissores sobre as propriedades químicas do solo foram observados nos teores de P disponível, resultados esses que apresentaram efeitos residuais após 1 ano da aplicação do BLE (Fachini et al., 2021a). O aumento de até 6,6 vezes do valor de P no solo após a aplicação do BLE foi encontrado por Yue et al. (2017), aumento este que foi de 4,83 mg kg^{-1} de P no solo não tratado para 32,02 mg kg^{-1} para o tratamento que recebeu a taxa de aplicação de 1% de BLE. O BLE foi eficaz em fornecer cerca de 4,5 a 7,2 vezes mais P total para o solo em comparação a adubação mineral, 6 a 7 vezes mais P disponível em comparação com o controle e 2 a 3 vezes em comparação com o tratamento com NPK após 5 anos de aplicação (Chagas et al., 2021).

Diferentemente do P, o BLE não é uma boa fonte de K (Kirchmann et al., 2016). Mesmo havendo um aumento da concentração de K durante a pirólise, os teores de K no BLE ainda são muito baixos (Yuan et al., 2016; Figueiredo et al., 2018). No trabalho de Faria et al. (2018) houve aumento do teor de K em BLEs de 300 e 500ºC, porém este aumento não foi suficiente para fornecer o conteúdo de K exigido pela cultura de milho, sendo necessário a complementação com suprimento de K por meio de fertilizante mineral. No trabalho de Sousa & Figueiredo (2016) apenas com a aplicação da maior dose de BLE (100 t ha^{-1}) foi possível suprir a demanda de K pela planta. Após um ano da aplicação de BLE a absorção de K pelas plantas foi semelhante ao tratamento controle, solo sem adubação, reforçando a necessidade da mistura de BLE com fontes de K (Fachini et al., 2021a). Chagas et al. (2021) afirmam que para fornecer K via aplicação isolada de BLE são necessárias altas doses o que inviabiliza sua aplicação do ponto de vista econômico, agronômico e perspectiva ambiental. Entretanto, deve-se ressaltar que biochars provenientes de outras matérias primas já resultaram no aumento significativo no valor de K do solo (Najafi-Ghiri et al., 2020; Zhang et al., 2020; Boostani et al., 2020). Neste caso, se o objetivo for fornecer K, deve-se buscar alternativas para fornecer o nutriente juntamente com a aplicação de BLE, ressaltando a necessidade e importância de estudos voltados para o enriquecimento do BLE com fontes potássicas.

2.3. Fertilizante à base de biochar (BBF)

2.3.1. Produção

Recentemente, trabalhos foram desenvolvidos com o objetivo de avaliar o potencial de enriquecimento de biochars com fontes minerais e orgânicas na busca de um produto mais completo e equilibrado nutricionalmente (Blackwell et al., 2015; Nguyen et al., 2017; Gondek et al., 2018; Farrar et al., 2018). De forma geral a produção de BBFs consiste na mistura de biochars como fonte de matéria orgânica e nutrientes com fertilizantes minerais para aumentar e/ou suprir a oferta de nutrientes.

Os estudos com BBFs são recentes. Por isso, há uma grande variação nos métodos empregados para a obtenção do produto final. De acordo com Melo et al. (2022), o BBF é um produto cuja tecnologia envolvida aproveita as características benéficas de distintos biochars e as diversas formas de enriquecer o biochar com nutrientes. Recentemente, Sim et al. (2021) descreveram três principais métodos utilizados para a produção de BBFs: 1) impregnação, que consiste em misturar o biochar em soluções ricas em nutrientes seguido pelo processo de secagem; 2) granulação mista, ou seja, mistura do biochar com fontes minerais em forma de pó e depois submetê-lo ao processo de granulação ou peletização, e; 3) co-pirólise, que resulta da mistura do biochar com fontes de nutrientes (geralmente da forma de pó) seguidas por pirólise.

Os processos de granulação e peletização dão origem a produtos com maior homogeneidade nos tamanhos de grânulos e pellets e nos teores de nutrientes, trazendo facilidade de aplicação ao campo. Além disso, essas tecnologias utilizadas juntamente com o processo de enriquecimento do biochar podem minimizar os riscos de poeiras e, consequentemente, possíveis problemas respiratórios causados pela aplicação de biochar em forma de pó (Vincevica-Gaile et al., 2019) e desenvolver um produto mais equilibrado nutricionalmente. Dumroese et al. (2011) afirmam que biochars peletizados apresentam maior facilidade de manuseio além de aumento da porosidade total e aeração. Em alguns processos de granulação há a necessidade de umedecer os materiais para que haja a formação dos grânulos, nesse caso o processo é denominado de granulação úmida. De acordo com Bowden-Green & Briens (2016) a granulação úmida em tambor é a mais indicada para a granulação de biochars por apresentar menor custo de operação. Nesta forma de produção a mistura do biochar já com a fonte mineral e o aglutinador (todos em forma de pó) é adicionada no tambor em rotação e posteriormente a água é pulverizada sobre a superfície do pó. Inicia-se então a formação de núcleos granulares e logo após a ativação do aglutinador, com isso os núcleos evoluem para grânulos maiores dando origem ao produto final com todas as matérias primas em um único grânulo.

O biochar, uma vez transformado em um BBF, pode reter nutrientes e funcionar como um fertilizante de liberação lenta, devido à interação do elemento enriquecido com a superfície do biochar, principalmente pela alta porosidade e grande área superficial presentes no biochar (Schmidt et al., 2017). Além disso, a superfície dos biochars é caracterizada principalmente por grupos funcionais com potencial para gerar cargas negativas, contribuindo para uma maior sorção de cátions, como o K (Mukherjee et al., 2011). Sendo assim, o enriquecimento do BLE com K para a produção de um BBF apresenta uma grande possibilidade em resolver o problema de fornecimento desse nutriente via aplicação de SSB isolado. Dessa forma, desenvolvendo um produto completo para a agricultura, mais eficiente e com menores taxas de aplicação, contribuindo para o aumento da sua viabilidade economica na agricultura.

2.2.2. Potencial agronômico

Segundo Joseph et al. (2013) BBFs são considerados produtos com baixa dose de aplicação e alta eficiência na utilização como fertilizante. Diferentes BBFs vem demonstrando potencial em aumentar a produção de biomassa e produtividade das culturas (Gunes et al., 2014; Kizito et al., 2019; Borges et al., 2020; Puga et al., 2020; Carneiro et al., 2021). A análise microestrutural de um biochar, após o enriquecimento para a produção de um BBF, revelou uma estrutura porosa rodeada por camadas de minerais, formando complexos organominerais, melhorando a concentração de nutrientes e promovendo maior crescimento das plantas em comparação com os biochars não enriquecidos (Chia et al., 2014).

O enriquecimento do biochar poderá fornecer ao solo um reservatório adicional de nutrintes para as plantas. No entanto deve-se atentar às possíveis modificações na composição química e nas propriedades físicas do biochar resultante da mistura do mesmo com outras fontes de nutrientes (Gondek et al., 2018). Modificações em diversas características físico-químicas de BBFs já foram relatados quando comparados com as suas respectivas matérias primas. Por exemplo, Blackwell et al. (2015) observaram mudanças significativas nos valores de pH, CTC e relação C/N após o enriquecimeno do biochar quando comparado ao biochar de madeira puro. O enriquecimento de biochar de trigo com sais minerais resultou no aumento dos teores de S e Mg e redução do pH comparado ao biochar puro (Gondek et al., 2018). Um organomineral de biochar de bambu e madeira também apresentou uma superfície rica em Al, sílicio (Si), K, Ca e P comparado ao biochar puro (Darby et al., 2016). Biochar de LE misturado com demais fontes orgânicas resultaram em um BBF com menor área da superfície e menor porosidade comparado ao BLE puro (Huang et al., 2017). Um BBF de BLE enriquecido com K garantiu um teor de 75 vezes mais K_2O do que o BLE puro, além de apresentar diferenças nas características físicas e morfológicas (Fachini et al., 2021b).

Devido às características do biochar como alta área superficial, porosidade, natureza hidrofóbica (Chia et al., 2015) e forte capacidade de adsorção (Li et al., 2018), após o enriquecimento, o biochar pode dar origem a um BBF de liberação lenta (Lustosa e Filho et al., 2020; Khajavi-Shojaei et a., 2020; Carnero et al., 2021) resultando em um fornecimento equilibrado e gradual de nutrientes durante todo o ciclo da cultura e aumentando da eficiência do uso de nutrientes (Lustosa Filho et al., 2020). Isso é possível porque os FBBs podem reduzir as perdas de nutrientes via lixiviação (Luo et al., 2021) e o uso de fontes minerais solúveis, além de contribuir para aumentar a absorção de nutrientes e a produtividade das culturas (Borges et al., 2020; Carneiro et al., 2021). No entanto, inúmeros trabalhos com BBFs avaliou o enriquecimento do biochar com N, P, NP ou NPK (Melo et al., 2021) sendo necessários estudos que avaliem o efeito do enriquecimento do biochar somente com fonte mineral de K nas caracteristicas fisico-quimicas do BBF, liberação de K e potencial agronômico.

Joseph et al. (2013) indicam que no futuro próximo BBFs serão desenvolvidos levando em consideração o tipo do solo e a sua fertilidade bem como a matéria prima disponível. A ideia da combinação de biochars com demais matérias primas para a produção de BBF surgiu recentemente. Pouco se sabe sobre os efeitos desses compostos no rendimento, nutrição de plantas e disponibilidade de nutrientes (Nguyen et al., 2017). Nesse sentido é crucial que mais estudos com BBFs sejam realizados para aumentar a viabilidade econômica desses produtos e contribuir para a adoção em larga escala em sistemas agrícolas brasileiro.

3. OBJETIVOS

3.1. Objetivo geral

Produzir, caracterizar e avaliar a dinâmica de liberação de K e o potencial agronômico de um fertilizante à base de biochar (BBF) enriquecido em K utilizando distintas tecnologias de enriquecimento.

3.2. Objetivos específicos

1) Realizar a caracterização físico-química, morfológica e mineralógica dos BBFs de biochar de lodo de esgoto (BLE) enriquecidos por diferentes tecnologias com duas fontes de K.

2) Avaliar a dinâmica temporal de liberação e lixiviação de K dos BBFs em sílica sob diferentes níveis de umidade.

3) Avaliar o desempenho agronômico dos novos fertilizantes, na forma de pellet e grânulo, nos indicadores de fertilidade do solo, nutrição, fisiologia e no índice SPAD da cultura do rabanete.

4. HIPÓTESES

1) Os BBFs são quimicamente semelhantes, apresentam características físicas e mineralógicas distintas conforme a fonte de K e a forma do fertilizante utilizadas no enriquecimento.

2) BBF na forma de pó libera o K em um período de tempo mais curto, seguido pelo grânulo e, por último, o pellet.

3) Independente do nível de umidade do solo, os BBFs na forma de grânulos e pellets atendem aos critérios de fertilizantes de liberação lenta.

4) Independente do nível de umidade da sílica, os BBFs retardam a lixiviação de K comparado ao fertilizante mineral.

5) BBFs, independente da forma, melhoram a disponibilidade de nutrientes no solo e a nutrição das plantas, contribuindo para um melhor índice SPAD, e melhor desenvolvimento e produtividade de rabanete, quando comparado ao fertilizante mineral solúvel.

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CHAPTER I

NOVEL K-ENRICHED SEWAGE SLUDGE BIOCHAR FERTILIZERS: CHEMICAL, PHYSICAL, MORPHOLOGICAL AND MINERALOGICAL CHARACTERIZATION

(Manuscript published in Waste Management – doi: https://doi.org/10.1016/j.wasman.2021.08.027)

6. NOVEL K-ENRICHED SEWAGE SLUDGE BIOCHAR FERTILIZERS: CHEMICAL, PHYSICAL, MORPHOLOGICAL AND MINERALOGICAL CHARACTERIZATION

6.1. ABSTRACT

The sewage sludge (SS) use in agriculture has been limited by the Brazilian legislation to a few situations, mainly as a precautionary measure due to inorganic pollutants and pathogens. Thermal treatment via pyrolysis has stood out as an option for SS recycling, transforming it into a carbon-rich product known as SS biochar (SSB). The SSB is a multi-nutrient fertilizer with very low K concentration. This study presents a novel K-enriched SSB fertilizer with the potential to increase K use efficiency by crops. The present study aimed to evaluate the influence of pyrolysis at 300°C on the SSB characteristics and to evaluate the physical-chemical, morphological and mineralogical characteristics of a biochar-based fertilizer (BBF) enriched with K. SSB was enriched with KCl and K_2SO_4 using three technological methods (granules, pellets and powders). In general, results of the present study showed that pyrolysis is a technological alternative to enable SS use as a sustainable input in agriculture. The enrichment of SSB with K ensured a K_2O content about 75 times higher than the pure SSB. BBF in powder form had higher levels of total nitrogen, calcium, sulfur, phosphorus and higher pH than granules and pellets. The morphology and physical characteristics of enriched BBFs were more influenced by the form of the fertilizer than by the source of K. In general, the enriched BBFs are influenced by the quantities of feedstocks and the enrichment technology.

6.2. INTRODUCTION

Compared to other biomasses, sewage sludge (SS) is considered a residue rich in nutrients and organic matter (Paz-Ferreiro et al., 2018). Sewage sludge can be used in agriculture as a soil amendment, among other functions (Kirchmann et al., 2021). Despite this potential, according to the Brazilian regulation, CONAMA Resolution 498 (Brazil, 2020), SS should be applied in a few situations, mainly as a precautionary measure due to the presence of inorganic pollutants and pathogens. Consequently, a large amount of SS is accumulated in landfills, with no prospect of use, generating great concern for governments and society. Therefore, technological alternatives must be sought so that the agricultural use of SS is not neglected. Thermal treatment via pyrolysis is a technological alternative to transform SS into a multi-nutrient fertilizer.

The solid product obtained by this process, called SS biochar (SSB), is free of pathogens and rich in C and nutrients including N, P, Ca and Zn (Paz-Ferreiro et al., 2018). There are multiple feedstocks used for biochar production such as manure, wood and crop residues, and urban waste. Sewage sludge biochar is considered a nutrient-rich material, with the exception of K (Figueiredo et al., 2018a). In general, the last step of sewage treatment precipitates N and P. At the end of the SS treatment, more than 90% of the total P is precipitated as iron (Fe) and/or aluminum (Al) salts, which are insoluble in water, generating a SS rich in P (Tontti et al., 2016). Thus, pyrolysis has great potential to transform SS into a multi-nutrient fertilizer, especially rich in P and N (Fristák et al., 2018; Jassal et al., 2015). Potassium is eliminated as soluble salts together with the liquid effluent and is not incorporated into the solid SS (Kirchmann et al., 2016) which results in SSB with low K contents (Gwenzi et al., 2016; Sousa and Figueiredo, 2016). Despite the increased K content due to the rise in pyrolysis temperature, it is not sufficient for the adequate supply of this nutrient to different crops (Fachini et al., 2021; Faria et al., 2018; Sousa and Figueiredo, 2016). This requires the complementation of K via mineral fertilization or by application of very high SSB doses.

Enriching SSB with K is an interesting alternative to make a complete fertilizer, with the potential to supply K to plants gradually and with greater efficiency. Recent studies have sought to develop mineral-enriched biochars to act as slow-release fertilizers (Jassal et al., 2015), balancing and enabling the supply of nutrients to plants (Darby et al., 2016; Farrar et al., 2018). Mixtures of biochars with other organic and/or mineral sources can give rise to mineral-enriched biochars (Chia et al., 2014; Gondek et al., 2018) or organomineral biochar (Farrar et al., 2018; Nguyen et al., 2017) giveing rise to one biochar-based fertilizers (BBFs).

Biochar-based fertilizers can be applied at low rates and have a higher efficiency than pure biochars, mineral or organic fertilizers (Farrar et al., 2018; Nguyen et al., 2017). Due to the high porosity and large surface area, as well as the interaction of the enriched element with the biochar surface, BBFs can retain nutrients and act as a slow-release fertilizer (Schmidt et al., 2017). Changes in several physical and chemical characteristics of BBFs have already been reported compared to their raw materials. For instance, the enrichment of wheat straw biochar with mineral salts resulted in increased levels of S and Mg and reduced pH compared to the pure biochar (Gondek et al., 2018). Increases of 2.7 and 56.6 times in N and P levels, respectively, were observed after the enrichment of wood biochar with mineral and organic sources (Blackwell et al., 2015). Larger pores coated with P, K, Ca and Mg were observed by Farrar et al. (2018) in manure and wood BBFs. On the other hand, the co-pyrolysis of SS with different organic biomass resulted in biochars with less surface area and porosity compared to pure SSB (Huang et al., 2017).

Studies with BBFs are relatively recent. Therefore, there is a wide variation in the methods used to obtain the final product (Farrar et al., 2018; Nguyen et al. 2017). Granulating and pelletizing biochars are the most common processes which have been used to minimize dust production, and consequently reduce respiratory problems caused by biochar application in the form of powder (Vincevica-Gaile et al., 2019). In addition, these products can facilitate the application of biochar in the field. Another advantage of producing BBFs is that these fertilizers can be enriched with specific nutrients and adapted according to the requirements of the crop (Farrar et al., 2018). Additionally, BBFs reduce the high doses of biochars that may cause soil pollution, hindering the adoption of biochar technology by farmers.

There is still a lack of information on the enrichment of SSB with soluble K sources using different technologies such as granulation and pelletizing. Contrasting results on the effectiveness of BBFs could be related to the physical formulation (e.g., powder, granular, pellet), physicochemical properties and composition of the mineral and organic sources used (Frazão et al., 2019). Furthermore, the physical formulation can affect the efficiency of storage, handling and application, as well as the plant responses. For instance, Sakurada et al. (2016) reported significant differences between granular and pelletized fertilizers applied to maize. However, the characterization of BBFs has been poorly performed in most studies, which compromises the interpretation of effectiveness results behind the reactions of BBFs in the soil. Therefore, studies on this subject are relevant for a better comprehension of the agronomic effectiveness of BBFs, which allow for future adjustments in terms of fertilizer formulation.

In this context, the present study sought to evaluate the effect of pyrolysis on the transformations of SS, predominantly domestic, and the physical, chemical, morphological and mineralogical characteristics of SS, SSB and BBFs from SSB enriched with two K sources and different physical forms. It was hypothesized that all BBFs enriched with K sources have similar compositions but have distinct physical and mineralogical properties, depending on the physical form and K source used.

6.3. MATERIALS AND METHODS

6.3.1. Preparation of sewage sludge biochar (SSB)

The SSB was produced from SS samples collected at the Melchior wastewater treatment plant, belonging to the Environmental Sanitation Company of Brasília, DF, Brazil. This wastewater treatment plant utilizes a tertiary treatment system, in which sewage decomposition is carried out in an anaerobic up-flow reactor (RAFA). In this type of system, nutrients such as P and N are removed from the liquid effluent by a coagulation process using aluminum salts. Therefore, these nutrients remain in the final SS biomass.

For SSB preparation, SS samples were air-dried (to approximately 10% moisture content), passed through a 4 mm sieve and then pyrolyzed at 300 °C. Based on our previous study (Figueiredo et al., 2018a), considering all variables together, the biochar produced at 300 ºC showed the greatest nutrients availability. Pyrolysis was performed in a muffle furnace (Linn ElektroTherm, Eschenfelden, Germany) at a mean temperature increase rate of 2.5 ºC min^{-1} and residence time of 5 h as described by Figueiredo et al. (2018a). The furnace was equipped with a mechanism to prevent oxygen flow (via forced draft fan, helping gas and oil vapors exit the furnace).

6.3.2. Experimental setup and BBFs production

The experiment was setup in a completely randomized design with 2x3 factorial treatments (2 K sources and 3 physical forms) and three replications, totaling 6 treatments. The K sources were KCl and K_2SO_4, whereas the physical forms were powder, granule and pellet. Thus, the treatments tested were: 1) BBF-KCl powder; 2) BBF-KCl pellet; 3) BBF-KCl granule; 4) BBF-K_2SO_4 powder; 5) BBF-K_2SO_4 pellet; and 6) BBF-K_2SO_4 granule. The description of the treatments is presented in Table S1.

The BBFs (treatments) were produced from a physical mixture of SSB, K sources and additives (e.g., binding agent). The feedstocks were mixed to obtain a final mass of 1.0 kg of each BBF. Considering the values of total nitrogen (TN) and P_2O_5 in SSB, the final K concentration in BBFs was fixed at 3% and the sum of NPK was 10% (Brazil, 2009). Thus, 50.0 and 59.0 g of KCl and K_2SO_4 were added, respectively, to supply 3% K_2O. As a binding agent, 65 g of pre-gelatinized starch was also added to produce granules and pellets. As a source of N and P, SSB was added to complete 1.0 kg of the formulation. Summary of the amount of each raw material used in the production of each BBF is in Figure S1.

The SSB and K sources were crushed in an industrial device (Philco PLQ 1400), and later passed through a 0.500 mm mesh sieve. The formulations SSB + KCl + starch (BBF-KCl) and SSB + K_2SO_4 + starch (BBF-K_2SO_4) were subjected to the granulation and pelleting processes. Additionally, powder mixtures of raw materials without starch were studied as BBF in a powder form. The BBFs in different forms are shown in Figure S2.

The pellets were produced in a laboratory pelletizer (ENG-MAQ, model ENG 0200 V, São Paulo, Brazil). For each 1.0 kg batch of BBF, 140 mL of distilled water was used to facilitate agglutination of the raw materials. At the end of this process, pellets with a diameter of 6 mm and 1 cm in length were produced. After this process, the pellets were dried in an oven at 65 ºC for 24 h.

The granules were produced in a laboratory granulator composed of a cylindrical tray measuring 7 cm high by 36 cm in diameter, inclined at an angle of approximately 70º, coupled to a motor operating at 40-rpm (Figure S3). During granulation, distilled water was also added by spraying it on the raw material. Afterward, the granules were passed through a set of 3 sieves with different meshes, according to the sequence: 4 mm, 2 mm and 1 mm. The granules > 4 mm and smaller than 1 mm were crushed again and granulated to obtain granules between 1.0 and 4.0 mm. Finally, the granules were dried in an oven at 65 °C for 24 h.

6.3.3. Physical, chemical, mineralogical and morphological characterization of SS, SSB and BBFs

6.3.3.1. Proximate analysis

The SS, SSB and BBFs samples were passed through a 0.250 mm mesh sieve. For proximate analysis, moisture, volatile matter, fixed carbon and ash contents were determined by heating the samples in a muffle furnace (Linn-ElektroTherm, model KK 260 SO 4060) according to the method proposed by ASTM international (2013).

6.3.3.2. Elemental analysis

Total carbon (TC) and TN were determined using an elemental analyzer (Euro EA3000 Elemental Analyser, Milano, Italy) equipped with a thermal conductivity detector. Samples (approximately 5 mg) were placed in an auto-injector for analysis.

6.3.3.3. pH, nutrients and heavy metals (HMs)

After drying, grinding and sieving through a 0.500 mm mesh sieve, pH and macronutrients contents of the samples were determined. The pH was determined in a 0.01 M $CaCl_2$ solution, using a 1:5 (w/v) solid: solution ratio suspension (USEPA, 1996). For the extraction of macronutrients (Ca, Mg and S), micronutrients and HMs, samples were subjected to acid digestion according to USEPA 3050B (USEPA, 1996), and quantified by ICP-OES (ICPE-9000, Shimadzu, Japan). The concentration of P was determined by the molybdovanadophosphoric acid colorimetric method (Brasil, 2017), following nitric-perchloric extraction. The P concentration was estimated in a spectrophotometer at 400 nm (Automatic Digital Spectrophotometer SP 22, China). The concentration of K was determined by flame photometry (Brasil, 2017).

6.3.3.4. Organic carbon and humic substances

The organic carbon (OC) content was determined by the volumetric method of potassium dichromate (Walkley and Black, 1934). Determination of humic substances was performed according to the differential solubility technique (Swift, 1996). Carbon levels of fulvic acid (FA), humic acid (HA) and humin (HU) were estimated by dichromatometry according to Yeomans and Bremner (1988).

6.3.3.5. Surface area and pore volume

The surface area (SA), pore volume (PV) and micropores volume (PMV) were determined by N_2 adsorption isotherms at - 196.2 ºC using a surface area analyzer, NOVA 2200 (Quantachrome Corp., Boynton Beach, FL, USA). Values were estimated automatically by the software Quantachrome NovaWin®, using the BET (Brunauer, Emmett and Teller) equation.

6.3.3.6. Scanning electron microscopy (SEM) images

To obtain SEM images, samples were attached to stubs with carbon adhesive tape and then metalized with an electrically conductive thin gold film by the sputtering method. Analyses were performed using a microscope of the brand Jeol KAL-70001F (Waltham, Massachusetts, USA).

6.3.3.7. X-ray diffraction (XRD) and energy dispersive X-ray spectrometry (EDX) analysis

The XRD analysis was carried out on a diffractometer (D8 Focus, Bruker, Germany). Powder XRD patterns were obtained using monochromatic Cu Kα radiation at 40 kV, 30 mA, with 2θ between 10 and 70º. The peak areas identified for the different minerals were compared with XRD patterns of standard minerals compiled by the ICDD (International Center Diffraction Data). Samples were also submitted for energy dispersive EDX analysis. EDX patterns were obtained using an EDX 720HS (Shimadzu) spectrometer. For both analyses (XRD and EDX) whole samples were used.

6.3.3.8. Apparent density and particle density of BBFs

The apparent density (AD) of the BBFs (granules and pellets) was determined according to British (1995). Cylinders measuring 50 cm^3 were filled with BBFs samples and the calculation of AD was performed according to equation (1) (Eq. (1)):

$$\text{Eq. 1: } \mathrm{AD} = \frac{\mathrm{w}}{\mathrm{v}}$$

where, AD = apparent density (g cm^{-3}); w = weight of fertilizer needed to fill the cylinder (g); v = volume of the cylinder (cm^{-3}).

The particle density (PD) of BBFs (granules and pellets) was also determined according to the British Standard Method (British, 1995). The individual volume of 10 granules and 10 pellets of the same granulometry were calculated using a digital caliper. Thereafter, the mass of each material (granule and pellet) was determined on a precision balance. Subsequently, calculation of PD was performed according to equation (2) (Eq. (2)):

$$\text{Eq 2: } \mathrm{PD} = \frac{\mathrm{w}}{\mathrm{v}}$$

where, PD = particle density of the granule or pellet (g cm^{-3}); w = weight of the granule or pellet (g); v = volume of the granule or pellet (cm^{-3}).

6.3.4. Statistical analyses

For the macronutrients and micronutrients, elemental composition, proximate analysis properties, surface area and pore volume, comparisons between the SSB and the SS were performed considering the relative enrichment factor (RE), where $C_{biochar}$ is the content of property in biochar and C_{feed} is the content of property in the SS, according to the Equation 3 used by Yuan et al. (2013):

$$\text{Eq 3: } RE = \frac{Cbiochar}{Cfeed}$$

Data normality was validated by the Shapiro-Wilk test (α = 0.05) and the homogeneity of variance by Bartlett's test. A two-way analysis of variance (ANOVA) and the Tukey posthoc honest significant difference test were used to compare treatment means at a 5% level of significance. All statistical analyses were performed using the XLSTAT software (Addinsoft, 2013).

6.4. RESULTS AND DISCUSSION

6.4.1. Physical and chemical characteristics of SS and SSB

The results obtained by physical-chemical analysis indicate a clear influence of pyrolysis on the properties of SSB. The pyrolysis process reduced moisture (RE = 0.81) and volatile matter (RE = 0.85), and increased ash (RE = 1.18) and fixed carbon (RE = 4.2) levels in samples (Table 1). The increase in ash content is expected, since up to 600 °C most of the mineral material is preserved and volatile compounds are lost, resulting in a higher ash concentration (Adhikari et al., 2019). The pH value was not altered by pyrolysis and it was close to neutrality (6.5), similar to results previously reported for biochars obtained at low temperatures (300 ºC) (Faria et al., 2018; Fachini et al., 2021a). Typically, increases in pH are observed at higher pyrolysis temperatures (> 400 °C). SSB had a fixed carbon content 4.2 times higher than SS, and a smaller increment was verified for TC, ranging from 25.1% in SS to 27.1% after pyrolysis. These results demonstrate that pyrolysis promotes a greater accumulation of more recalcitrant forms of C, due to the reorganization of aliphatic chains into condensed C forms (Lehmann, 2007).

The TN content increased from 3.9% to 4.3% after pyrolysis (RE = 1.17). This increase indicates the presence of compounds in SSB with structures that are not easily decomposed up to 300 °C (Figueiredo et al., 2018a). Thus, the higher TN concentration in SSB can be explained by the volatilization losses of other elements and water. As expected, SS showed low K concentration, being little altered by pyrolysis. Consequently, SSB was poor in K, as reported previously (Figueiredo et al., 2021). This is the main limitation when using SSB as a fertilizer. In this case, further studies should search alternatives to provide K sources together with SSB. Enriching SSB with K and co-pyrolysis of SS with K-rich raw materials (Najafi-Ghiri et al., 2020) or produce of K-enriched fertilizer from SSB are some promising technologies.

Except for K, SS pyrolysis enriched macro and micronutrients levels. The total P_2O_5 concentration in SSB was 5.5%. This value was14% higher than in SS. This increase usually occurs up to 700 °C, at which P losses start due to volatilization (Yuan et al., 2013). Compared with biochar from multiple feedstocks (Li et al., 2019) and with other types of soil amendments (Cajamarca et al., 2019), SSB has higher P levels, with great potential for use as a P fertilizer. Increases of Ca, Mg, S and micronutrients levels have also been reported in previous studies with SSB at 300 ºC (Fachini et al., 2021a; Figueiredo et al., 2021; Chagas et al., 2020).

Table 1. Physical and chemical characteristics and relative enrichment factor (RE) from sewage sludge (SS) and biochar (SSB).

Property[a]	**SS**	**SSB**	**RE**[b]
pH ($CaCl_2$)	6.4±0.05	6.5±0.02	1.02
Moisture (%)	10.4±0.11	8.4±0.03	0.81
Volatile matter (%)	55.7±0.32	47.2±0.49	0.85
Ash (%)	32.4±0.17	38.1±0.18	1.18
FC (%)	1.5±0.19	6.3±0.64	4.20
OC (%)	18.3±0.11	18.3±1.06	1.08
H (%)	4.1±0.17	2.7±0.04	0.65
TC (%)	25.1±0.17	27.1±0.08	1.10
TN (%)	3.9±0.17	4.3±0.13	1.17
C/N	6.4±0.11	6.3±0.17	0.80
Total P_2O_5 (%)	4.7±0.07	5.5±0.08	1.15
Total K_2O (%)	0.05±0.01	0.04±0.01	1.10
Ca (g kg $^{-1}$)	6.0±0.03	6.9±0.04	1.25
Mg (g kg $^{-1}$)	1.40±0.2	1.54±0.01	1.14
S (g kg $^{-1}$)	1.30±0.4	1.62±0.01	1.18
Fe (g kg $^{-1}$)	17.5±1.06	20.0±2.1	1.13
B (mg kg $^{-1}$)	26.4±3.0	31.2±1.1	1.18
Mn (mg kg $^{-1}$)	88.6±4.2	100.0±11.3	1.14
Zn (mg kg $^{-1}$)	414.2±19.1	453.9±2.1	1.23
Cu (mg kg $^{-1}$)	88.1±5.5	100.0±2.3	1.25
Co (mg kg $^{-1}$)	9.7±0.6	11.9±1.9	1.22
Mo (mg kg $^{-1}$)	33.9±0.1	42.4±2.5	1.25
Cd (mg kg $^{-1}$)	18.1±0.7	19.3±3.5	1.07
Cr (mg kg $^{-1}$)	47.3±2.7	53.0±0.1	1.12
Ni (mg kg $^{-1}$)	14.4±1.3	28.4±0.6	1.96
Pb (mg kg $^{-1}$)	414.2±19.1	148.5±0.7	0.36
FA (g kg^{-1})	35.0±0.85	33.7±0.82	1.00
HA (g kg^{-1})	14.9±0.55	9.3±1.60	0.62
HU (g kg^{-1})	179.1±0.58	229.4±8.08	1.28
SA (m^2/g^{-1})	21.9	27.8	1.02
PV (cm^3/g^{-1})	0.096	0.102	1.10

[a]: average values ± standard deviation (n = 3); [b]: relative enrichment factor; FC = fixed carbon; OC = organic carbon; TC = total carbon; TN = total nitrogen. FA: fulvic acid; HA: humic acid; HU: humin; SA: specific surface area; PV: pore volume.

Pyrolysis also increased HMs levels (Table 1). Similar results also indicated higher HM content in SSB than in SS (Chagas et al., 2020). During the SS pyrolysis process, there may be an increase in the concentration of non-volatile elements in the temperature range used, leading to higher HMs contents (Yuan et al., 2015). Therefore, because HMs have a higher boiling point than the pyrolysis temperature employed, they are concentrated in the final biochar (Chagas et al., 2020). Pyrolysis also increases the thermostability of HMs, where examples may include the various forms in which HMs can exist in SS, salts and hydroxides are generally converted to oxides or sulphides, which are more stable at elevated temperatures (Yaun et al., 2015). Despite this, the HMs concentration was below the maximum limits acceptable by Brazilian legislation (Brazil, 2020) and the European Union (Concil of the European Union, 1986) for SS and the maximum limits allowed by the International Biochar Initiative for biochar (IBI, 2015). The origin of the SS produced in Brasília, Brazil, is predominately domestic with low HMs concentration. Therefore, biochar produced from SS generated in this city has a low risk of soil contamination, as demonstrated in our previous works, including short-term (Figueiredo et al., 2019) and long-term assessments (Chagas et al., 2020).

The pyrolysis process reduced the TC and FA and HA contents and increased HU concentration. Lower levels of FA and HA may result from thermal degradation of organic compounds during the pyrolysis process (Cybulak et al., 2019), thus increasing the C content in HU, which is the most recalcitrant fraction of organic matter. In addition, biochars contain highly aromatic polycondensed compounds very similar to the HU fraction (Figueiredo et al., 2018b), which may increase this fraction compared to SS.

The pyrolysis increased SA and PV (Table 1). The increase was 27 and 6.25% for SA and PV respectively. The increase in PV is due to the increase in SA after a pyrolysis (Figueiredo et al., 2019). In the present study, SSB, produced at 300 °C, had SA (27.8 m^2/g) and PV (0.102 cm^3/g) similar to or higher than values presented by other studies with SSB (Figueiredo et al., 2019; Figueiredo et al., 2021; Yuan et al., 2015). In addition, the SA value is generally related to the porosity of the material, mainly with the micropore volume (Hsu et al., 2019). In the present work, this relationship became clear because the material with the highest PV was also that with the highest SA (SSB).

Nitrogen adsorption and desorption isotherm models described by Brunauer–Enmett–Teller (BET) Model for the SS and SSB are shown in Figure S4. BET-analysis is widely used for SA and porosity measurements. The isotherms of both materials were Type IV(a) with Type H3 loop, according to the International Union of Pure and Applied Chemistry (IUPAC) classification. This indicates that SS and SSB predominantly present mesopores and macropores (Weber and Quicker, 2018; Huang et al., 2017; Wang, et al., 2016). Larger total PV and SA are desirable characteristics since they promote greater contact between the biochar and soil colloids and water, favoring the release of plant nutrients (Antille et al., 2013). In addition, larger pores can serve as an adequate shelter for microorganisms, increasing their survival and spread, in addition to improving water retention and soil aeration (Gao et al., 2016).

6.4.2. Spectra by energy dispersive spectrometry of SS and SSB

In the X-ray spectra it is possible to confirm the low presence of K in both SS (Figure 1A) and SSB (Figure 1B). Contrarily, the spectra of both materials confirmed the presence of P and other nutrients such as S, Ca, manganese (Mn), Fe and Al. Small increases in intensity were observed after pyrolysis, 0.028 cps/u.A and 0.1656 cps/u.A for K and P, respectively. These results demonstrate that pyrolysis at 300 °C promoted little change in the composition of these elements. Previous studies reported that the most significant changes in these SSB elements, compared to SS, were only found in biochars obtained at higher temperatures (Figueiredo et al., 2018a; Yuan et al., 2015).

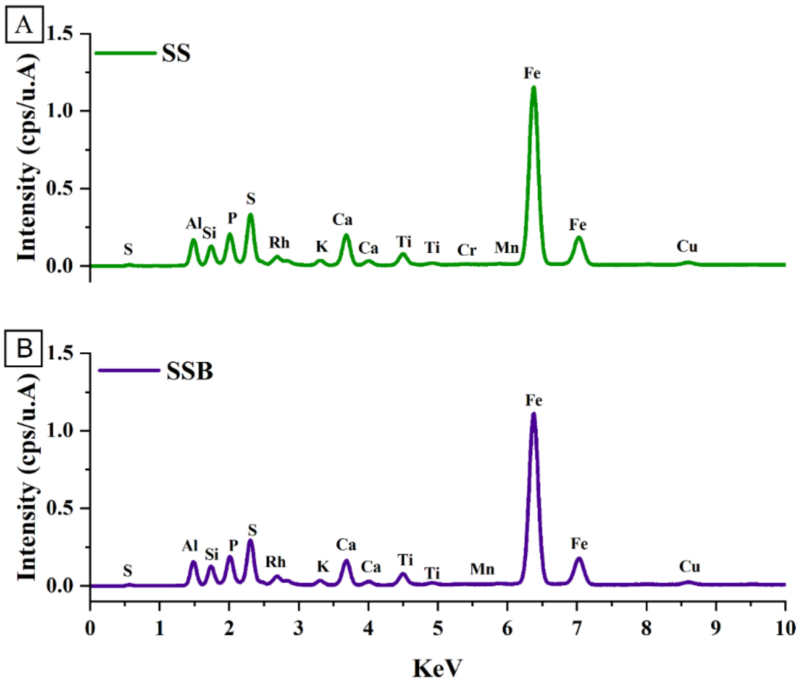

Figure 1. Energy dispersive X-ray spectrometry (EDX) spectra of sewage sludge (SS) and biochar (SSB).

6.4.3. X-ray diffraction (XRD) spectra of SS and SSB

The X-ray diffraction spectra (XRD) (Figure 2) demonstrated that quartz (SiO_2) was the main mineralogical component of SS (Figure 2A) and SSB (Figure 2B), with peaks close to 21°, 26º, 31°, 36°, 41°, 55°, 60°, 64° and 68° for SS and 21°, 26°, 45° and 68° for SSB. Usually, quartz is the most abundant mineral in SS and SSB samples, mainly due to clay and sand that remain in the sludge after the sewage treatment (Wang et al., 2017; Shen et al., 2018). Less intense peaks were also observed, in SS and SSB, at 18°, 22°, 25°, 27° and 29°, which show, respectively, the presence of gibbsite [$Al(OH)_3$], variscite ($AlPO_4$), dolomite [$CaMg(CO_3)_2$], calcite ($CaCO_3$) and albite ($NaAlSi_3O_8$) (Shen et al., 2018). In SSB, the increase in peaks during the range of $2\Theta = 20$ to 30°

indicates a C-rich structure with graphite-like amorphous structures stacked in layers (Hsu et al., 2019). In general, after the pyrolysis, SSB maintained the mineralogical characteristics of SS, probably due to the low temperature used. The only difference found was the presence of more intense peaks of quartz in SSB compared to SS. The XRD spectra reinforce the results obtained in chemical analyzes (Table 1) and the EDX spectra (Figure 1B) that demonstrated the presence of silicon (Si), Fe, Al, P, Ca and Mg in SSB.

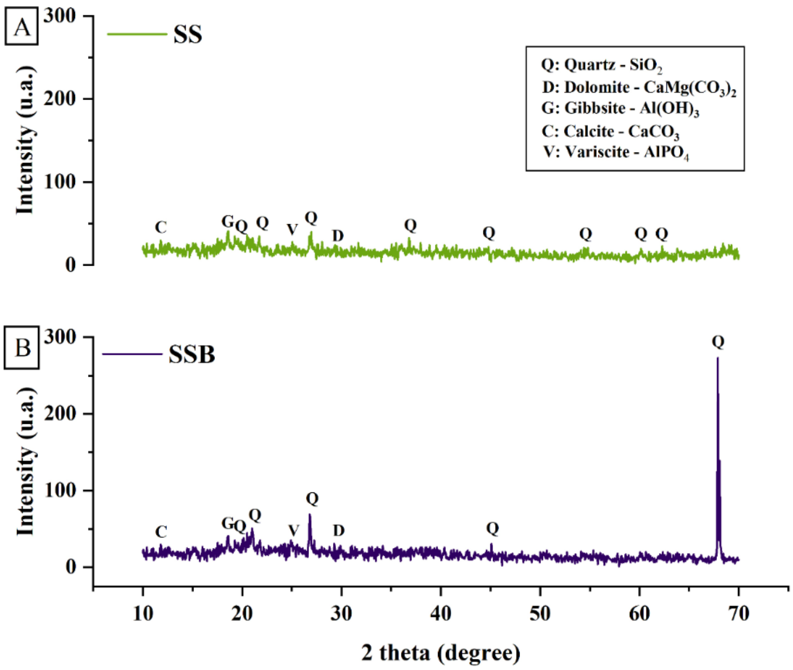

Figure 2. X-ray diffraction (XRD) spectra of SS (A) and SSB (B).

6.4.4. Scanning electron microscope images of SS and SSB

SEM images of the SS and SSB samples are shown in Figure 3. The SSB sample has a darker color with a typical charcoal appearance (Figure 3D) compared to the SS images (Figure 3A).

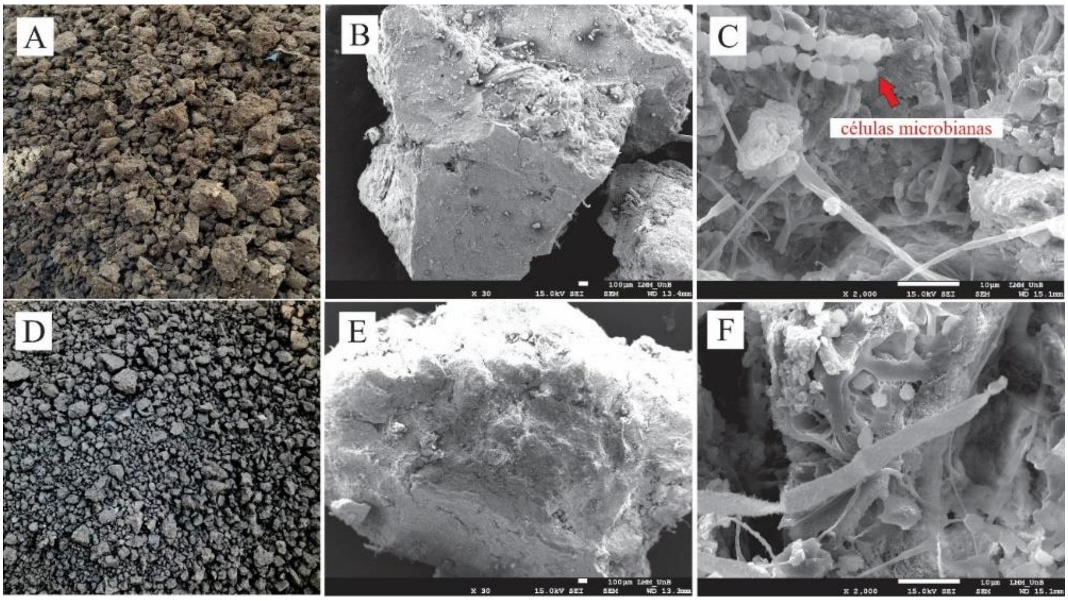

Figure 3. Scanning electron microscopy images of the SS and SSB surfaces. A: crushed SS; B: SS surface with a 30x magnification; C: SS surface with 2000x magnification. D: SSB; E: SSB with a 30x magnification. F: SS surface with 2000x magnification.

Figures 3B and 3E show the irregular shape of the SS and SSB samples, in addition to showing a greater presence of impurities on the SS surface and the presence of very small aggregates and stabilized particles on the SSB surface. The greater presence of pores in SSB (Figure 3F) than in SS (Figure 3C) can also be observed, contributing to a greater SA in biochars (Karim et al., 2016).

The presence of microbial cells in abundance in the SS sample should also be noted (Figure 3C), possibly composed of pathogenic microorganisms that persist even after the SS has dried. Pyrolysis temperatures ≥ 300 °C can inactivate helminths and thermotolerant coliforms, as demonstrated in our previous study (Figueiredo et al., 2019).

6.4.5. Chemical and mineralogical characterization of BBFs

6.4.5.1. Proximate analysis and pH

The BBFs pH values were affected by the interaction between K sources and forms ($P < 0.05$; Table 2). In general the BBF powder showed higher pH than pellets and granules, and BBF-K_2SO_4 pellets presented values between the granules and powder. The addition of water in the granulation and pelletization processes may have solubilized part of the mineral fertilizer (KCl or K_2SO_4), promoting ion exchange between the fertilizers and the SSB. Thus, there may have been a change in pH of the medium due to the marked increase in concentration of ions supplied by fertilizers to the microenvironment, resulting in the displacement, release or solubilization of other ions of an acid character (Du et al., 2010).

Table 2. Volatile matter (VM), pH, ash, fixed carbon (FC), total C and N contents of BBFs.

Form	Source				
	BBF-KCl		BBF-K_2SO_4		
	pH ($CaCl_2$)				
Granule	5.7 b B		5.8 c A		
Pellet	5.7 b B		6.1 b A		
Powder	6.6 a A		6.6 a A		
Source	VM (%)	Ash (%)	FC (%)	TC (%)	TN (%)
BBF-KCl	49.7 a	39.6 a	4.2 a	25 a	3.3 a
BBF-K_2SO_4	50.6 a	39.6 a	3.2 b	25 a	3.4 a
Form					
Granule	51.3 a	39.7 ab	2.1 b	25 a	3.0 b
Pellet	52.3 a	38.6 b	3.9 b	25 a	3.4 ab
Powder	47.0 b	40.6 a	5.1 a	24 a	3.6 a

Means followed by equal letters, uppercase in the row and lowercase in the column, do not show statistical differences according to the Tukey test ($P < 0.05$). Reference values (range) of various enriched biochar reported in literature: pH = 5.7 – 9.9; TC = 5.6 – 39.5 %; TN = 0.9 – 1.2% (Blackwell et al., 2015; Darby et al., 2016; Farrar et al., 2018; Gondek et al., 2018; Nardis et al., 2020).

Although KCl has a neutral acidity/basicity index (Coelho, 1994), the BBF-KCl, compared to BBF-K_2SO_4, resulted in lower pH values in all forms (except in powder form). In addition, KCl has a greater solubility (300 g L^{-1}) than that of K_2SO_4 (110 g L^{-1}) at 20 ºC (Coelho, 1994). Thus, the same amount of water added in the granulation and pelletization process can promote greater KCl solubilization, resulting in a pH reduction for BBF-KCl in the form of granules and pellets compared to BBF-K_2SO_4.

Volatile matter, ash and fixed carbon were not influenced by the interaction between K sources and forms ($P > 0.05$; Table 2). No differences in volatile matter were found between BBF-KCl and BBF-K_2SO_4 ($P > 0.05$; Table 2). BBFs in the form of granules and pellets showed a higher value of volatile solids than the powder form, probably because corn starch was used as a binding agent. According to Novak et al. (2009), high temperatures contribute to the dehydration of hydroxyl groups in starch, which may have resulted in greater volatilization of C, hydrogen (H) and oxygen (O) in BBFs formed with the addition of this binder. No differences in ash contents were found between K sources ($P > 0.05$; Table 2). Powder BBFs had higher ash contents than pellets. Likewise, BBFs in powder form had the highest fixed carbon levels. The K source also influenced the fixed carbon content, where BBF-KCl had a higher fixed carbon than BBF-K_2SO_4, probably due to the higher percentage of SSB used in the production of BBF-KCl.

6.4.5.2. Elemental composition

The TC contents in the BBFs were similar between sources of K and physical forms of the fertilizers ($P > 0.05$). In general, the TC contents for all BBFs were close to 25% (Table 2). The levels of TN were affected only by the physical form of the fertilizers. The only source of N used in the production of BBFs was SSB. Therefore, because powdered fertilizers have a higher percentage of SSB (Figure S1), they had a higher TN content compared to granules. In general, all fertilizers had on average 3.3% of TN. This value is above the levels typically found in enriched biochars obtained from different raw materials such that have a TN content ranging from 0.9 – 1.2% (Blackwell et al., 2015; Darby et al., 2016; Farrar et al., 2018; Gondek et al., 2018; Nardis et al., 2020).

6.4.5.3. Macronutrients and heavy metals (HMs) composition

The Ca content was influenced by the interaction between K sources and fertilizer form ($P < 0.05$; Table 3). The BBF powder showed higher Ca contents than pellets and granules. Because the fertilizers KCl and K_2SO_4 do not have Ca in their constitution, the Ca present in BBF fertilizers comes only from SSB. The BBFs in powder form showed higher Ca contents than granules and pellets, resulting from the higher proportion of SSB in their composition (Figure S1).

Only the fertilizer form had a significant effect on the Mg and total P_2O_5 contents in BBFs (Table 3). Of the total BBF mass, 88.5 and 87.6% of SSB were used for enrichment with KCl and K_2SO_4, respectively, resulting in similar values of Mg and total P_2O_5 between the sources of K. Powdered fertilizers showed the highest contents of Mg and total P_2O_5 compared to the granules and pellets which showed no differences amongst each other. For enrichment of the BBFs powder, a higher percentage of SSB was used in the final mass (Figure S1), contributing to a higher content of these nutrients. In general, SSB has a higher P content than biochars from other raw materials (Kim et al., 2018), representing a good option for the composition of BBF. It is currently well known that SSB is a source of P for crops, potentially replacing soluble mineral fertilizers (Faria et al., 2018; Fachini et al., 2021). As a fertilizer, SSB can supply from 4.5 to 7.2 times more P to soil than conventional P fertilizers (Chagas et al., 2021). Additionally, the P content in maize leaves cultivated in soil amended with SSB was around 67% higher compared to chemical fertilizers.

Table 3. Macronutrients and organic carbon (OC) in BBFs.

Form	Source				
	BBF-KCl			$BBF-K_2SO_4$	
	Ca ($g\ kg^{-1}$)				
Granule	5.5 b B			6.2 ab A	
Pellet	5.5 b A			5.8 b A	
Powder	7.0 a A			6.6 a A	
Source	Mg	S	K_2O	P_2O_5	OC
	$g\ kg^{-1}$		%		$g\ kg^{-1}$
BBF-KCl	1.4 a	1.3 b	3.0 a	5.3 a	178 a
$BBF-K_2SO_4$	1.4 a	2.2 a	3.0 a	5.3 a	173 a
Form					
Granule	1.4 b	1.6 c	3.0 a	5.1 b	175 ab
Pellet	1.4 b	1.7 b	3.0 a	5.1 b	194 a
Powder	1.5 a	1.9 a	3.0 a	5.4 a	158. b

Means followed by equal letters, uppercase in the row and lowercase in the column, do not show statistical differences according to the Tukey test ($P < 0.05$).

Sulfur contents were influenced by the sources and form ($P < 0.05$; Table 3). Regardless of the fertilizer form, the highest S levels were found in $BBF-K_2SO_4$ (Table 3). When enriched with K_2SO_4, the S levels in BBFs were higher because S came from both SSB and K_2SO_4. The KCl source resulted in BBFs with an S content similar to the pure SSB, 1.6 $g\ kg^{-1}$ (Table 1). Powdered BBFs, regardless of the K source, presented higher S levels than granules and pellets, resulting from the higher percentage of SSB in the composition of the BBFs.

The K_2O contents were similar between BBFs regardless of the source of K and the physical form of the fertilizer ($P > 0.05$; Table 3). The enrichment of SSB with K guaranteed a 75 fold increase in K_2O content of BBFs compared to pure SSB (Table 1). According to the percentage added in the production of these fertilizers, all BBFs presented 3% K_2O. Powdered BBFs had a higher SSB percentage in the final mass. However, the low content of K_2O in the SSB (0.04%) did not increase the content of this nutrient in powder BBFs compared to granules and pellets. These results prove the efficiency of enriching SSB with K sources to supplement the low K supply when using the pure SSB.

The HMs contents are shown in Table S2. All BBFs enriched with K source, regardless of the form and source used, showed HMs levels below the maximum acceptable value by Brazilian legislation for SS (Brasil, 2020), of the European Union (Council of the European Union, 1986) for SS and IBI (IBI, 2015) for biochars. The HMs values were close to those reported for pure SSB (Table 1). Furthermore, considering that the doses of enriched SSB will be lower than those normally used for pure SSB, the BBFs of the present work do not present risks of contamination with HMs when applied to the soil.

6.4.5.4. X-ray spectra by energy dispersive spectrometry

As expected, the most prominent effect of SSB enrichment was the observed increase in K levels (Figure 4.). Potassium peaks (Figure 4) with an increase of 6.8 and 7.2 times, respectively, for the enrichment of the SSB with KCl and K_2SO_4, compared to the pure SSB (Figure 1), prove the efficiency of enrichment with K sources to supplement the deficiency of this nutrient in the SSB.

The intensities of the Ca peaks were similar among K sources, with averages of 0.27 and 0.29 cps/uA for KCl and K_2SO_4, respectively. As a result of the higher SSB composition, powdered BBF, regardless of the K source, showed Ca peaks with an intensity of 0.34 cps/uA, similar to that of SSB (Figure 1). On average, the characteristic peaks of P for KCl (1.8 cps/uA) and K_2SO_4 (1.9 cps/uA) were similar to those found in the SS and SSB (Figure 1). These results prove that pyrolysis preserves or increased P concentration, representing a desirable feature for the production of sustainable fertilizers.

The BBF-K_2SO_4 showed more intense S peaks than BBF-KCl. As expected, peaks of chlorine (Cl) were observed only in BBF-KCl due to the presence of Cl in the KCl fertilizer. The peaks of Fe, Al and Si are due to the presence of these elements in the SS and consequently in the SSB (Figure 1). X-ray photoelectron spectroscopy spectra obtained by Shen et al. (2018) proved that the main elementary components in the pure SSB were Fe, Al and Si. This composition results from inorganic compounds such as Si, and Fe and Al salts in SS (Yuan and Dai, 2015).

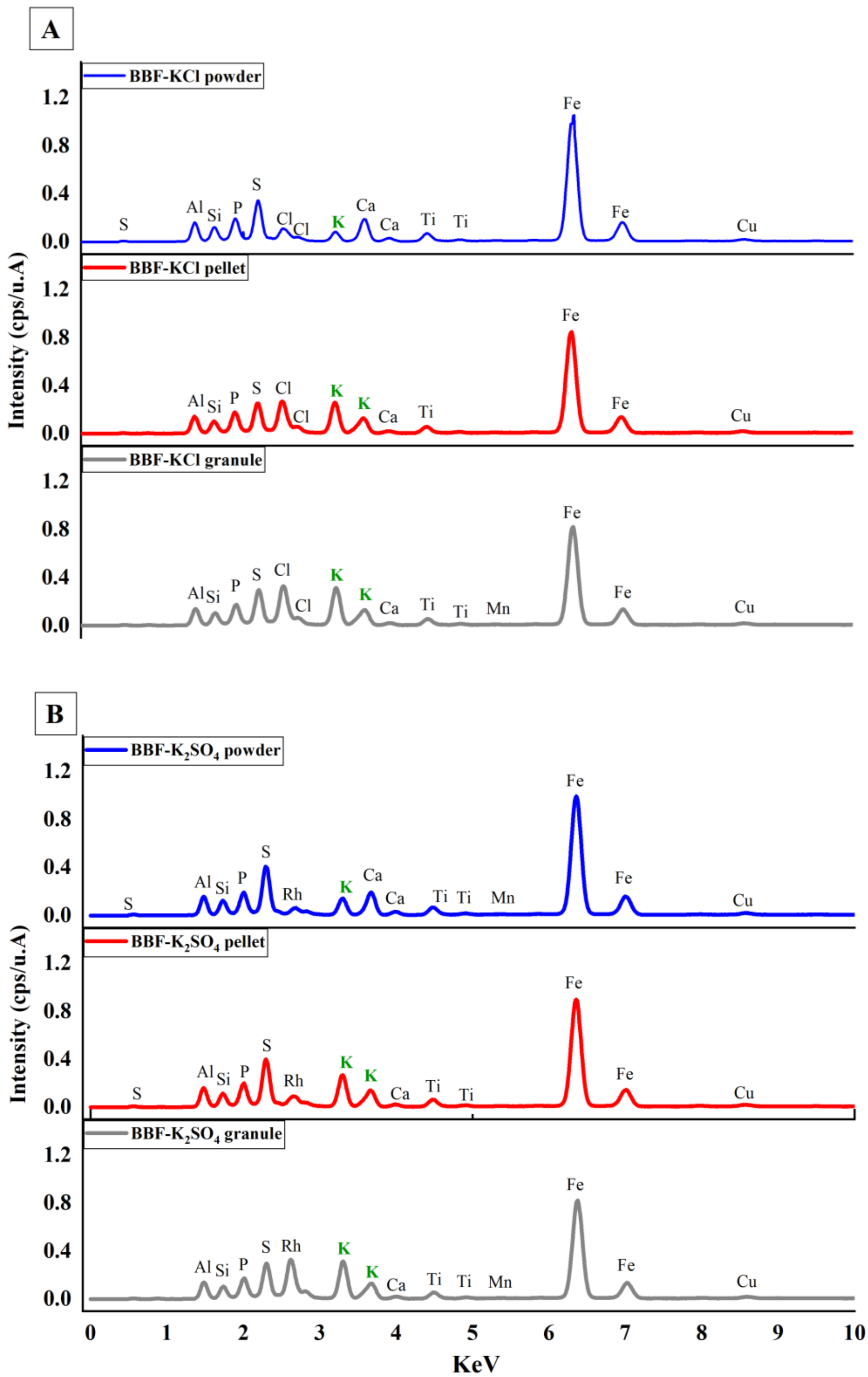

Figure 4. Energy dispersive X-ray spectrometry (EDX) spectra of BBFs fertilizers enriched with KCl (A) and K2SO4 (B) in the form of granules, pellets and powder.

6.4.5.5. X-ray diffraction (XRD) spectra

Figure 5 shows the XRD spectra of BBF enriched with KCl (Figure 5A) and K_2SO_4 (Figure 5B). In general, there is a wide range of typical peaks that indicate a wide variety of mineral components. Like SSB (Figure 2), the BBFs showed an increase in peaks in the range of 2θ = 20° to 30°, indicating C in graphite-like amorphous structures (Hsu et al., 2019). In addition, all BBFs showed peaks that indicate the presence of quartz (SiO_2), gibbsite [$Al(OH)_3$], variscite ($AlPO_4$), calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$], confirming previous studies (Liew et al., 2004; Shen et al., 2018; Wang et al., 2018). The mineralogical composition of the fertilizers was very similar to the pattern observed in pure SSB (Figure 2). On the other hand, after enrichment peaks at 28°, 41° and 50° were seen in the BBF-KCl (Figure 5A), indicating the presence of silvite (KCl) according to previous studies (Wang et al., 2018). In the BBF-K_2SO_4 (Figure 5B), peaks close to 16°, 30° and 40° confirmed the presence of the arcanite mineral (K_2SO_4) (Francello et al., 2019; Kim et al., 2012).

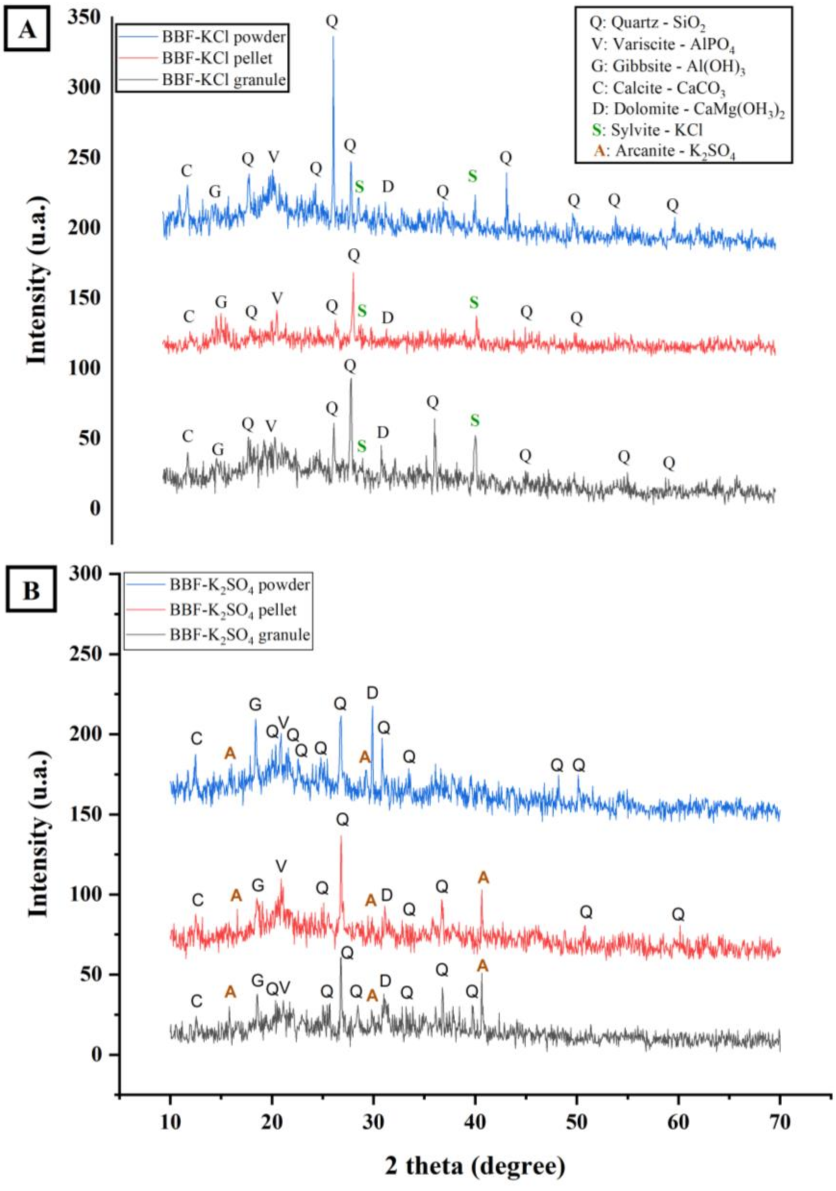

Figure 5. X-ray diffraction (XRD) spectra of BBFs fertilizers enriched with KCl (A) and K2SO4 (B) in the form of granules, pellets and powder.

Enrichment with K did not change the mineralogical composition of BBFs except for the sylvite and arcanite minerals from K sources (KCl or K_2SO_4). More intense peaks of quartz are observed in BBF in the powder form due to the higher percentage of SSB in the final mixture formulation.

6.4.5.6. Organic matter and humic substances

Humic fractions of the BBFs were not affected by interaction of the K source and the physical form of the fertilizer, nor by the isolated factors (Table S2). The humic fractions values ranges from 32.2 g kg^{-1} up to 33.9 g kg^{-1} for FA, 10.4 g kg^{-1} up to 11.5 g kg^{-1} for HA and 177.6 g kg^{-1} up to 220.2 g kg^{-1} for HU. There was an effect only of the fertilizer form on the OC content. SSB and starch, used in granules and pellets, were the sources of OC in BBFs. Because they have similar percentages of SSB and starch, BBF-KCl and BBF-K_2SO_4 showed similar OC contents. Organic C concentrations in BBFs were similar to those of SSB and SS, approximately 18.3% for both (Table 1). Pellets showed a higher OC content than the powder form. These results may be related to the addition of starch in the granulation and pelletization processes.

The high OC concentration in BBFs (Table 3) represents an essential substrate for soil microbial activity and the processes of immobilization and mineralization of nutrients. Although the increase in soil C contents after applying biochars is already well established (Yang et al., 2017; Yue et al., 2017), there are still doubts about the effect of using biochar-based fertilizers on soil C stocks. Therefore, BBF, in addition to the supply of nutrients, can contribute over time to the increase in soil organic matter fractions, increasing soil biota, aggregate stability and formation of humic substances.

6.4.6. Physical and morphological characterization

6.4.6.1. SEM images of BBFs

In Figure 6 it is possible to visualize the different structures of the granulated, pelletized and powdered BBFs and differentiate their pore-filled surfaces. Figure 6A and 6G show the joining of several particles of varying sizes and shapes to form a single granule of BBF-KCl and BBF-K_2SO_4. Unlike granules, BBF pellets showed a more compact and regular structure, with a smoother surface but with cracks (Figure 6B and 6H).

In addition to the binder, compressing of raw materials in the pelletizer promotes a surface with less roughness and greater uniformity when compared to granules (Reza et al., 2012). Cracks on the surface of biochar pellets of different materials have also been reported in previous studies (Reza et al., 2014; Santos et al., 2015). The more compact structure with a smooth surface may be related to the decrease in pore volume of the pellets compared to other forms of BBFs.

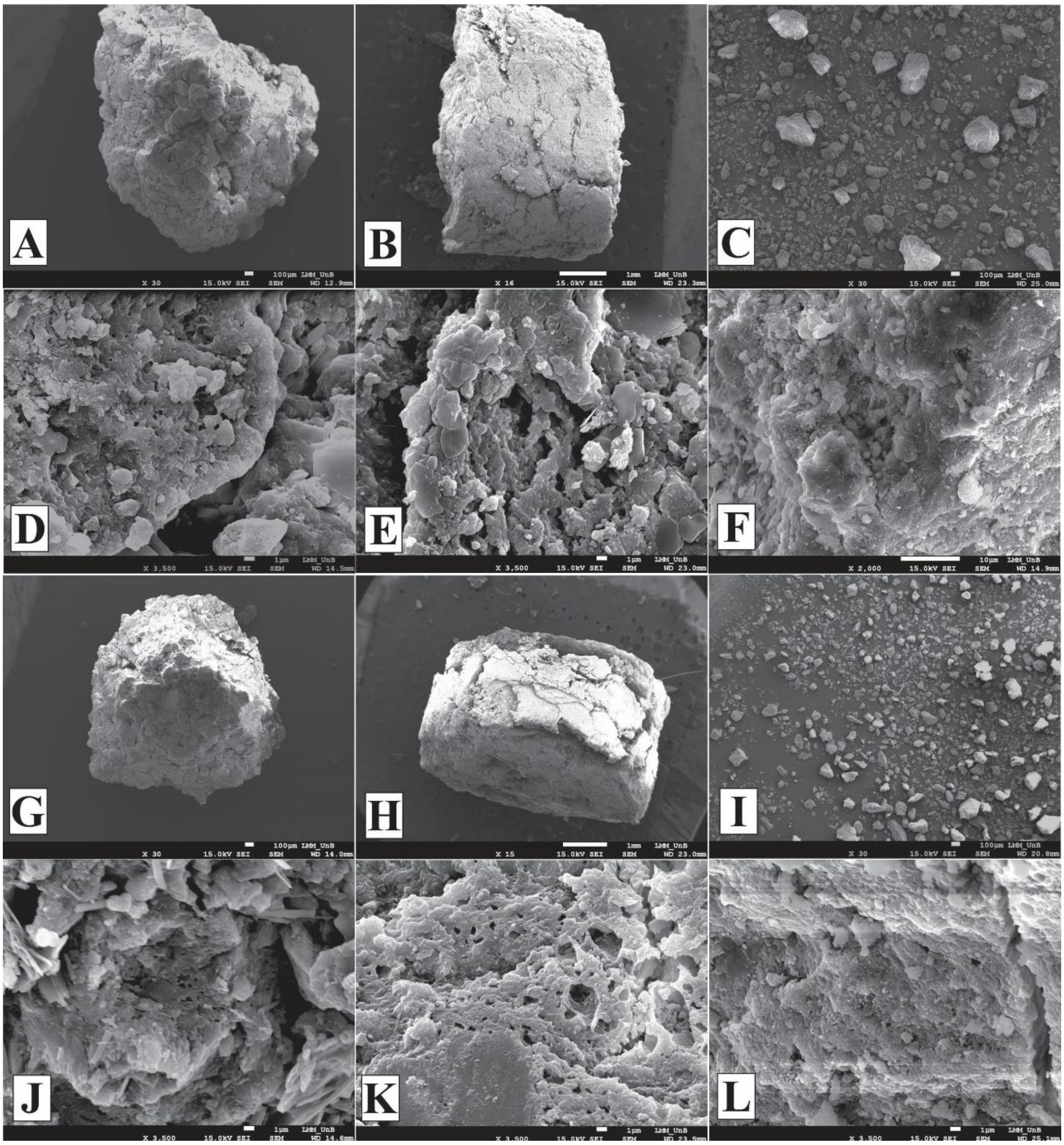

Figure 6. Scanning electron microscopy images (SEM) of the BBFs granules, pellets and powders. A, B and C: BBF-KCl in the form of granules (with 30x magnification), pellets (with 15x magnification) and powder (with 30x magnification), respectively; D, E and F: BBF-KCl in the form of granules, pellets and powder, respectively, with 3500x magnification; G, H and I: BBF-K_2SO_4 granules (with 30x magnification), pellets (with 15x magnification) and powder (with 30x magnification), respectively; J, K and L: BBF-K_2SO_4 in the form of granules, pellets and powder, respectively, with 3500x magnification.

Figure 6C and 6I show the BBFs in powder form (BBF-KCl and BBF-K_2SO_4, respectively), which present a physical mixture of different particles with different sizes and shapes representing SSB and K sources. In general, K sources did not influence the shape of the granules, pellets and powders, since they were the smallest proportion in the BBFs mixture.

Figure 6D, 6E, 6F, 6J, 6K and 6L with 3500x magnification show the surface roughness dominated by pores of varying sizes and well-distributed slits in the three different shapes of the BBF-KCl and BBF-K_2SO_4. Also observed was the presence of particles of the minerals KCl (Figure 6D, 6E and 6F) and K_2SO_4 (Figure 6J, 6K and 6L) on the surface of the SSB, and pores filled with minerals, indicating that the K fertilizer was adequately incorporated during the mixing of raw materials (Lin et al., 2013).

6.4.6.2. Surface area and pore volume

Nitrogen adsorption and desorption isotherm models described by BET-analysis for the different BBFs are shown in Figure 7. BET-analysis is widely used for surface area and porosity measurements. However, this method bears some limitations as diffusion problems in micropores (diameter < Å=2 nm) can occur and the surface area might therefore be underestimated (Weber and Quicker, 2018). In the present study, the isotherms of all materials (Figure S4 and Figure 7) were Type IV(a) with Type H3 loop, according to the IUPAC classification. This indicates that SSB and BBFs predominantly present mesopores and macropores (Huang et al., 2017; Wang et al., 2016). In general, BBFs production reduced SA, PV and micropores volume (PMV). Regarding the PV, SSB presented 39% micropores and regardless of the K source, the BBFs reduced the PV, presenting average values of 26, 27 and 23% micropores, in granules, pellets and powders, respectively. Among BBFs, pellets showed the lowest SA, PV and PMV, confirming the effect of compaction promoted during pelletization, as observed in the SEM images (Figure 6). In this sense, granulation showed higher values of SA, PV and PMV than the pellet, but lower than the product in a powder form.

Lower SA in BBF (Figure 7) compared to SSB (Table 1) may also be related to the presence of mineral particles on the surface of the SSB and the filling of SSB pores with the K source after the enrichment process. In addition, the SA value is generally related to the porosity of the material (Hsu et al., 2019), mainly with the micropore volume (Frazão et al., 2019). In the present work this relationship became clear because the material with the highest PMV was also that with the highest SA (SSB).

Micropores (< 2 nm) contribute to SA and are considered essential for nutrient adsorption. On the other hand, mesopores can provide adequate shelters for microorganisms, increasing their survival and spread, and macropores can increase water infiltration and soil aeration (Gao et al., 2016). The greater the pore volume the easier it is for water and plant roots to penetrate, facilitating contact with the material particles and favoring the release and absorption of nutrients. Fertilizers with higher porosity tend to have a higher rate of nutrient release when compared to fertilizers with thicker and smoother layers (Hermawan and Adipati, 2018).

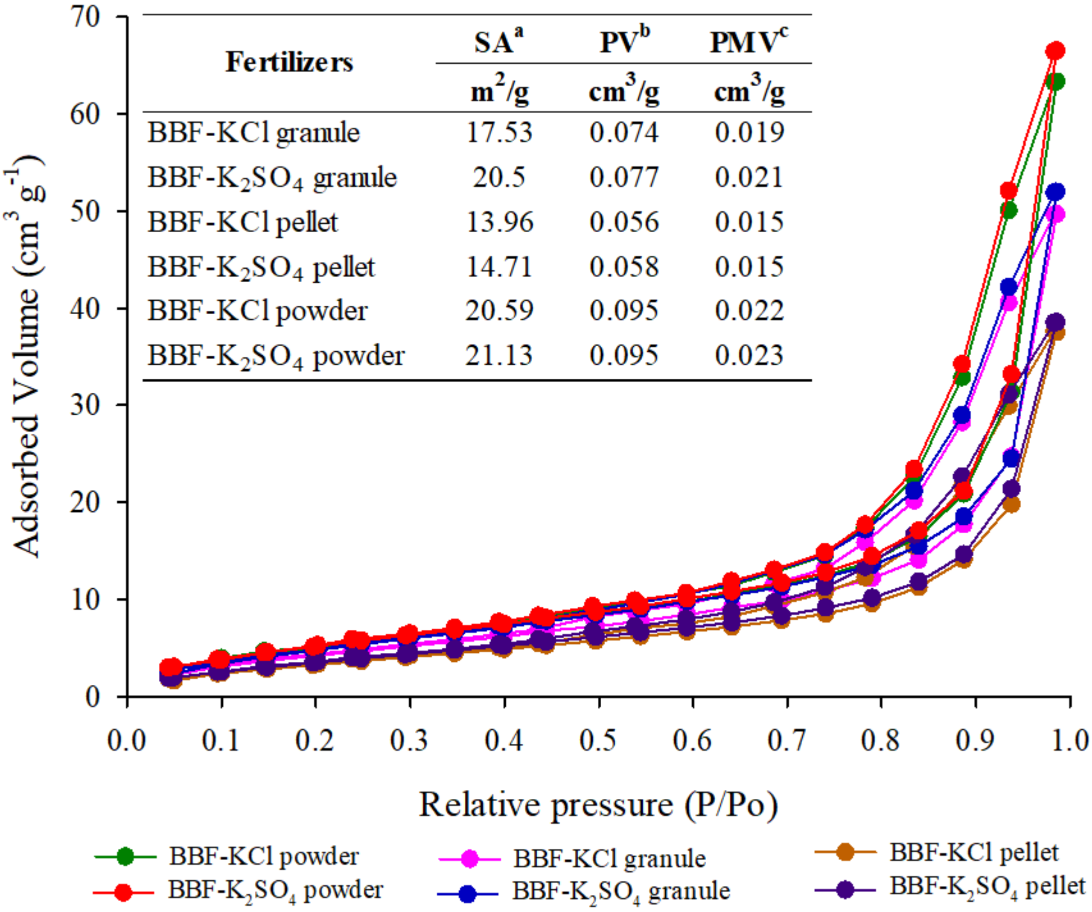

Figure 7. Nitrogen adsorption/desorption isotherms of BBFs fertilizers enriched with KCl (BBF-KCl) and K2SO4 (BBF-K2SO4) in three physical forms: granules, pellets and powder. a: surface area; b: total pore volume; c: micropores volume.

6.4.6.3. Apparent density (AD) and particle density (PD)

The K source did not affect the AD and PD of BBFs. On the other hand, the AD was affected by the physical form of the fertilizer (Table 4). The powdered BBFs showed a higher AD, and the granules presented the lowest values. The pellet showed an intermediate AD value. The higher AD of the BBFs in a powder form is related to the predominance of small particles (< 0.500 mm). As a consequence, a larger mass of powdered fertilizer can be stored per unit volume.

Table 4. Apparent density (AD) and particle density (PD) of BBFs

Source	AD (g cm $^{-3}$)	PD (g cm $^{-3}$)
BBF-KCl	0.56 a	1.0 a
BBF-K_2SO_4	0.55 a	1.0 a
Form		
Granule	0,45 c	0,9 a
Pellet	0,50 b	1,0 a
Powder	0,74 a	-

Means followed by the same letter are not statistically different according to the Tukey test ($P < 0.05$).

There was no difference between the forms of BBFs in terms of PD values. Contrary to our results, pellets usually have a higher PD than granules due to the pelletizing process. Compression reduces gaps and voids between the particles of the material (Reza et al., 2012), requiring a larger amount of biomass to form a pellet. In the granulation process the material is not subjected to compression, presenting a more porous structure in the middle of the granule when compared to the pellet structure (Vincevica-Gaile et al., 2019). According to Hu et al. (2016), a higher PD indicates a lower percentage of empty spaces and gaps within the material. In the present study, the PD values of BBFs, pelletized and granulated, are within the PD range already reported in other studies with biochars, with values varying between 0.6 and 1.7 g cm^{-3} for pellets and granules, respectively (Hu et al., 2016; Reza et al., 2014; Vincevica-Gaile et al., 2019).

Apparent density, PD and granulometry are important physical characteristics of fertilizers that influence the storage and application of the product. The development of new fertilizers requires the determination of physical properties of the materials, because they affect storage, spreading, behavior in the soil and agronomic efficiency (Antille et al., 2013). Thus, the BBFs in the form of granules and pellets need a larger storage space to store the same mass of powdered BBFs.

However, in its powder form, biochar can have very fine particles (1–600 μm) (Bowden-Green and Briens, 2016) that can be transported by the air. This causes health risks to people exposed to the product, such as respiratory irritation and pulmonary damage, thus making its application in the field unviable. Additionally, its low density promotes the accumulation of biochar in the upper soil layers, hindering its interaction in the soil profile (Vincevica-Gaile et al., 2019). Granulation and pelletization of SSB enriched with K are therefore means of minimizing the risks of dust and respiratory problems caused by the application of powdered biochars. Additionally, granules and pellets are easier-to-apply materials.

6.5. CONCLUSIONS

Sewage sludge pyrolysis increased the TC, TN and macro and micronutrient contents in SSB. Biochar preserved the mineralogical characteristics of the raw material, whose main mineral was quartz. The pyrolysis process also increased the SA and PV, which are desirable characteristics for a sustainable-based fertilizer. The SS pyrolysis at 300 °C was insufficient to increase the concentration of K in SSB, due to the low presence of this element in the raw material. The enrichment of SSB with soluble sources of K produces one biochar-based fertilizer with great potential for agriculture. The K source influenced both the chemical and mineralogical composition of the BBFs due to the proportions of raw materials used. The morphology and physical characteristics of BBFs were more influenced by the shape of the fertilizer (powder, pellet or granule) than by the source of K (KCl or K_2SO_4). Future studies are needed to evaluate the release dynamics of K from BBFs in the soil and the K uptake by crops. In addition, the scaling-up process and economic analysis need to be better understood.

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CHAPTER II

ASSESSING POTASSIUM RELEASE IN NATURAL SILICA SAND FROM NOVEL K-ENRICHED SEWAGE SLUDGE BIOCHAR FERTILIZERS

(Manuscript published in Journal of Environmental Management – https://doi.org/10.1016/j.jenvman.2022.115080)

7. ASSESSING POTASSIUM RELEASE IN NATURAL SILICA SAND FROM NOVEL K-ENRICHED SEWAGE SLUDGE BIOCHAR FERTILIZERS

7.1. ABSTRACT

Enrichment of biochars to produce slow nutrient release fertilizers with minimal losses to the environment is a promising strategy. However, the release of K from biochar-based fertilizer produced from SS is still poorly studied. In the present 30-day incubation study, the dynamics of K release were evaluated from SS biochar-based fertilizers enriched with potassium chloride (BBF-KCl) in different forms, subjected to two levels of silica sand moisture (10 and 20%). The BBF-KCl was evaluated in the form of granules, pellets and powder, in addition to pure KCl mineral fertilizer. During the incubation period water-soluble K extractions were performed, where the K contents were adjusted to K release kinetic models. An additional experiment was performed to assess the effect of BBF-KCl and KCl on K leaching. In general, at both moisture levels all BBF-KCl presented a slower K release compared to pure KCl mineral fertilizer, reducing the release rate by up to 77%. The K release dynamics were affected by the type of biochar fertilizer (granule, pellet and powder) and the silica sand moisture level. The behavior of BBF-KCl as slow-release fertilizers is strongly dependent on the silica sand moisture level. At the 10% moisture level, biochar fertilizers in the form of pellets and granules can be classified as slow-release fertilizers with the potential to increase the efficiency of K use in agriculture. Furthermore, compared to the chemical fertilizer, BBF-KCl reduced the amount of leached K, diminishing the risk of this nutrient polluting the groundwater. Our results must be further assessed in real conditions using soil as a suitable medium for agronomic and environmental evaluation. Therefore, future studies should consider the dynamic of K and other nutrients from BBF-KCl in distinct soil types.

7.2. INTRODUCTION

Pyrolysis has been used in the treatment of SS. The solid product of SS pyrolysis, called SSB, can contribute to the recycling of SS in agriculture, providing significant amounts of nutrients such as P, N, Ca and Zn (Paz-Ferreiro et al., 2018). However, low K levels are normally found in SSB which may limit its use in agriculture. The SS raw material has low K contents resulting from the sewage treatment process, where K is eliminated in the form of soluble salts along with the liquid effluent (Kirchmann et al., 2016). Thus, as a consequence of the low K concentration in the SS, SSBs typically do not have adequate K contents to meet crop demands (Faria et al., 2018; Fachini et al., 2021a) and it is necessary to complement with mineral fertilizer. Previous studies with biochars from other raw materials have also reported the need to apply mineral fertilizers combined with biochars for a complete and balanced supply of nutrients to plants (Subedi et al., 2016; Arif et al., 2017; Shin et al., 2019).

The use of nutrient-enriched biochars has increased in recent years with the objective of enabling and balancing the supply of nutrients to plants. Enriching biochars to produce slow nutrient release fertilizers is one of the strategies used in recent years (Carneiro et al., 2021). When compared to highly soluble mineral fertilizers, BBFs contribute to increase the fertilizer use efficiency (Lustosa Filho et al., 2020). This is possible because BBFs can reduce nutrient losses via leaching (Luo et al., 2021) and the use of soluble mineral sources, in addition to contributing to increased nutrient uptake and crop productivity (Borges et al., 2020).

The surfaces of biochars are mainly characterized by negatively charged functional groups, such as carboxyl and phenolic, which can contribute to greater sorption of cations such as K (Mukherjee et al., 2011). Therefore, K-enriched SSB can act as a slow-release fertilizer and minimize K losses by leaching. Furthermore, the organic fraction of biochar and the presence of pores in its structure can contribute to protect the more soluble fractions of the mineral fertilizer (Kim et al., 2014; Luo et al., 2021). This minimizes its losses and provides a better synchronization of nutrient release with the plant's nutritional demand, increasing the efficiency of the applied fertilizer (Adu-Gyamfi et al., 2019). Thus, the enrichment of SSB with mineral K sources may result in a slow K release BBFs, resolving the low supply of this nutrient with the application of pure SSB, in addition to reducing K losses from highly soluble sources. In general, weathered soils from tropical regions have low cation exchange capacity. As a consequence, K losses by leaching are common in these regions. Therefore, slow-release fertilizers are crucial for increasing K use efficiency in agriculture.

Studies on BBFs are relatively recent. Therefore, there is a wide variation in the methodologies used to obtain the final product (Karim et al., 2016; Farrar et al., 2018). Biochar granulation and pelleting processes are the most common for nutrient enrichment and have been used as a way to minimize the risk of dust and respiratory problems caused by the application of biochar in its powder form (Vincevica-Gaile et al., 2019). In the case of SSB, to date there are no published studies evaluating the release and availability of nutrients from SSB-based fertilizers enriched with soluble K sources. Furthermore, enrichment technologies can affect the release of nutrients by the fertilizer as well as its agronomic efficiency, and they need to be better studied. Soil is the most appropriate medium to assess nutrient release from fertilizers. However, in this preliminary study, silica sand was used as a pure medium to avoid the influence of the soil matrix on K sorption (Adams et al., 2013).

The present study sought to evaluate the dynamics of K release from BBF enriched with KCl (BBF-KCl), subjected to distinct silica sand moisture levels. For this, the following hypotheses were tested: i) K release dynamics are affected by the physical form of the BBFs-KCl; ii) BBFs-KCl act as K slow-release fertilizers regardless the silica sand moisture level.

7.3. MATERIALS AND METHODS

7.3.1. Production of K-enriched biochar fertilizers

The BBF-KCl were the same used in Chapter I (BBF-KCl) in the form of granule, pellet and powder. Therefore, details of the production and characterization of SS, SSB and BBF-KCl are presented in Chapter I and in our previous work (Fachini et al., 2021b).

7.3.2. Incubation study

To assess the K-release dynamics from BBF-KCl, an incubation experiment was performed as described in Bley et al. (2017). Natural silica sand (SiO_2), with fine granulometry (< 0.2 mm and > 0.06 mm) according to the ABNT classification (NBR 6502/1995), was used to ensure that the released K levels resulted only from the studied fertilizers as previously adopted by Luo et al. (2021). Silica sand presented the following characteristics: apparent density (1.15 g cm^{-3}); Moisture content (0.60%); SiO_2 (97.0%); Al_2O_3 (1.50%); Fe_2O_3 (0.30%); and other unspecified components (0.60%).

In the incubation assay, silica sand was placed in 200 cm^3 plastic containers. In each container 100 g of silica sand and 5 g of each BBF-KCl were added. In addition to BBF-KCl, pure KCl mineral fertilizer was also evaluated. The BBF-KCl used in this study contained 3% K (Fachini et al., 2021b). Thus, 5 g of each material was applied to silica sand to provide 1500 mg kg^{-1} of K_2O, which corresponds to 1245 mg kg^{-1} of K. To ensure the same mass of K in the treatment with mineral fertilizer, 0.25 g of KCl mineral fertilizer (60% K_2O) was added to 100 g of silica. The same KCl source used to enrich the BBF-KCl was used, presenting analytical purity that meets the purity standards defined by the American Chemical Society (PA-ACS).

The BBF-KCl and KCl were placed in containers with permeable polyester mesh < 0.500 mm, measuring 5 × 4 cm and sealed at the ends with 100% polyester thread, referred to as “sachets” (Figure S5). All sachets were sealed at the end with polyester thread. The sachets containing the fertilizers were placed in plastic bottles, previously filled with 50 g of silica sand and covered with another 50 g of silica sand (Figure 8).

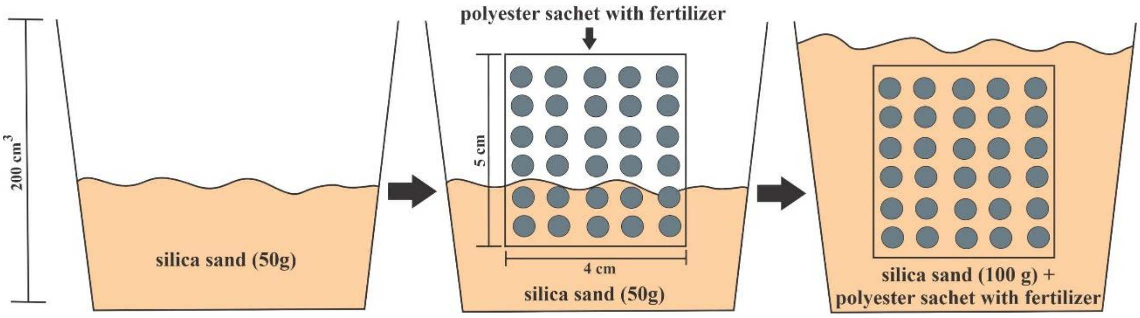

Figure 8. Schematic representing the 200 cm^3 plastic containers with 100 g of silica sand and polyester sachet containing the fertilizer.

Two levels of moisture in silica sand were tested. The moisture level of 10% corresponds to the moisture content of sandy soils at field capacity (Laboski et al., 1998). A soil water content of 20% was also chosen to simulate a moisture level with the potential to promote K losses by leaching in sandy soils. Thus, the total mass of 100 g of silica sand was moistened with distilled water, to reach 10 and 20% water, which corresponded to 0.1 g g^{-1} and 0.2 g g^{-1}, respectively. Moisture was monitored every 5 days by assessing the total mass of the flasks using a precision scale model AY220 (Shimadzu), and when necessary distilled water was added to maintain a constant water content in the silica sand. Flasks containing the silica sand and treatments were incubated in an incubation room equipped with a temperature and humidity controller. Incubation was conducted at an average temperature of 25 °C, and the following periods were assessed: 12 h and 1, 2, 3, 4, 5, 10, 20 and 30 days after initiating the incubation. After the incubation period established for each treatment, the flasks were removed from the incubation room, separating the sachet from the silica sand. The water-soluble K content released in the silica sand mass was then determined.

7.3.3. Determination of the K concentrations

After removing the sachets, the mass of silica sand from the container was air-dried and homogenized. The silica sand samples were then analyzed and the K contents determined. The K was extracted in a mixture with distilled water in a 1:10 (w/v) silica sand: distilled water ratio (Wang et al., 2018).

For the extraction of K, 1 g of silica sand and 9 mL of distilled water were mixed in a 50 mL beaker, then the mixture was agitated for about 5 min at 150 rpm on a horizontal circular agitation table, model Tec-1401 (Tecnal, Piracicaba, SP). Next, the mixture decanted for 30 min until finally the extract was filtered and the K reading was taken in a digital flame photometer (Benfer PHS, São Paulo, SP, Brazil).

7.3.4. Evaluated treatments

The following treatments were evaluated, with three replications: 1) control: only silica sand without fertilizer addition, 2) granulated BBF-KCl, 3) pelletized BBF-KCl, 4) BBF-KCl powder and 5) powder KCl mineral fertilizer. The treatments were submitted to two moisture levels (10 and 20%) and evaluated in 9 incubation periods.

7.3.5. Potassium release kinetics

After the determination of K, the K release rate (%) during the incubation period was calculated according to equation (4) (Eq. (4)).

$$\text{Eq. 4: K release (\%)} = \left(\frac{\text{Kt}}{\text{Kt0}}\right) \text{x } 100$$

where, Kt = K content released during the incubation period (mg kg^{-1} K); Kt0 = total initial K content (mg kg^{-1}) added to the sachet.

Next, the K release data (%) was submitted to non-linear regression analysis to determine the K release dynamics over time. Different models were tested to best represent the data, using the SigmaPlot 12.5 program. According to the values of the R^2 coefficient and the P value (< 0.0001), the best model to represent the K release data was the first-order exponential equation (Eq. (5)).

$$\text{Eq. 5: } y = a(1 - b^x)$$

where, y = K release (%) and x = incubation time (days).

7.3.6. BBF-KCl as a slow-release fertilizer

The fitted equation (Eq. (5)) was used to determine the release dynamics of the fertilizers. According to the Association of American Plant Food Control Officials (AAPFCO, 1997), a slow- or controlled-release fertilizer is a fertilizer containing a plant nutrient in a form which delays its availability for plant uptake and use after application, or which extends its availability to the plant significantly longer than a reference ‘rapidly available nutrient fertilizer’ such as ammonium nitrate or urea, ammonium phosphate or potassium chloride. In addition, according to regulations of the European Committee for

Standardization (CEN), fertilizer may be described as slow-release if the nutrient or nutrients declared as slow-release meet, under defined conditions, each of the following criteria (Trenkel, 2010): i) no more than 15% released in 24 h; ii) no more than 75% released in 28 days.

7.3.7. Colum leaching experiment

Leaching of K from fertilizers (BBF-KCl and KCl) in natural silica sand was assessed during a 6-day trial. The column leaching experiment, with 3 replications, was carried out in polyvinyl tubes (20 cm length x 5.0 cm diameter), with a barrier made of filter paper fitted near the base (Yuan et al., 2016). A valve was inserted at the base for the control of leachate collection (Figure 9). The columns were packed with 375 g of silica sand.

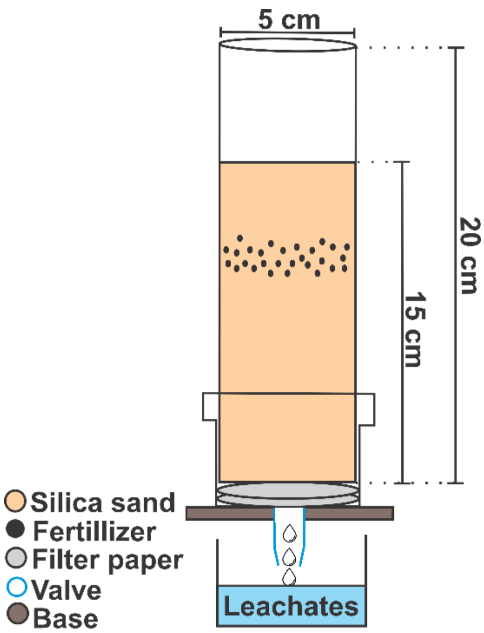

Figure 9. Schematic of the experimental setup used in the column leaching test.

The same amount of BBF-KCl and KCl used in the incubation experiment was added into the columns (5 g of BBF-KCl and 0.25 g of KCl). Distilled deionized water was added gently across the surface of the column. At the start of each experiment, the columns were saturated by the addition of 130 mL of distilled deionized water, and then they were immediately drained. Each column was leached once a day with 30 mL of the distilled deionized water, and a total of 180 mL of water was added to the columns over the 6-day experimental period. This volume corresponds to the average precipitation in February in the Central region of Brazil. The leachates were filtered via filter paper (JP42, Prolab) and the K concentration was determined using a digital flame photometer (Benfer

PHS, São Paulo, SP, Brazil). The effect of the treatments (fertilizers) on the cumulative amount of leached K was tested by a one-way ANOVA, followed by the Tukey test ($P < 0.05$).

7.4. RESULTS AND DISCUSSION

7.4.1. Cinética de liberação de K

The dynamics of K release from BBFs-KCl and pure KCl at the two different moisture levels is shown in Figure 10. For all fertilizers, the first-order exponential model adequately described the K release process with high significance ($P < 0.0001$) and a R^2 value greater than 0.85. The first-order kinetic equation also provided the best correlation to describe the release mechanism of K into water and soil in the work conducted by Pang et al. (2018).

For the two moisture levels, 10% (Figure 10A) and 20% (Figure 10B), all BBFs-KCl showed slower K release compared to pure KCl fertilizer. Among the BBFs-KCl, the K release rate followed the order of powder > granule > pellet, regardless of the moisture content. For the 10% moisture level, the KCl fertilizer showed a rapid K release, totaling 1078.4 mg kg^{-1} (86.6%) of K released after the first day (Figure 10A). Afterwards, the release remained constant until the end of the solubilization process. On the other hand, the enriched fertilizers showed slower K release than KCl, suggesting that BBFs-KCl has the ability to control K release. The enriched fertilizer types also presented different K release rates in the initial incubation period. Until the fourth day of incubation, the release was 501.4, 605.2 and 703.0 mg kg^{-1} of K for the pellet, granule and powder, respectively. In the final incubation phase, at 30 days, BBFs-KCl in the pellet, granule and powder form released only 54, 65 and 78% respectively, while the KCl fertilizer released 100% of K by the twentieth day of incubation.

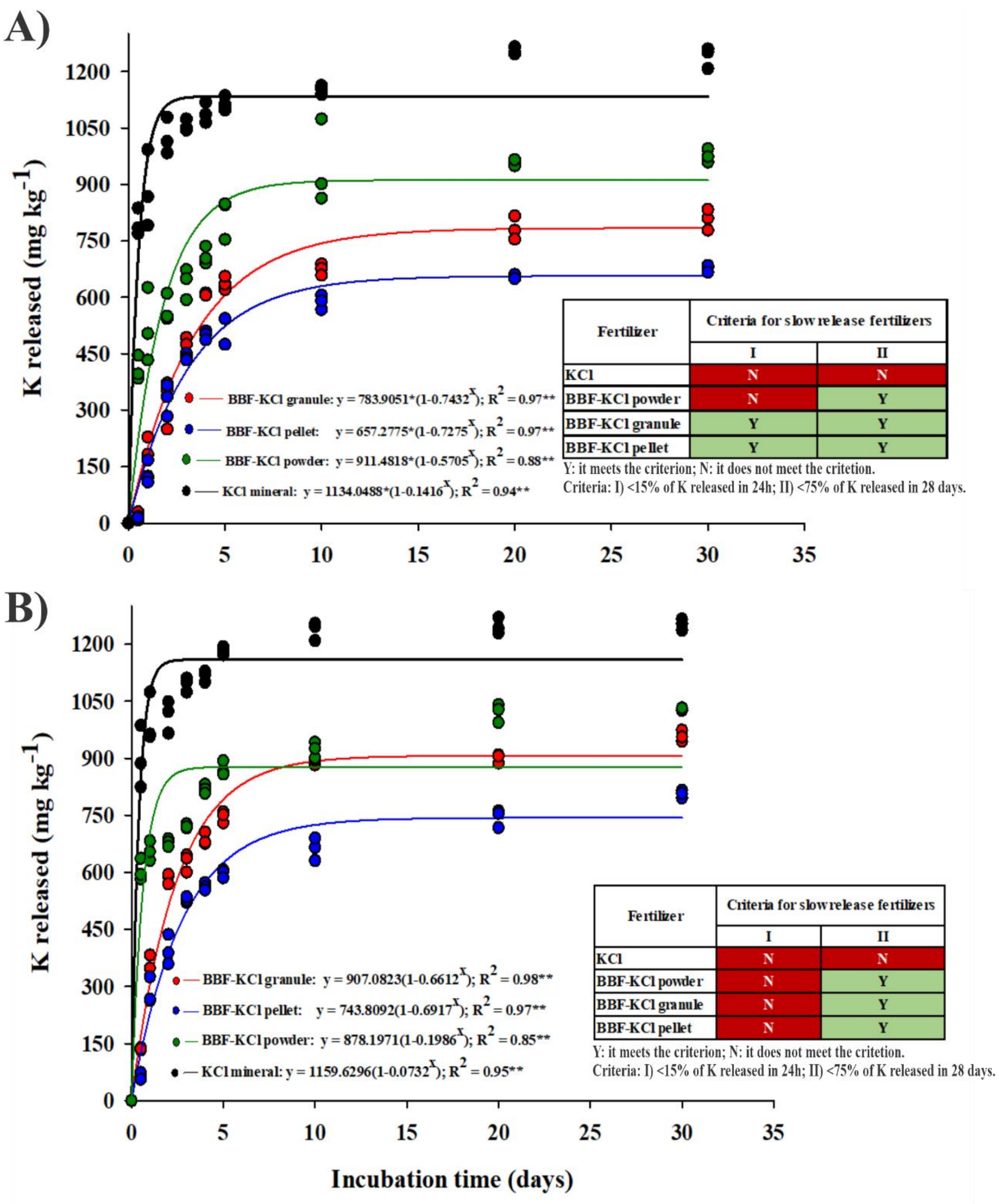

Figure 10. K release (mg kg-1) from BBFs-KCl and mineral KCl over time (days) in silica sand with 10% moisture (A) and 20% moisture (B). **P < 0.0001. Tables show the criteria for fertilizer to be considered slow-release according to the European Committee for Standardization (CEN).

The two moisture levels showed similar K release dynamics from the fertilizers. At the 20% moisture level, in just 1 day of incubation the KCl fertilizer released almost 90% of K, reaching 1049.30 mg kg^{-1} of K on the second day of the experiment (Figure 10B). From the second day onwards, release remained practically constant. At this same moisture level, the accumulated release of K by the enriched fertilizers at 30 days was 65, 77 and 83% for the pellet, granule and powder, respectively. This greater presence of water anticipated by 10 days the total release (100%) of K from the mineral fertilizer KCl (1245 mg kg^{-1} of K), proving that the rate of K solubilization is very dependent on the soil moisture level. Increasing the moisture level from 10 to 20% also increased K release from BBFs-KCl, with increases of 19, 18 and 5% for the pellet, granule and powder, respectively. The fertilizer nutrient release mechanism depends, among other factors, on the fertilizer solubility in solution, granule physical form and soil/substrate water content (Adms et al., 2013). KCl has a high water solubility, around 300 g/L (Coelho et al., 1994). In the present work, a greater supply of water in silica resulted in a higher rate of K release from fertilizers considering the same period of time under the same conditions of temperature, substrate and fertilizer doses. According to Du et al. (2006), the highest K release rate was obtained when the fertilizer was immersed in water, followed by water-saturated silica and finally, the lowest release rate was verified when the fertilizer was released onto silica with the water content at the field capacity.

7.4.2. Slow-release mechanism of K from BBF-KCl

The models used to describe the K release kinetics (Figure 10) demonstrated that BBFs-KCl have a slower K release when compared to KCl mineral fertilizer. According to the European Committee for Standardization (CEN) regulations for slow or controlled release fertilizers, the product must not release more than 15% in 24 h, and no more than 75% in 28 days (Trenkel, 2010). In the present study, when submitted to 10% moisture the BBF-KCl both in the form of granules and pellets can be classified as a slow-release fertilizer. On the other hand, BBF-KCl in powder form, despite not releasing more than 75% in 28 days, released more than 15% K in 24 h, therefore it did not fully meet the requirements to be considered a slow-release fertilizer according to CEN classification (Trenkel, 2010).

When BBFs-KCl were subjected to 20% moisture, none of the fertilizers meet the criterion I and released more than 15% of the K in 24 h. However, in this higher moisture level, only biochar fertilizers (granule, pellet and powder) met the second criterion of not releasing more than 75% in 28 days. Considering that biochar has different physicochemical characteristics from other raw materials used so far for the development of a controlled or slow-release fertilizer, and studies with fertilizer biochar are recent, there is a need to create new regulations for these new fertilizers that utilize biochar as a raw material.

Potassium is one of the nutrients most subject to leaching losses, especially in sandy soils (Rosolem and Steiner, 2017). As a consequence, in addition to reducing the efficiency of using this nutrient (Cheng et al., 2017), K losses can promote pollution of waterways (Borges et al., 2017). The use of a BBFs-KCl can thus contribute to the slow release of K, reducing the social and environmental problems caused by the high solubility of K mineral fertilizers.

The release of K from chemical fertilizers is normally proportional to the applied dose (Adebayo et al., 2017). However, organic fertilizers (Soremi et al., 2018), organominerals (El-Mageed and Semida, 2015) and pure biochar (Wang et al., 2018) may not release K proportionally to the fertilizer dose due to complexity of K interactions with the organic and inorganic compounds of these fertilizers. The effect of BBFs-KCl dose on K release needs to be better understood.

The results of this work prove that, depending on the soil moisture level, the efficiency of enriching sewage sludge biochar with KCl is increased since this combination resulted in a K slow-release fertilizer. When the moisture is at field capacity, BBFs-KCl in the pellet and granule forms were classified as slow-release fertilizers. Recent studies with biochars from other biomasses enriched with mineral nutrient sources have also proven the effectiveness of transforming biochar into a slow-release fertilizer for which it was enriched, mainly N, P and K (Zhao et al., 2016; Gwenzi et al., 2017; Shin et al., 2019; Lustosa Filho et al., 2020; Pogorzelski et al., 2020; Carneiro et al., 2021; Luo et al., 2021). This slower release of the nutrient from a biochar fertilizer resulted in an increase in agronomic efficiency of up to 15% in clayey soils when compared to mineral fertilizer (Borges et al., 2020); and in sandy soils the agronomic efficiency was the same as that of a highly soluble mineral fertilizer (Carneiro et al., 2021). Similarly, a P-enriched biochar fertilizer was more effective in providing P to plants in clayey soil when compared to conventional high-solubility phosphate fertilizer (Pogorzelski et al., 2020).

The slower release of nutrients from biochar fertilizers, when compared to highly soluble mineral fertilizers, has been related to several factors such as: i) formation of new low solubility precipitates on the surface of the biochar (Luo et al., 2021), i.e., elements present on the surface of the biochar can bind with highly soluble nutrients from the mineral source and form new compounds with lower solubility (Carneiro et al., 2021); ii) strong electrostatic attraction between the negatively charged biochar surface and positively charged elements (Gwenzi et al., 2017; Luo et al., 2021); iii) physical protection of the soluble fraction by biochar pores (Pogorzelski et al., 2020); iv) presence of micropores, complex pore geometry and the hydrophobic nature of the biochar (Chia et al., 2015) which limits water access inside the biochar fertilizer, hindering the diffusion and dissolution of the more soluble fertilizer (Limwikran et al., 2018); and v) strong biochar adsorption capacity (Li et al., 2018). Based on these factors and considering the K release kinetics obtained in the present study (Figure 10), a representative schematic was elaborated (Figure 11) that seeks to clarify the mechanisms that can explain the release of K from the enriched BBFs-KCl.

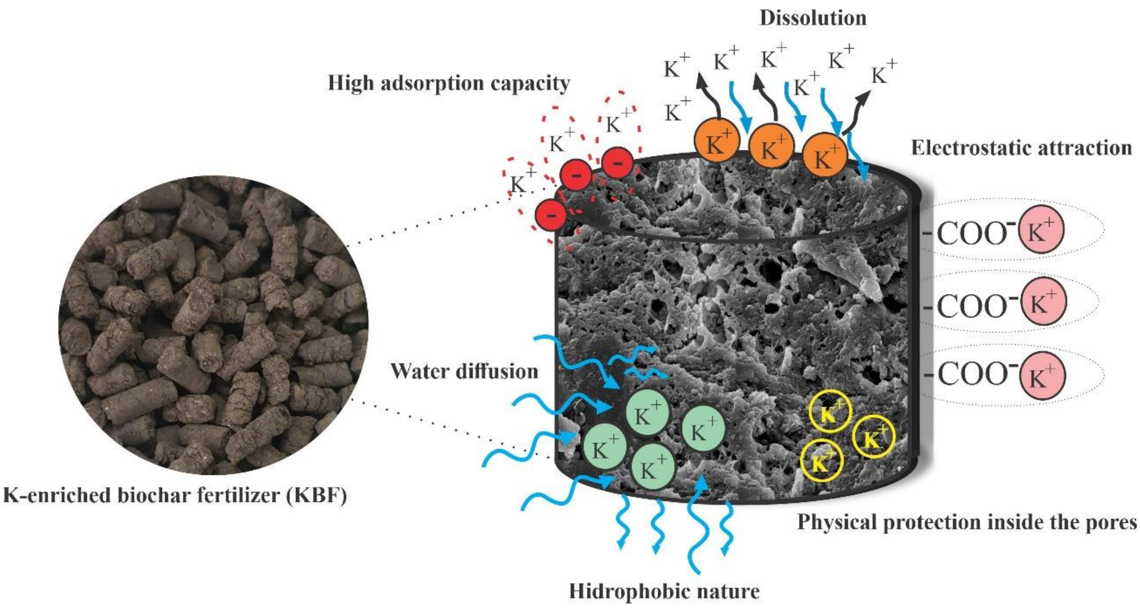

Figure 11. Schematic representing the interactions between biochar and K that interfere with the release of K in BBFs-KCl.

Several mechanisms act simultaneously which cause the slower K release from BBFs-KCl when compared to KCl fertilizer. The kinetics (Figure 10) obtained in the present study indicated that K release occurs in two distinct phases. The first (Phase 1) was characterized by a faster initial release of K. This behavior may be associated with dissolution of readily available and water-soluble KCl present on the surface of BBF-KCl. The dissolution of K present on the surface can promote the formation of channels on the fertilizer surface through which water will start to diffuse into the fertilizer (Pogorzelski et al., 2020). This water diffusion can be limited and slow, due to a very tortuous path and flow and the presence of varied pores (Gwenzi et al., 2017). Next, a slower release of K begins (Phase 2). This second phase occurs due to the physical protection of the biochar pore network (Dias et al., 2018) and its hydrophobic nature (Chia et al., 2015) which hinders and limits the access of water to the minerals found inside the fertilizer or inside the biochar pores (Gwenzi et al., 2017). Furthermore, a part of the already dissolved K can be readsorbed on the biochar surface due to electrostatic attraction and its strong adsorption capacity (Luo et al., 2021).

This behavior with two distinct phases has also been reported in other works with biochar fertilizers (Kim et al., 2014; Gwenzi et al., 2017, Shin et al., 2019; Pogorzelski et al., 2020). Biochar fertilizers are often little soluble in water and short-term availability is low (Lustosa Filho et al., 2020). However, it can increase over time due to the fertilizer dissolution process that occurs after water diffuses into the biochar fertilizer matrix and releases the nutrient through its pore structure (Luo et al., 2021). Pogorzelski et al. (2020) reported that the use of biochar as a compound in the production of fertilizers, combined or not with synthetic polymers, improves the recalcitrance and porosity characteristics of the fertilizer. Recalcitrance reduces the structural degradation of the soluble fertilizer, providing greater stability over time. Porosity, on the other hand, controls the flow of water in the fertilizer matrix, directly influencing the release of nutrients. According to Kim et al. (2014), the low surface area and reduced pore size of biochar are fundamental properties that influence the interaction between water and the soluble fertilizer associated with biochar. Another important factor to be reported is that biochar has humic substances in its composition (Fachini et al., 2021b) that can act as chelating and complexing agents in the formulation of mineral, organic and organomineral fertilizers, forming complex molecules with metal ions. Thus, the presence of humic substances in biochar may have complexed K and contributed to a slower release of this nutrient in BBFs-KCl compared to the KCl mineral fertilizer.

7.4.3. Influence of granulation and pelletizing technology on K release

The results of the present study show that K release dynamics are affected by the enrichment process of BBF-KCl. The BBF-KCl in a powder form released K faster than other enriched fertilizers (Figure 10).

Figures S6 and S7 show the BBFs-KCl during the incubation period. Note that the pellets and granules in the sachets did not fall apart, i.e., they maintained their initial shapes throughout the incubation time. Even the 20% moisture level (Figure S7) was not sufficient to break up the BBF-KCl granules and pellets. This indicates that, at field capacity (moisture level of 10%), both granulation and pelletization promoted protection of the soluble K source found inside the granules and pellets. The presence of starch in the granulation and pelletization process may have contributed to the fact that the BBFs-

KCl did not break up, promoting protection of the soluble K source. In a work by Kim et al. (2014), increasing the percentage of starch resulted in pellets that promoted slower nutrient release. Another work carried out with biochar fertilizer granules showed that even after 72 days of leaching the granules maintained the same structure due to the presence of starch and this resulted in lower nutrient leaching losses (Gwenzi et al., 2017).

In addition to the presence of starch, the pelletization process may also have contributed to the slower release of K by the pellets when compared to other enriched fertilizers. In general, during the pelleting process, the particles are forced against each other by the applied pressure (Reza et al., 2014), producing smaller pores and reducing the total pore volume (Kim et al., 2014). According to Pogorzelski et al. (2020), porosity controls the water flow in the fertilizer matrix, directly influencing the release of nutrients, i.e., fertilizers with greater porosity will tend to have a higher rate of nutrient release due to the greater ease of water diffusion to their interior.

The isotherms of all materials were Type IV(a) with a Type H3 loop according to the IUPAC classification (Figure 7). This indicates that in general the pores of BBF-KCl are predominantly mesopores and macropores (Wang et al., 2016; Huang et al., 2017). The BBF-KCl in pellet form had the lowest values of SA, PV and MPV, confirming the effect of compaction promoted during pelletization. In this sense, granulation presented higher values of SA, PV and MPV than pellets, but much lower than BBF-KCl in powder form.

This reduction in total pore volume reduces the SA and water contact to solubilize the K source present in enriched fertilizers. On the other hand, the higher the PV the easier the diffusion of water into the fertilizer and its contact with the material particles, favoring solubilization of the soluble source and contributing to the release of nutrients. According to Hermawan and Adipati (2018), fertilizers with greater porosity tend to have a higher rate of nutrient release when compared to fertilizers with thicker and smoother layers. Carneiro et al. (2021) evaluated two biochar fertilizers and found that the greatest P release occurred in the biochar fertilizer that presented the highest SA, which allowed greater fertilizer dissolution. Thus, different biochar fertilizers, even if enriched with the same mineral nutrient source but with different biochars, can result in different nutrient release rates due to different physical characteristics of the enriched fertilizer. Biochar fertilizer pellets with K, P and lignin showed slower release of K and P due to higher stability/durability promoted by lower SA and PV (Kim et al., 2014). Slower biochar N release was also observed in granules with lower PV (Chen et al., 2018).

In this sense, granules presented higher values of SA, PV and MPV than pellets, but much lower than the product in powder form, which may have resulted in slower release in the order pellet < granule < powder.

BBF-KCl in a pellet form had a higher PD (1.0 cm^3/g) than in granule form (0.9 cm^3/g) (Fachini et al., 2021b). In general, a higher PD indicates a lower percentage of voids and gaps within the material (Hu et al., 2016). This occurs because in the pelletizing process the press reduces gaps and empty spaces between the material particles (Reza et al., 2012), requiring a greater amount of raw material to form a pellet. In the granulation process, the amount of powder material needed to form a granule is smaller and there is also no pressing process, resulting in a more porous structure of the granule when compared to the pellet structure (Vincevica-Gaile et al., 2019). The PD results (Fachini et al., 2021b) once again prove the effect of pelletizing on the physical characteristics of the pellet and its effect on the K release dynamics. On the other hand, greater pore volume is observed in BBFs-KCl in the form of granules and powder, facilitating the entry of water into the fertilizer which causes greater contact with the material particles and favors a greater release of nutrients when compared to BBF-KCl in the pellet form (Figure 10).

The results of the present study indicate that enriching SSB with K sources is a promising practice for the production of a slow K release BF. The BBF-KCl exhibited excellent slow K release performance compared to the KCl mineral fertilizer, which contributes to reducing K loss through leaching and increasing the efficiency of fertilizer use. In addition to resolving the low K supply via application of pure SSB and contributing to the recycling of SS in agriculture, this work presents a sustainable alternative for the production of new SSB-based fertilizers, recycling of SS, rational use of highly soluble K mineral fertilizer and reduces Brazil's dependence on potassium fertilizer imports.

7.4.4. Potassium leaching from BBF-KCl and KCl

Figure 12 shows the cumulative amount of K leached over six days in the leaching column experiment. The cumulative K leached followed the order of KCl > powder = granule > pellet > control ($P < 0.05$). In general, BBFs-KCl reduced the total amount of leached K compared to the chemical fertilizer (KCl). From the total amount of K applied (130 mg), 128 mg were leached from the chemical fertilizer after 6 days. Both granule and powder fertilizers showed intermediate values, leaching 96 mg of K. In 6 days, BBF-KCl in the pellet form reduced the total leached of K to 33.6 mg, showing the great potential of this type of fertilizer for reducing K leaching. Additionally, these results indicate that biochar-based fertilizers retain K for a longer period than chemical fertilizers. As mentioned previously, the lower rate of leached K in biochar-based fertilizers is due to their ability to release this nutrient slower, mainly when the pellet form was used, possibly due to the higher K retention capacity of biochar (Yuan et al., 2016). In the work by Shin et al. (2019), pelleting was efficient for reducing N and P leaching when compared to the same non-pelleted material with and without mixing with biochar. Mohammadi (2021) stated that one of the benefits of pelleting biochar is to reduce nutrient losses via the leaching process.

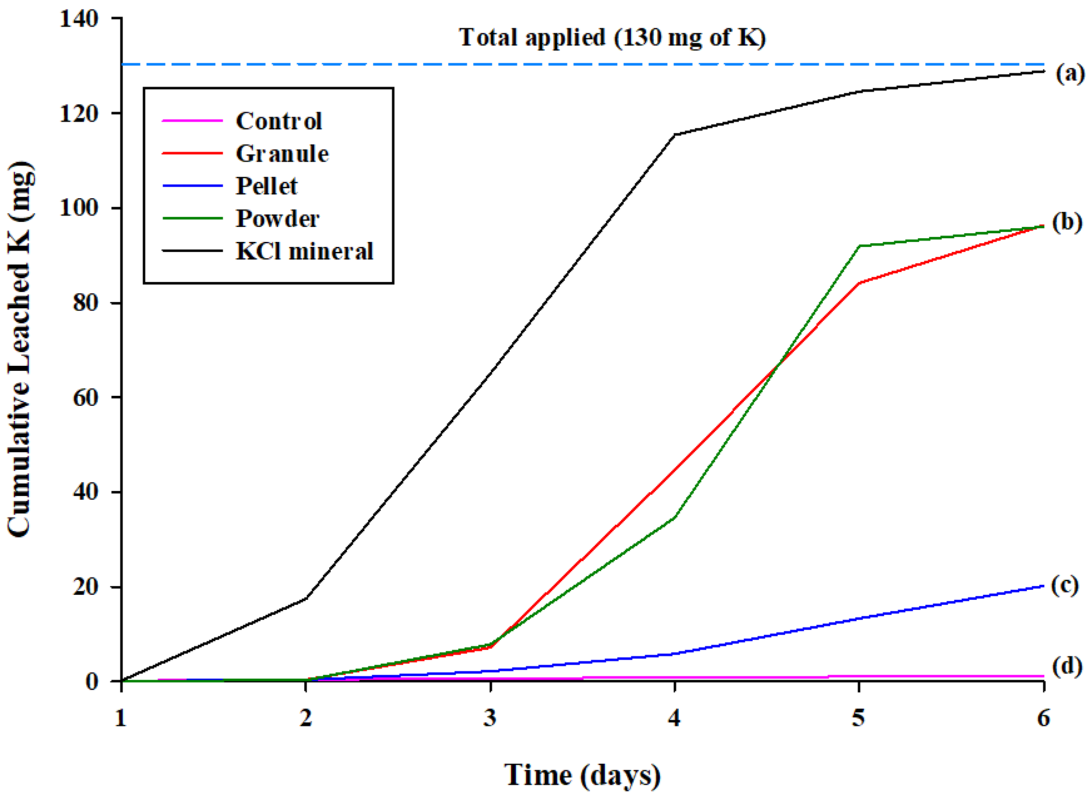

Figure 12. The amount of K+ leached from biochar-based fertilizers and KCl in leaching columns filled with silica sand. Different letters indicate that the fertilizers differed significantly by the Tukey test ($P < 0.05$).

Due to the high solubility of conventional fertilizers, about 50 – 70% is lost to the environment (Trenkel, 2010), being unsuitable for sustainable agricultural ecosystems and requiring that their properties are improved (Timilsena et al., 2014). In addition, the greatest loss of K in agriculture via highly soluble fertilizer application is through the leaching process (Buresh et al., 2010). Therefore, in the present study biochar fertilizers, mainly those in pellet form, presented good properties to be used as sustainable fertilizers with minimum risk of polluting groundwater through leaching processes.

7.5. CONCLUSION

The results confirm the hypothesis that biochar-based fertilizers delay K release. In the first four days after application, BBFs-KCl reduced K release by up to 77% compared to the KCl mineral fertilizer. K release dynamics were affected by the enrichment process of BBFs-KCl. Performance of the K slow-release pellets was attributed to their physical characteristics after going through the pressing process during pelletizing, such as lower surface area, pore volume, micropore volume and particle density compared to BBFs-KCl in powder form. At the 10% moisture level, biochar fertilizers in the pellet and granule forms can be classified as slow-release fertilizers. Furthermore, compared to KCl, BBF reduced the amount of leached K highlighting their function as sustainable fertilizers. The scaling-up process and economic analysis need to be better understood. All results presented in the current study are valid for the silica sand medium. For agronomic and environmental applications, an additional evaluation must be performed in soils. Therefore, future works should evaluate the performance of BBFs-KCl on K release and uptake dynamics for plants in different soil types.

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CHAPTER III

PERFORMANCE OF K-ENRICHED BIOCHAR-BASED FERTILIZERS FOR IMPROVING POTASSIUM UPTAKE IN RADISH PLANTS

(Manuscript submitted to Nutrient Cycling in Agroecosystems – Under Review)

8. PERFORMANCE OF K-ENRICHED BIOCHAR-BASED FERTILIZERS FOR IMPROVING POTASSIUM UPTAKE IN RADISH PLANTS

8.1. ABSTRACT

Biochar-based fertilizers (BBFs) enriched with potassium (K) can increase the efficiency of K use by plants. This study evaluated the effect of a new K-enriched sewage sludge biochar in the pellet and granule forms, applied in full and reduced dose (50%), compared with a conventional K fertilized control (KCl), on soil chemical attributes, nutrition and relative chlorophyll content (SPAD index) of radish plants grown in a greenhouse. Both forms of BBF (granule and pellet) showed good performance in supplying K and other nutrients to the plants. On average, BBF in the granule form increased the concentration of K in radish sap by 30% compared to BBF in the pellet form and KCl. Even when applied at half the recommended dose (210 kg ha^{-1} of K_2O), BBFs were efficient in supplying K and other nutrients to the plant. BBF in the pellet form increased the tuber dry mass, which was on average 150% higher than KCl and BBF in the granule form. In general, the results of the present study indicate that the better supply of K promoted by the BBF also contributed to higher SPAD index values in the radish crop. More studies should be carried out to better understand the effect of BBF on the performance of crops with different cultural cycles (short and long).

8.2. INTRODUCTION

Studies on biochar have been conducted in several areas of research in the last two decades (Islam et al., 2021). In agriculture it shows great potential as a soil conditioner and fertilizer, promoting the recycling of nutrients and the accumulation of carbon in the soil (Chagas et al., 2022). The concentration of nutrients in the biochar depends on the type of raw material and pyrolysis conditions, including temperature and residence time (Najafi-Ghiri et al., 2020). When produced from sewage sludge (SS), biochar may contain up to 6% phosphorus (P), approximately 3.2% N, 0.82% Ca and 540 mg kg^{-1} of Zn (Figueiredo et al., 2018; Faria et al., 2018). However, SS biochar (SSB) is deficient in potassium (K), because SS has low K levels in its composition (Tontti et al., 2016); this requires a combination with mineral fertilizer or application of very high SSB doses for the adequate supply of K.

When applied in high doses, SSB may deliver large amounts of nutrients that can be toxic to plants. In addition, high doses of SSB may contain levels of heavy metals above national regulations for land application, restricting the application of SSB to soils (Figueiredo et al., 2019). Furthermore, high doses of biochar may not be economically viable (Bach et al., 2016). Studies with biochars from other raw materials have also reported the need to apply mineral fertilizers in combination with biochars for the complete and balanced supply of nutrients to plants (Arif et al., 2017; Shin et al., 2019).

The development of enriched fertilizers is one of the strategies to improve the use of biochar as a fertilizer. Biochar enrichment with mineral fertilizers can be achieved using different techniques such as simple mixing in powder form, granulation, pelletizing and others (Ndoung et al., 2021; Melo et al., 2022). When compared to highly soluble mineral fertilizers, biochar-based fertilizers (BBFs) can improve the efficiency of plant nutrient use (Lustosa Filho et al., 2020; Puga et al., 2020). This is possible because SSBs can reduce K and nitrogen (N) losses via leaching by acting as slow-release fertilizers (Luo et al., 2021; Fachini et al., 2022). Additionally, SSBs can reduce N losses by volatilization (Puga et al., 2020), minimize the specific adsorption of P in the soil, and increase the P availability for plants (Lustosa and Filho et al., 2020). As a result, SSBs can increase crop yields by 10% and 186% compared to fertilized and unfertilized controls, respectively (Melo et al., 2022).

There are several techniques to enrich biochar with nutrients including pre- and post-pyrolysis procedures. K-enriched BBFs were obtained via pre-pyrolysis; and composite biochars showed slow-release characteristics (Wu et al., 2021). However, post-pyrolysis is the most used technique to produce BBFs (Ndoung et al., 2021). In recent years new BBFs enriched with mineral fertilizers have been evaluated, with an emphasis on P enrichment (Chia et al., 2014; Nguyen et al., 2017; Lustosa Filho et al., 2019). In the specific case of BBF from SS the biochar itself is the source of P (up to 6%) and N (approximately 3.2%); this reduces the production cost since only K sources are needed for its enrichment. In this sense, a K-enriched sewage sludge BBF was recently developed (Fachini et al., 2021a). This new fertilizer ensured a 75-fold increase in soluble K_2O content when compared to pure biochar. Under laboratory conditions, this new fertilizer functioned as a slow-release K fertilizer, reducing K leaching rates in pure silica (Fachini et al., 2022). Therefore, BBFs provide better synchronization of nutrient release and the nutritional demand by plants, increasing the K use efficiency (Adu-Gyamfi et al., 2019). However, both the release dynamics and the K uptake of BBF need to be evaluated under real conditions in the presence of plants where nutritional, physiological and productivity aspects of the crop are investigated.

Despite the potential of using K-enriched biochar fertilizers, there is still a lack of information on the agronomic performance of these inputs. Given this lack of studies, the present work sought to evaluate the effect of SSB enriched with K, in the pellet and granule forms, applied in two doses, compared with a conventional K fertilized control (KCl), on potassium absorption, nutrition and on the SPAD index of radish plants. It was hypothesized that BBFs, in granules and pellets form, improve the soil available nutrients and plant nutrition, contributing to a better SPAD index, and increased radish productivity.

8.3. MATERIALS AND METHODS

The study was carried out in a greenhouse located at Embrapa Hortaliças, Brasília, DF, Brazil, with radish plants grown in 1.5-liter pots with diameter and height of 11.28 cm and 15 cm, respectively. Pots were filled with 1.5 kg of soil. Fertilizers based on sewage sludge biochar enriched with K (using KCl) were produced in the granule and pellet forms, using starch as a binding agent, whose production details are presented in Fachini et al. (2021a). For SSB preparation, SS samples were air-dried (to approximately 10% moisture content), passed through a 4 mm sieve and then pyrolyzed at 300 °C. Pyrolysis was performed in a muffle furnace (Linn ElektroTherm, Eschenfelden, Germany) at a mean temperature increase rate of 2.5 ºC min^{-1} and residence time of 5 h as described by Figueiredo et al. (2018a). The furnace was equipped with a mechanism to prevent oxygen flow (via forced draft fan, helping gas and oil vapors exit the furnace). The chemical and physical characteristics of the fertilizers are presented in Table 5.

Table 5. Characteristics of K-enriched biochar fertilizers (FBBs).

Variable[a]	FBBs	
	Granule	Pellet
pH ($CaCl_2$)	5.73±0.05	5.77±0.02
Moisture content (%)	7.14±0.27	4.79±0.44
Volatile matter (%)	51.11±0.63	52.90±1.22
Ash (%)	39.58±0.14	38.74±1.09
Fixed carbon (%)	1.91±0.45	3.90±0.04
OC (%)	17.64±0.55	19.48±1.28
TC (%)	25.31±0.40	25.50±1.49
TN (%)	3.02±0.12	3.66±0.31
C/N	8.25±0.40	7.77±0.62
P_2O_5 total (%)	5.21±0.14	5.22±0.13
K_2O total (%)	3.0±0.02	3.0±0.03
Ca (g kg^{-1})	5.57±0.001	5.57±0.001
Mg (g kg^{-1})	1.63±0.001	1.42±4.7
S (g kg^{-1})	1.24±0.001	1.3±2.5
Fe (g kg^{-1})	17.3±0.001	18.3±1.0
B (mg kg^{-1})	25.6±0.4	27.2±1.1
Mn (mg kg^{-1})	89.0±2.2	89.0±0.3
FA (g kg^{-1})	33.85±0.22	33.20±0.32
HA (g kg^{-1})	11.08±0.19	11.86±0.64
HU (g kg^{-1})	204.83±3.34	211.51±6.54

[a]: average values ± standard deviation (n = 3); OC = organic carbon; TC = total carbon; TN = total nitrogen. FA = fulvic acid; HA = humic acid; HU = humin. Adapted from Fachini et al. (2021a).

8.3.1. Soil and laboratory analysis

Samples from a Red Latosol (Santos et al., 2018), with 82% clay, were collected from the 40-100 cm layer in a profile located at the Experimental Farm of the University of Brasília (15° 56' 45" S, 47° 55 ' 43" W; 1095 m), Brasília, DF, Brazil. Before and after the experiment, the soil samples were chemically characterized for pH, CEC, P, K^{+}, Ca^{+2}, Mg^{+2} and Al^{+3} according to the methodologies of Teixeira et al. (2017).

8.3.2. Conducting the experiment

Based on the results of soil chemical analysis before the experiment, a rate equivalent to 4 Mg ha^{-1} of dolomitic limestone was applied to raise the base saturation to 80% as required by the radish crop (Raij et al., 1997). Next, as corrective fertilization, a dose of 420 kg ha^{-1} of P_2O_5 was applied in the form of monobasic calcium phosphate (26.5% of P_2O_5), according to Sousa and Lobato (2004). Soil chemical parameters before and after acidity correction and P correction fertilization are presented in Table 8.

Radish seeds (*R. sativus* L.), variety Saxa (ISLA seeds®), were sown in commercial substrate and later transplanted into 1.5-liter pots containing the corrected soil. Seeds of the variety Saxa take 30-35 days to mature and present a yield potential of 10-15 tonnes per hectare.

The recommended fertilization for radish was carried out according to Raij et al. (1997). The total amounts of N (source: Urea), P (source: Monobasic calcium phosphate) and K_2O (source: Potassium chloride) applied were 130, 360 and 210 kg ha^{-1}, respectively. In addition to these nutrients, to supply zinc (Zn), boron (B), sulfur (S) and magnesium (Mg), fertilization was also carried out via a nutrient solution with zinc sulfate (20% of Zn and 10,5% of S), boric acid (17% of B) and magnesium sulfate (9% of Mg and 12% of S).

Two levels of K supply via the BBFs were evaluated: 0.5 and 1 times the recommended K_2O dose for the radish crop. The BBFs in the form of granules and pellets had the same concentration of K_2O (3%). Thus, to provide 0.5 and 1 times the recommended dose of K_2O for the radish crop, doses equivalent to 3.5 and 7 Mg ha^{-1} of BBF were applied, respectively. The quantities of BBF applied for the two different fertilization levels are shown in Table S4. A commercial KCl treatment was applied as a reference (fertilized control) to provide the recommended K_2O dose for the crop (210 kg ha^{-1} K_2O or 0.262 g pot^{-1} of KCl).

In order for all treatments to receive the same nutrient quantities, for the supply of P and N via solution the amount of these nutrients supplied via the BBF was discounted. The BBF composition presented an average of 3.3 and 5.2% of total N and total P_2O_5, respectively (Table 5). To consider the contribution closest to real, the soluble P and N contents of the SSB were considered. In SSB pyrolyzed at 300°C, 24% of the total P is soluble in citric acid (Figueiredo et al. 2021) and 1.4% of the total N is mineral N (nitrate and ammonium) (Figueiredo et al. 2019). Therefore, in Table S5 the doses applied are presented as a function of the concentrations of P_2O_5 soluble in citric acid and mineral N in the BBFs.

The application of fertilizers (BBFs and KCl) was carried out on the same day as the seedlings were transplanted. Fertilization of P, N, Zn and B was carried out via a solution at 7 days after transplanting for a total supply of 360, 40, 3 and 4 kg ha^{-1}, respectively. After 13 days of transplanting, one more topdressing was carried out via solution to supply 40, 80 and 41 kg ha^{-1} of N, sulfur (S) and magnesium (Mg), respectively. The last topdressing fertilization was performed 28 days after transplanting to supply 50 kg ha^{-1} of N. All recommendations were performed according to Raij et al. (1997).

Irrigation management was performed by controlling the water tension in the soil (15 kPa) using the Irrigas® device. When necessary, irrigation was performed by drip (flow rate of 2 L/h) for an average of 3 minutes per day. The insecticide Pirate (Clorfenapir®) was applied to control whitefly. The radish was harvested 38 days after transplanting.

8.3.4. Treatments and experimental design

The experimental design was completely randomized, with 5 treatments and four replications, totaling 20 pots. The treatments evaluated were: KCl (210 kg ha^{-1} of K_2O via granulated mineral KCl), BBF-G0.5 (105 kg ha^{-1} of K_2O via granulated BBF), BBF-G1 (210 kg ha^{-1} of K_2O via granulated BBF), BBF-P0.5 (105 kg ha^{-1} of K_2O via pelleted BBF) and BBF-P1 (210 kg ha^{-1} of K_2O via pelleted BBF). All BBFs were enriched with the same KCl used in the control as the K source.

8.3.5. Crop agronomic indices and nutrient absorption

At radish harvest, 38 days after transplanting, the following biometric characteristics of the plant were evaluated: height, leaf area, K content in the sap, fresh aerial part mass and mass of the commercial part (tuber). The plant height was measured using a millimeter ruler. To determine the leaf area, a fully healthy and expanded leaf of each plant was used to perform the calculation in the ImagemJ™ software (PMC5554542) (Schneider et al., 2012). To determine K in the sap of the leaves, the collection of samples (one leaf with petiole per plant) was carried out in the most recent fully expanded leaf and in the morning period between 8 and 11 am. According to Vitosh and Silva (1996), it is suggested that sap sampling be performed in the morning to minimize data variability, since differences in nutrient concentrations may occur due to variations in leaf water potential during the day (Esteves et al., 2021). The leaves with petioles were pressed/crushed immediately after collection. A stainless-steel crusher was used and fluid measurement was performed with the Horiba LAQUATwin 741 device (HORIBA, Japan) after calibration.

The fresh mass (FM) of the aerial part and of the tuber was determined using a precision scale, and weighing was done immediately after harvest. The dry mass (DM) of the aerial part and of the radish was determined after drying in an oven for 72 hours at 60°C. Leaf thickness was evaluated 25 days after transplanting, using the MultispeQ device (PhotosynQ INC, USA).

The levels of macro and micronutrients absorbed by the plant were determined according to methodologies described in Malavolta et al. (1989). Briefly, leaves with petiole samples were stored in paper bags and dried in an oven with air circulation at 65°C until constant weight. Then, grounded samples were submitted to nitric-perchloric acid digestion. N was determined by the semi-micro-Kjeldahl analysis, and titration with H_2SO_4. P by colorimetry of metavanadate. K by atomic absorption spectrometry, with a K hollow cathode lamp. S content by barium sulfate turbidimetry. The contents of Ca and Mg by atomic absorption spectrophotometry. The micronutrients manganese (Mn), cobalt (Co) and Zn were estimated by atomic absorption spectrophotometry, with direct determination in the nitric-perchloric extract of vegetables.

8.3.6. Relative chlorophyll content (SPAD Index)

The radish SPAD index was evaluated 25 days after transplanting, using the MultispeQ device (PhotosynQ INC, USA) by means of the PhotosynQ platform (http://www.photosynq.org). The SPAD index measurement after 25 days was based on previous studies whose values ranged from 19 to 30 days after transplanting (Stagnari et al., 2018; Kalaji et al., 2018; Kushwah et al., 2019). Readings were taken on 2 healthy and fully expanded leaves per plant. The SPAD index was evaluated in the morning when the average temperature inside the greenhouse was 33.6°C and humidity of 49.3%.

8.3.7. Statistical analyses

Data was initially analyzed for residual normality and homoscedasticity using the Lilliefors and Cochran test. When presenting a normal distribution, the data was submitted to analysis of variance (ANOVA) and the means were compared by Fisher's LSD test (P < 0.05) using the XLSTAT software (Adinsoft, 2013).

8.4. RESULTS

8.4.1. Radish biometric indices and nutrient absorption

BBF in the pellet form increased the DM of the tubers, which was on average 150% higher than KCl and BBF in the granule form. The other biometric indicators of the plant were not affected by the fertilizers (Table 6).

Table 6. Biometric characteristics of the radish plants fertilized with biochar based fertilizers and KCl.*

Treatments	Height		Leaf area		Leaf thickness	
	cm		cm^2		mm	
KCl	28.20 ± 4.00	a	44.69 ± 7.03	a	0.68 ± 0.04	a
BBF-G0.5	22.20 ± 0.92	a	49.75 ± 6.85	a	0.64 ± 0.06	a
BBF-G1	25.00 ± 2.18	a	51.89 ± 2.29	a	0.70 ± 0.07	a
BBF-P0.5	21.90 ± 0.98	a	54.79 ± 6.22	a	0.80 ± 0.10	a
BBF-P1	22.20 ± 1.84	a	57.18 ± 9.00	a	0.68 ± 0.10	a

Treatments	Fresh mass (FM)				Dry mass (DM)			
	Aerial part		Tuber		Aerial part		Tuber	
	(g)							
KCl	14.13 ± 2.06	a	2.11 ± 1.09	a	1.27 ± 0.26	a	0.14 ± 0.06	b
BBF-G0.5	15.58 ± 0.87	a	2.16 ± 1.15	a	1.29 ± 0.16	a	0.13 ± 0.06	b
BBF-G1	15.73 ± 1.39	a	2.14 ± 0.08	a	1.49 ± 0.15	a	0.14 ± 0.01	b
BBF-P0.5	14.27 ± 0.70	a	1.79 ± 0.53	a	1.29 ± 0.09	a	0.15 ± 0.05	ab
BBF-P1	15.35 ± 1.46	a	4.87 ± 2.02	a	1.53 ± 0.13	a	0.35 ± 0.12	a

Means with the same letters do not show statistical differences according to Fisher's LSD test (P<0.05). * average values±standard error (n=4).

K uptake by plants, estimated from leaf + petiole biomass, in response to the application of BBFs is shown in Figure 13. The fertilizers behaved differently and can be grouped into three groups. Full dose BBFs (BBF-G1 and BBF-P1) promoted greater K uptake in plants (average of 47%) than mineral fertilizer (KCl). The reduced BBF dose (BBF-G0.5 and BBF-P0.5) showed an intermediate behavior and did not differ from the other fertilizers. Despite promoting differences in K uptake, all fertilizers maintained adequate levels of K in the plant (15 to 30 g kg^{-1}) for the radish crop (Burdine, 1976; Sanchez et al., 1991; Hochmuth et al., 2022).

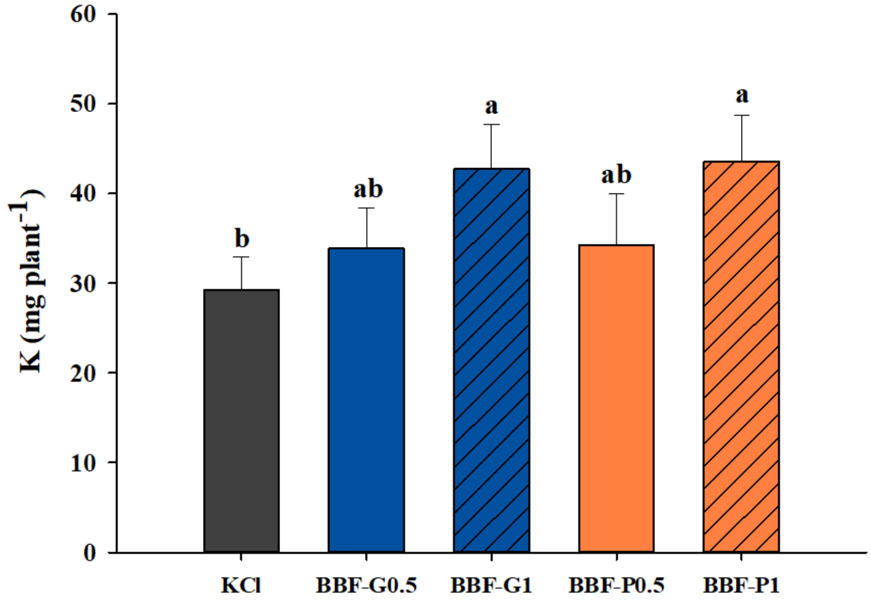

Figure 13. K uptake by the radish plant in response to BBF application. Means with the same letters do not show statistical differences according to Fisher's LSD test (P<0.05). Error bars represent the standard error (n = 4).

The contents of the other macronutrients (N, P, S, Ca and Mg) in the plant are shown in Table 7. In addition to K absorption, only the N and S contents were affected by the application of the fertilizers (P<0.05). In general, the BBFs promoted N and P concentrations in the plant similar to the conventional fertilizer. Among biochar-based fertilizers, BBF-P0.5 had lower N content than both BBFs in granule form and lower S content than BBF-G1.

Table 7. Nutrient content in radish plants fertilized with biochar-based fertilizers.*

Treatments	N		P		S	
	g kg^{-1}					
KCl	42.00 ± 0.40	ab	4.80 ± 0.29	a	9.40 ± 0.44	ab
BBF-G0.5	43.50 ± 0.86	a	4.95 ± 0.62	a	9.10 ± 0.77	ab
BBF-G1	44.25 ± 1.49	a	5.05 ± 0.38	a	8.02 ± 0.37	ab
BBF-P0.5	29.50 ± 1.45	b	3.65 ± 0.59	a	6.25 ± 0.78	b
BBF-P1	40.00 ± 1.08	ab	4.72 ± 0.33	a	9.72 ± 0.54	a

Treatments	Ca		Mg	
	g kg^{-1}			
KCl	29.52 ± 2.04	a	6.00 ± 0.12	a
BBF-G0.5	31.47 ± 1.08	a	5.67 ± 0.27	a
BBF-G1	31.80 ± 0.72	a	6.02 ± 0.45	a
BBF-P0.5	21.72 ± 1.59	a	4.15 ± 0.41	a
BBF-P1	31.10 ± 0.40	a	5.32 ± 0.34	a

Means with the same letters do not show statistical differences according to Fisher's LSD test (P<0.05). * average values±standard error (n=4).

8.4.2. Potassium in plant sap and the Relative Chlorophyll Index (SPAD)

The K concentrations in the sap of radish plants (K-sap) in response to different fertilizers are shown in Figure 14. Plant sap analysis provides an early determination of the plant nutrient status since it relies on real-time information (Esteves et al., 2021). Plants fertilized with BBF-G1 showed a higher concentration of K-sap than the other fertilizers (Figure 14; P<0.05), remaining within the appropriate range for several vegetables in different development periods, with values between 1800 and 5000 mg L^{-1} (Hochmuth et al., 2022). The other fertilizers resulted in similar K-sap concentrations which were below the appropriate range (<1800 mg L^{-1}), regardless of the dose applied. Therefore, half of the applied BBF dose promoted a K-sap concentration equivalent to the full dose of KCl.

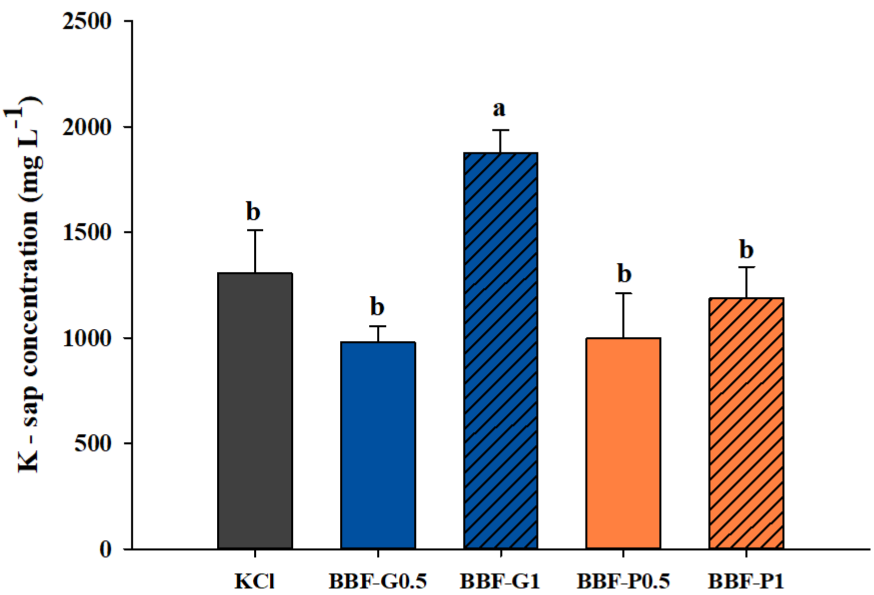

Figure 14. K content in the sap of radish leaves fertilized with different fertilizers and their respective doses. Means with the same letters do not show statistical differences according to Fisher's LSD test (P<0.05). Error bars represent the standard error (n = 4).

The relative chlorophyll content (SPAD index value) of radish plants is shown in Figure 15. The SPAD index was 18% higher in plants fertilized with BBF-G1 in relation to KCl (P<0.05), with no difference among the other fertilizers.

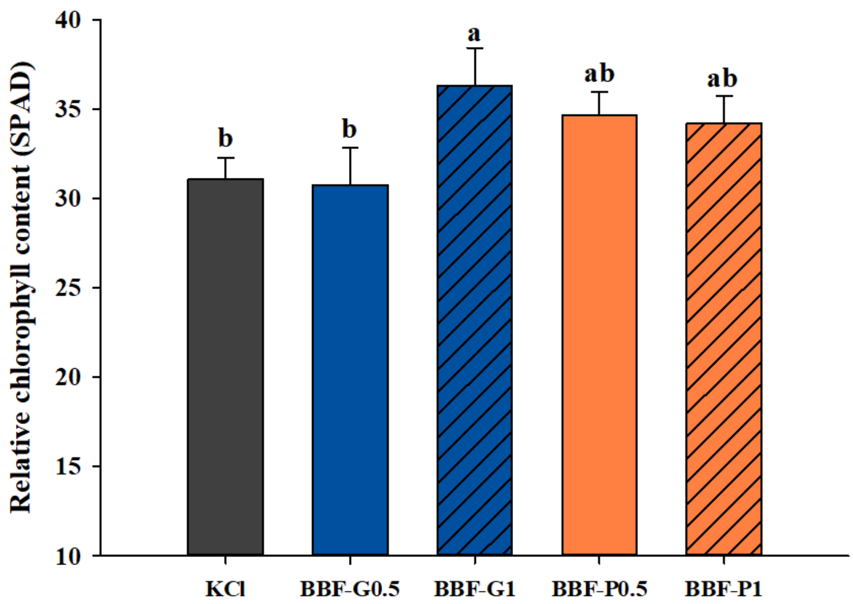

Figure 15. SPAD index in radish leaves fertilized with biochar-based fertilizers. Reading was performed 25 days after transplanting. Means with the same letters do not show statistical differences according to Fisher's LSD test ($P<0.05$). Error bars represent the standard error (n = 4).

8.4.3. Soil fertility indicators

The chemical attributes related to soil fertility after radish harvest are presented in Table 8. In general, fertilizers affected pH and contents of OM, P and Ca. The fertilizers did not change the base saturation (V value) of the soil during radish cultivation, but the BBF-P0.5 reduced the pH when compared to BBF-G0.5. A 50% reduction in the dose of pelletized BBF (BBF-P0.5) resulted in a small reduction in OM, Ca and P contents compared to the full BBF dose.

At the end of cultivation, the soil showed similar levels of available K in the soil. In general, after radish harvest, the K contents (Table 8) were similar to the K contents of the soil before fertilizer application (Table 8). The application of BBF-G1 promoted higher P content than the other fertilizers, with the exception of BBF-G0.5 ($P<0.05$). Soil P content in BBF-G1 was 29% higher than in KCl. When reducing the dose by 50%, BBF-P0.5 reduced the Ca supply by 22 and 26% compared to BBF-G1 and BBF-P1, respectively. Soil Mg levels were not affected by the fertilizers applied ($P>0.05$).

Table 8. Effect of biochar-based fertilizers on soil chemical attributes after radish harvest.*

Treatments	pH		Al^{3+}		H+Al		CEC	
	$CaCl_2$		$cmol_c\ dm^{-3}$		$cmol_c\ dm^{-3}$		$cmol_c\ dm^{-3}$	
KCl	6.12 ± 0.04	ab	0.00 ± 0.00	a	1.10 ± 0.06	a	4.80 ± 0.26	a
BBF-G0.5	6.17 ± 0.04	a	0.00 ± 0.00	a	1.00 ± 0.00	a	4.69 ± 0.06	a
BBF-G1	5.97 ± 0.11	ab	0.00 ± 0.00	a	1.10 ± 0.05	a	5.08 ± 0.29	a
BBF-P0.5	5.92 ± 0.08	b	0.00 ± 0.00	a	1.10 ± 0.05	a	4.40 ± 0.46	a
BBF-P1	6.05 ± 0.04	ab	0.00 ± 0.00	a	1.10 ± 0.05	a	5.15 ± 0.24	a
Prior[a]	4.4		0.14		5.4		7.0	
After	5.9		0.0		2.0		6.2	
Treatments	OM		V		K^+		P	
	$g\ kg^{-3}$		%		$mg\ dm^{-3}$			
KCl	12.00 ± 0.01	a	77.25 ± 0.01	a	22.00 ± 0.81	a	18.75 ± 0.75	b
BBF-G0.5	11.00 ± 0.05	ab	79.25 ± 0.57	a	17.00 ± 1.29	a	20.75 ± 1.10	ab
BBF-G1	12.50 ± 0.12	a	78.50 ± 1.25	a	22.50 ± 2.63	a	24.25 ± 1.75	a
BBF-P0.5	10.00 ± 0.01	b	74.75 ± 0.01	a	19.50 ± 4.50	a	20.00 ± 0.81	b
BBF-P1	11.50 ± 0.04	ab	79.25 ± 0.43	a	22.00 ± 3.48	a	19.75 ± 1.43	b
Prior[a]	21		23		19.5		1.94	
After	12		78		22.0		18.7	

Treatments	Ca^{2+}		Mg^{2+}	
	$cmol_c\ dm^{-3}$			
KCl	2.77 ± 0.13	ab	0.92 ± 0.12	a
BBF-G0.5	2.85 ± 0.05	ab	0.80 ± 0.04	a
BBF-G1	2.97 ± 0.11	a	0.97 ± 0.17	a
BBF-P0.5	2.42 ± 0.33	b	0.85 ± 0.16	a
BBF-P1	3.07 ± 0.06	a	0.95 ± 0.17	a
Prior[a]	1.13		0.44	
After	3.10		1.00	

Means with the same letters do not show statistical difference according to Fisher's LSD test ($P<0.05$). * average values±standard error (n=4). [a] prior and after liming (4 Mg ha^{-1} of limestone) and phosphorus (420 kg ha^{-1} of monobasic calcium phosphate) correction. CEC: cation exchange capacity; OM: organic matter; V: base saturation.

8.5. DISCUSSION

8.5.1. Chemical characteristics of the enriched fertilizers

In general, the two fertilizers (granules and pellets) showed similar chemical characteristics. Enrichment of the SSB with K ensured a 75-fold increase in K_2O content compared to pure SSB, with a content of 3% K_2O. The BBFs had an average content of 5.25% of total P_2O_5, indicating that SSB is a good option for supplying P via BBFs since SSB has a higher P content than biochars obtained from other raw materials (Kim et al., 2018). Mean values of pH, and elemental C and N were 7.75, 25.4% and 3.34%, respectively, and are within the range of reference values of several enriched biochars: pH = 5.7 – 9.9; TC = 5.6 – 39.5%; TN = 0.9 – 1.2% (Blackwell et al., 2015; Darby et al., 2016; Farrar et al., 2018; Gondek et al., 2018; Nardis et al., 2020). Other physicochemical, mineralogical and morphological characteristics of the BBFs are shown in Fachini et al. (2021a).

8.5.2. Effect of the fertilizers on biometric indices, nutrient uptake and K-sap in the radish plant

In the present study there did not appear to be K deficiency in plants fertilized with the different fertilizers (Table 6). All fertilizers maintained adequate levels of K in the plant (15 to 30 g kg^{-1}) for the radish crop (Burdine, 1976; Sanchez et al., 1991; Hochmuth et al., 2022), demonstrating that the radish plants had a good supply of K, even when half of BBF dose was available. K deficiency would limit plant growth, development and reproduction (Kusaka et al., 2021), as this nutrient is involved in most of the plant metabolism (Hasanuzzaman et al., 2018). Overall, for all fertilizers both the FM and DM of the radish aerial part (Table 6) were similar to the results reported by Sakamoto et al. (2021) in their experiment with radish in hydroponics, where the plant received all nutrients in a balanced dose.

The results of the present study indicate that BBF, regardless of the form (granule or pellet) and even with a 50% reduction in the application dose, had a similar effect to KCl on development of the radish plant. Previous studies have demonstrated the positive effects of BBFs on the DM of the aerial part of plants with values equivalent to mineral P fertilizer (Lustosa Filho et al., 2019) and other mineral fertilizers (Zhang et al., 2017; Khajavi-Shojaei et al., 2020; Borges et al., 2020; Carneiro et al., 2021), as well as when compared to unenriched biochar (Gunes et al., 2014; Kizito et al., 2019).

The physical characteristics of BBF in pellet form, such as a lower surface area, lower pore and micropore volume (Fachini et al., 2022), may have contributed to a more gradual release of K, increasing the efficiency of nutrient use by the plant, resulting in the highest tuber DM value of plants fertilized with BBF-P1 (Table 6). Lustosa Filho et al. (2020) also claim that the balanced and gradual supply of nutrients throughout the crop cycle increases the efficiency of nutrient use, in addition to contributing to increase nutrient absorption and crop productivity (Borges et al., 2020; Carneiro et al., 2021). Results from a recent meta-analysis indicate that BBF increases crop yields by 10% and 186% when compared to fertilized and unfertilized controls, respectively (Melo et al. 2022).

Even when half the recommended dose was applied, the BBFs provided similar K absorption to the full KCl dose (Figure 13). This better performance of BBF in supplying K is probably a result of the slow K release mechanism provided by this fertilizer (Fachini et al., 2022). This slower release may have contributed to the increased K uptake. Several studies indicate possible explanations for this slower release of BBFs, such as the formation of new low-solubility precipitates after biochar enrichment (Luo et al., 2021), strong electrostatic attraction on the surface of the biochar (Gwenzi et al., 2017), physical protection of the soluble fraction by the pores (Lustosa Filho et al., 2020), action of the micropores (Kim et al., 2014), hydrophobic nature of the biochar (Chia et al., 2015) and strong nutrient adsorption capacity (Li et al., 2018). Additionally, biochar has humic substances in its composition that can act as chelating and complexing agents that may have complexed K and contributed to a slower release of this nutrient (Fachini et al., 2022). Moreover, considering the soil nutrient contents after radish harvest, in the present study there was no leaching of nutrients from the pots. This may be considered a further indication of higher K use efficiency promoted by the FBBs.

Biochar-based fertilizers produced from different raw materials combined with N and P have also shown greater nutrient use efficiency than conventional mineral fertilizers. In the study of Carneiro et al. (2021), BBF resulted in P uptake by plants similar to the mineral source of the same nutrient in the short term, however in the long term BBF increased P uptake by plants. This greater P absorption was related to protection and consequent slower release of this nutrient (Lustosa Filho et al., 2020). Greater N uptake was also found when a N-enriched BBF was used (Khajavi-Shojaei et al., 2020). According to the authors, this increase in uptake was related to slower N release and reduced losses via leaching when compared to the mineral nitrogen fertilizer.

For the absorption of other macronutrients, in general the BBFs promoted N and P concentrations in the plant similar to the conventional fertilizer. It must be highlighted that the total amount of N and P in the conventional fertilizer treatment was in soluble forms. On the other hand, N and P in BBF treatments came from both soluble fertilizers and undefined chemical forms (present in the BBFs). The lower N content in BBF-P0.5 when compared to the granule forms may have been the result of lower N mineralization in the pellet, since in calculation of the applied N dose the concentration of this nutrient in the biochar was likely considered better protected by pelleting. In the case of S, the lowest dose of BBF-P0.5 was not sufficient for the adequate supply of this nutrient. In general, the results indicate that the use of BBF did not limit the absorption of nutrients by the radish, in addition to providing K more efficiently.

Despite the lack of difference among the BBFs with regards to K uptake by the plant, the higher K content in the sap of plants fertilized with BBF in the form of granules (Figure 14) indicates that this fertilizer was more efficient for the continuous and adequate supply of K during the entire plant development period. Plant sap analysis provides an early determination of the plant nutrient status since it relies on real-time information (Esteves et al., 2021). Furthermore, granules have characteristics that facilitate the diffusion of water into the fertilizer, such as a lower apparent and particle density (Fachini et al., 2021a), contributing to a greater KCl solubility and a higher K release than pellets. In the present work the K-sap values of the radish (Figure 14) fertilized with BBF-G1 (1875 mg L^{-1}) were within the adequate range for several vegetables in different development periods, with values between 1800 and 5000 mg L^{-1} (Hochmuth et al., 2022), while for the other fertilizers the values were below the reference range. These lower values may be due to remobilization of K from the leaves to the storage organs, the tubers, reinforced by the higher tuber dry mass promoted by BBF-P1 than BBF-G1 (Table 6).

8.5.3. Effect of the fertilizers on the relative chlorophyll content of radish plants

Potassium availability has previously been positively correlated with plant photosynthetic production, however the effect of its limitation on the process and efficiency of photosynthesis is still not fully understood (Kusaka et al., 2021). Nutritional deficiency negatively influences the structure of the photosynthetic apparatus in different plants, such as the brassica family, resulting in reduced SPAD index and chlorophyll fluorescence (Kalaji et al., 2018; Sakamoto et al., 2021). In the radish crop the low supply of nutrients resulted in a decrease in both the quantum yield of photosystem II and the SPAD index (Sakamoto et al., 2021). In fact, there is a potential relationship between the characteristics of leaf nitrogen content, chlorophyll a fluorescence, photosynthetic pigments and the SPAD index (Netto et al., 2005). In the present work it was possible to observe an increase in the SPAD index in the BBF-G1 treatment, coincident with a high foliar nitrogen content.

In the leaves of K-deficient plants there may occur chloroplast degradation and decrease in chlorophyll content (Jin et al., 2011). Therefore, the higher K content in the leaf sap (Figure 14) and higher K absorption (Figure 13) of the radish plant fertilized with BBF-G1 may have influenced the higher SPAD index values compared to KCl and BBF-

G0.5. In the present study, all fertilizers, regardless of dose, promoted leaf SPAD indices typical of radishes grown with adequate nutrient supply (Yousaf et al., 2021; Sakamoto et al., 2021; Kusaka et al., 2021).

Based on the results of the present study, better supply of K promoted by the BBF allows for speculating improved performance of the plant photosynthetic system. Nevertheless, future studies should evaluate photosynthetic indicators throughout the plant cycle since different responses were observed in younger and older radish leaves (Kusaka et al., 2021).

8.5.4. Soil fertility attributes after radish harvest

The pH values of all samples are within the ideal range (5.5 to 6.3) for soils in the Brazilian Cerrado region (Sousa and Lobato, 2004). In literature, many works report the alkaline power of pure biochar, especially that obtained at high temperatures (>500 °C) (Figueiredo et al., 2018). However, in the present study the previous application of lime to the soil may have limited the alkalizing effect of biochar.

The small differences in reductions of OM, Ca and P contents with the use of BBF-P0.5 compared to the full BBF dose (for Ca) and BBF-G1 (P and OM) may have resulted from the lower applied dose of BBF-P0.5, which also reduced carbon input into the soil from biochar. Although the increase in soil C levels with the use of biochars is already well established (Chagas et al., 2022), there are still doubts about the effect of BBF on the accumulation of C in the soil. In the study of Winarso et al. (2020) the enrichment of biochar with NKP accelerated the decomposition of biochar, decreasing its stability in the soil and resulting in lower supply of organic C in the soil compared to pure biochar. Carneiro et al. (2021) affirmed that the enrichment of biochar with a mineral source is efficient for sustaining agricultural production in the medium and long term, in addition to contributing to the addition of a stable carbon fraction in the soil.

After radish harvest the K contents were close to the K contents of the soil before fertilizer application (Table 8), showing a good relationship between the applied doses and consumption by the crop, without the appearance of K deficiency symptoms in the plant. Similar performance of BBFs compared to mineral sources for providing the nutrient with which the biochar was enriched has also been reported previously (Lustosa Filho et al., 2019; Carneiro et al., 2021).

The application of fertilizers provided similar amounts of P. Despite this, the available P content of the soil in BBF-G1 was higher than the other fertilizers, demonstrating that P of the biochar present in the fertilizer granule can become available in the soil, even in a short cultural cycle. This synchronized release of P from SSB has already been demonstrated by Figueiredo et al. (2020). In the mineral KCl treatment, all P was supplied via solution, i.e., all P was applied in the available form so a portion may have been adsorbed in the soil since soils of tropical regions have a high P adsorption capacity. When compared to treatments in the form of pellets, the granules, because they have a greater specific surface area and greater porosity (Fachini et al., 2021), may have facilitated the entry of water into the fertilizer, increasing the release of P via supply of SSB when compared to pelletized BBF. This may have occurred because high levels of available P are present in SSB (Figueiredo et al., 2021a) and are released directly in soluble forms, thus increasing the amount of P in the soil and its availability to plants (Fachini et al., 2021b). Results of the present study show the potential of SSB for the production of BBF, in which enrichment would be necessary only to supply K, since SSB efficiently supplies P in the soil.

According to Faria et al. (2018), SSB is efficient in replacing the use of inorganic fertilizers, but the authors highlighted the need for mineral supplementation to supply K. By presenting a slower release of K when compared to the mineral fertilizer KCl (Fachini et al., 2022a), BBF contributes to a better use of this nutrient by the plant and minimizes K losses by leaching. In addition to reducing the need for applications of large amounts of KCl in all crops, this also reduces Brazil’s dependence on fertilizer imports. Therefore, the practice of pyrolyzing SSB followed by enrichment with a mineral source of K contributes to the recycling of SS in agriculture, yielding a final product that is environmentally friendly, in addition to developing a sustainable fertilizer with great potential in agriculture.

8.5.5. CONCLUSIONS

This study presents the first report on the performance of special K-enriched sewage sludge biochar-based fertilizers for nutrition and growth of radish plants. Both fertilizer forms (granule and pellet) showed good performance in supplying K and other nutrients to the plants. In general, the application of half the K dose via BBF showed efficiency similar to a full dose of the KCl mineral fertilizer. Among the BBF forms, the pellet promoted greater tuber production and the granule promoted greater accumulation of nutrients in the soil. The results obtained in this work demonstrate the potential of sewage sludge BBFs to make more efficient use of K in agriculture, thus contributing to an adequate and sustainable destination of sewage sludge, in addition to reducing the use of soluble mineral fertilizers in agriculture. More studies should be carried out to better understand the effect of BBFs on the performance of crops with different cycles (short and long). In addition, a full economic feasibility assessment must be carried out.

8.5.6. REFERENCES

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9. CONSIDERAÇÕES GERAIS

O presente estudo relata pela primeira vez a produção, caracterização e avaliação da liberação de K e potencial agronômico de um fertilizante de BLE enriquecido com K em diferentes formas físicas. Os resultados obtidos indicam o potencial do enriquecimento do BLE em aumentar o teor de K em até 75 vezes quando comparado ao BLE puro. Além do mais o enriquecimento resultou em um novo BBF de liberação lenta de K que quando aplicado ao solo além de promover o fornecimento gradual e contínuo de nutrientes ao longo do ciclo da cultura, reduz as perdas de K via processo de lixiviação em até 4 vezes comparado ao fertilizante mineral KCl, contribuindo para aumentar a eficiência do uso do fertilizante.

A forma do fertilizante (grânulo e pellet) que é formado após diferentes tecnologias de enriquecimento resulta em BBF com características físicas distintas que fornece ao BBF enriquecido com K uma grande versatilidade de uso na agricultura. Devido uma maior porosidade e área da superfície especifica, o BBF na forma de grânulo apresentou uma liberação de K mais rápida quando comparado ao BBF na forma de pellet, podendo apresentar melhor desempenho para culturas de ciclos mais curtos. Já o BBF na forma de pellet, devido suas características físicas decorrentes da prensagem durante o processo de peletização, resultou em um fertilizante de liberação mais lenta de K, podendo apresentar melhor desempenho para a redução das perdas de K via processo lixiviação comparado ao fertilizante na forma de grânulo, além de melhor fornecimento de nutriente para culturas de ciclo mais longos.

Um fertilizante de liberação mais lenta pode reduzir a necessidade da aplicação de altas doses de fertilizantes a cada safra, contribuindo para redução do custo de produção da lavoura e minimizando a dependência do Brasil frente às importações de fertilizantes. De forma simplificada o custo (R$) de produção de uma tonelada de BBF de BLE enriquecido com KCl, é estimado em R$ 1.080,07 (Table S6). No entanto, devido os estudos de produção de BBFs serem recentes, e em relação a produção de BBF de BLE enriquecido com KCl este trabalho ser pioneiro, há a necessidade de novos estudos para testar novas proporções de matérias-primas para o enriquecimento e novas tecnologias para reduzir o custo de produção, tanto no processo de pirólise do LE quanto para o processo de enriquecimento do BLE. Além do mais, uma melhor avaliação de viabilidade econômica completa deve ser realizada, uma vez que a produção desse novo fertilizante contribui para resolver o problema de grande acúmulo de LE nas estações de tratamento de esgoto e o processo de pirólise resulta em mais dois subprodutos como o biogás e o bio-oleo que também podem gerar retornos financeiros. Somando a isso, e o BBF fornece macro e micronutrientes, além de ser uma fonte de C para o solo, reduzindo a operação na lavoura onde em muitos casos ocorre a aplicação separada de fertilizantes minerais e orgânicos, dobrando o custo operacional.

De forma geral, os resultados do presente estudo comprovaram: i) que o enriquecimento do BLE com K é eficiente em produzir um BBF com fornecimento de N, P e K, contribuindo para a reciclagem do LE na agricultura, resultado em um produto final ecologicamente correto; ii) Resolve o baixo fornecimento de K via BLE puro, que necessita de altas doses para suprir a demanda de K pela planta, inviabilizando sua aplicação do ponto de vista econômico e ambiental; iii) produz um fertilizante especial que é classificado como fertilizante de liberação lenta, que contribui para melhorar a eficiência do fornecimento e uso de K na agricultura, minimizando as perdas de K por lixiviação. Estudos futuros devem ser realizados para avaliar a dinâmica de liberação e lixiviação K em diferentes solos, avaliar o potencial agronômico dos BBFs em condições reais de campo e com diferentes culturas de ciclos curtos e longos e a realização de uma melhor avaliação de viabilidade econômica.

SUPPLEMENTAL MATERIAL

CHAPTER I

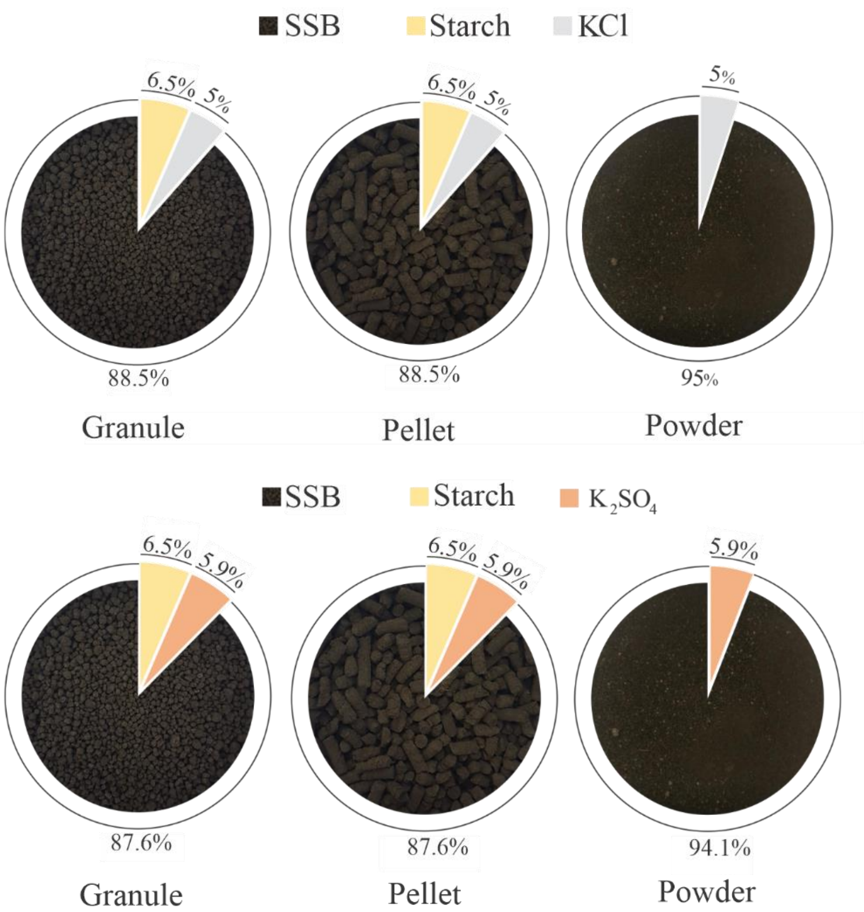

Figure S1. Summary of the amount of each raw material used in the production of each BBF.

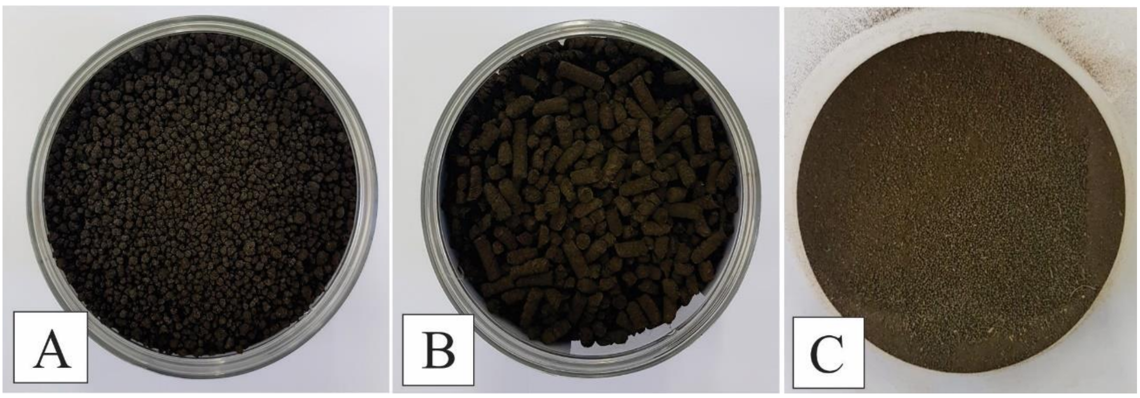

Figure S2. The BBFs in granulo (A), pellet (B) and powder (C) form.

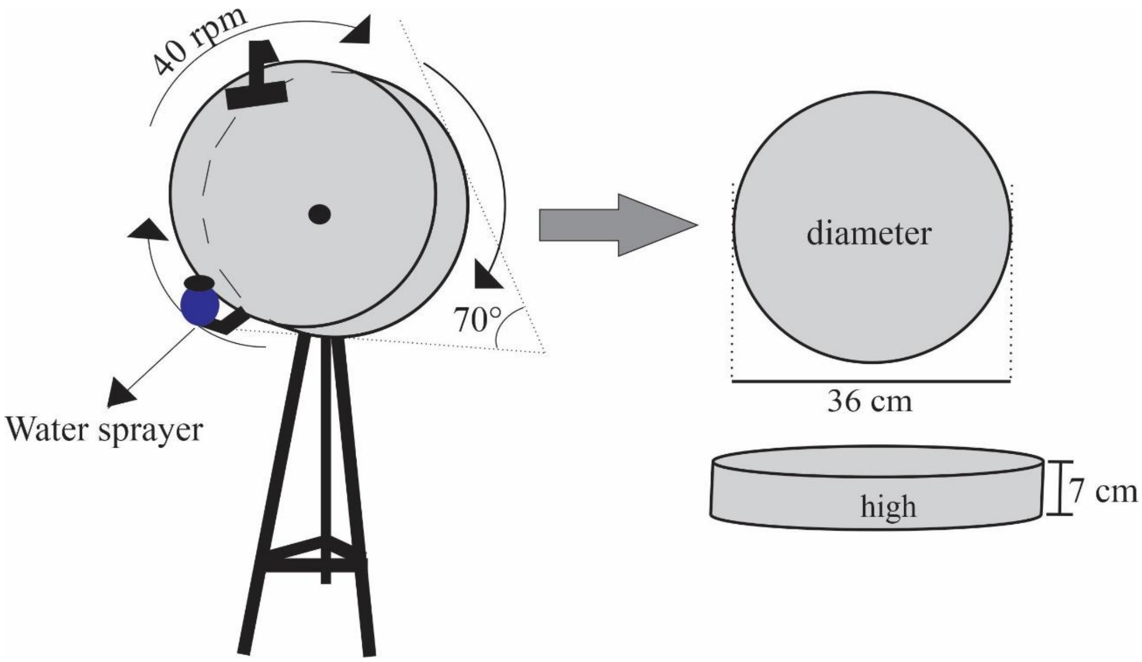

Figure S3. The granulator used in the granulation of BBFs.

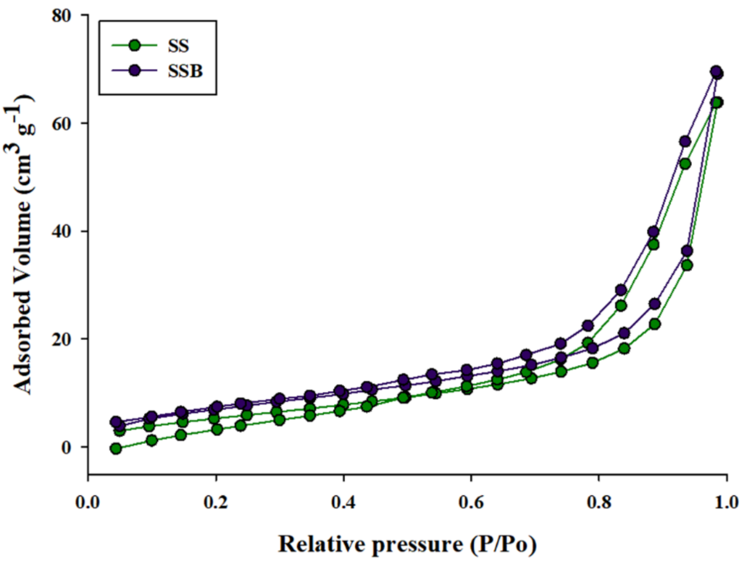

Figure S4. Nitrogen adsorption/desorption isotherms of SS and SSB.

Table S1. Description of the treatments tested.

Treatments	Description
BBF-KCl powder	SSB enriched with KCl in powder form
BBF-KCl pellet	SSB enriched with KCl in pellet form
BBF-KCl granule	SSB enriched with KCl in granule form
BBF-K_2SO_4 powder	SSB enriched with K_2SO_4 in powder form
BBF-K_2SO_4 pellet	SSB enriched with K_2SO_4 pellet form
BBF-K_2SO_4 granule	SSB enriched with K_2SO_4 in granule form

Table S2. The humic fractions of BBFs enriched with KCl and K_2SO_4.

Source	FA (g kg^{-1})	HÁ (g kg^{-1})	UH (g kg^{-1})
BBF-KCl	32.7 a	11.0 a	188.4 a
BBF-K_2SO_4	32.2 a	10.8 a	192.1 a
Form			
Granule	33.3 a	10.4 a	200.2 a
Pellet	33.9 a	11.5 a	192.9 a
Powder	32.4 a	10.9 a	177.6 a

Means followed by equal letters, uppercase in the row and lowercase in the column, do not show statistical differences according to the Tukey test ($P < 0.05$).

Table S3. The heavy metals contents of BBFs enriched with KCl and K_2SO_4.

Form	Source		
	BBF-KCl		BBF-K_2SO_4
		Co (mg kg^{-1})	
Granule	9.8 bA		9.6 aA
Pellet	9.8 bA		9.1 aA
Powder	11.8 aA		9.6 aB
Form		Li (mg kg^{-1})	
Granule	431.3 aA		415.3 aA
Pellet	400.6 aA		446.0 aA
Powder	441.3 aA		332.3 bB
Form		Pb (mg kg^{-1})	
Granule	102.4 abA		93.9 aA
Pellet	98.7 bB		96.3 aA
Powder	131.3 aA		92.7 aA
Source	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Ni (mg kg^{-1})
BBF-KCl	16.2	49.9 a	20.6
BBF-K_2SO_4	16.2	47.3 b	19.0
Form			
Granule	15.2	46.6 b	18.5
Pellet	17.0	48.7 ab	19.5
Powder	16.2	50.6 a	21.4

Means followed by equal letters, uppercase in the row and lowercase in the column, do not show statistical differences according to the Tukey test ($P < 0.05$).

CHAPTER II

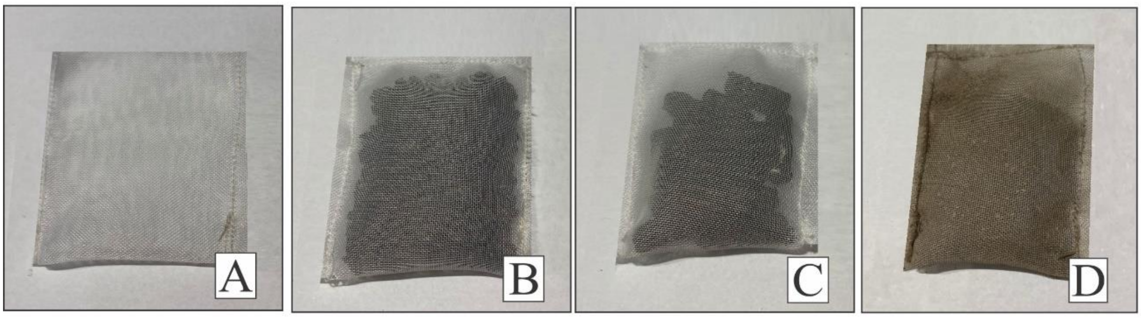

Figure S5. Polyester sachets sealed at the ends with 100% polyester thread. A: sachet without fertilizer; B: sachet with 5 g of BBF-KCl in the form of granules; C: sachet with 5 g of BBF-KCl in the form of a pellet; D: sachet with 5 g of BBF-KCl in powder form.

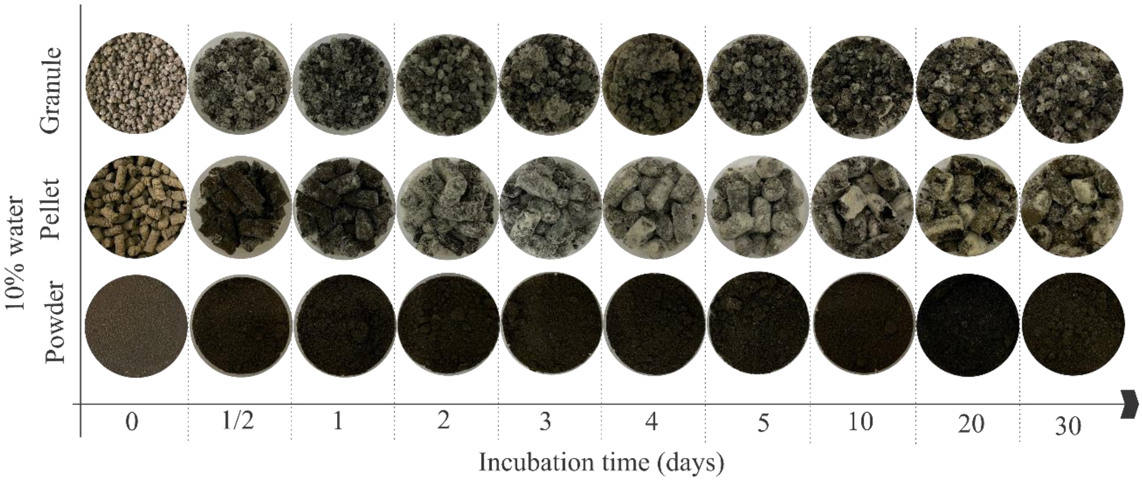

Figure S6. The BBFs-KCl during the incubation period on the 10% moisture level.

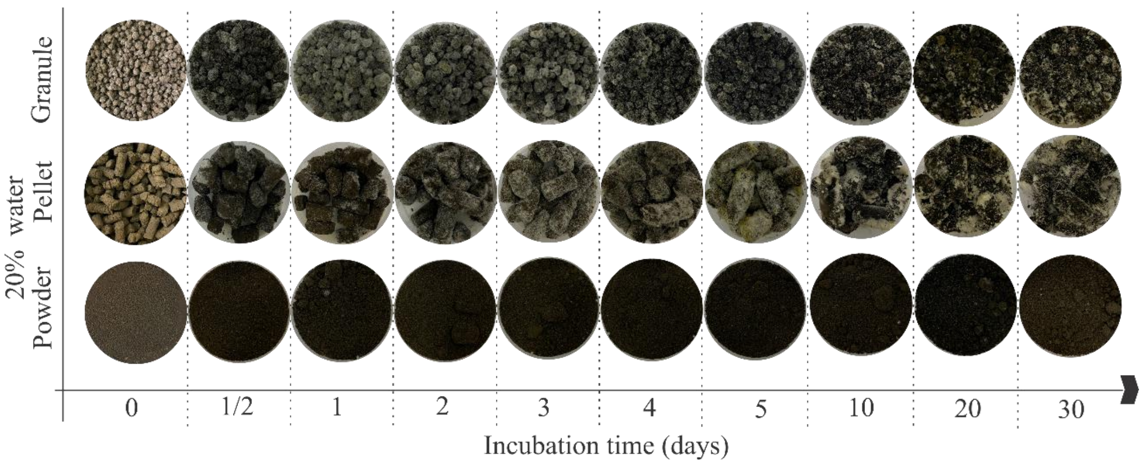

Figure S7. The BBFs-KCl during the incubation period on the 20% moisture level.

CHAPTER III

Table S4. Amount of fertilizer applied.

Fertilizer level	K_2O (kg há$^{-1}$)	BBF		KCl
		(Mg há$^{-1}$)	g pot^{-1}	g pot^{-1}
0.5	105	3.5	2.62	0.0
1.0	210	7.0	5.24	0.262

Table S5. Citric acid-soluble phosphorus and mineral N supplied via BBFs for each level of fertilization and the amount necessary for complementation applied via solution.

Fertilizer level	BBF	P_2O_5 (kg há$^{-1}$)			N (kg há$^{-1}$)		
	Mg há$^{-1}$	Total	Soluble[a]	Solution[c]	Total	Mineral[b]	Solution[c]
0.5	3.5	182	43.7	316.3	115.5	1.6	148.4
1.0	7.0	364	87.4	272.6	231.0	3.2	146.8

[a]: citric acid-soluble phosphorus; [b]: nitrate and ammonium; [c]: Amount of nutrient applied via solution.

CONSIDERAÇÕES FINAIS

Tabela S6. Custo de produção de uma tonelada de BBF de BLE enriquecido com KCl.

Matéria-prima	R$/tonelada
Lodo de esgoto	R$ 0,00
Amido de milho[a]	R$ 3.120,00
Cloreto de potássio (KCl)[a]	R$ 4.242,00
Serviço	**R$**
Pirólise para a produção do BLE[b]	R$ 300,00
Granulação/peletização	R$ 400,00

Custo de produção de uma tonelada de BBF de BLE enriquecido com KCl

Matéria-prima e serviço	Massa (kg) em 1 tonelada	R$
BLE	885	R$ 265,80
Amido de milho	65	R$ 202,80
KCl	50	R$ 212,10
Granulação ou peletização		R$ 400,00
Total	1000	R$ 1.080,70

[a]: valor da tonelada cotada no dia 25/11/2021; [b]: custo da pirólise do LE calculada para as nossas condições como capacidade e modelo do forno, temperatura, tempo de residência e tarifa de energia (0,61 R$/kWh).