pXRF ANALYSIS OF TROPICAL SOILS TREATED WITH SEWAGE SLUDGE BIOCHAR

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ABSTRACT: This study evaluated the application of portable X-ray fluorescence spectroscopy (pXRF) for the chemical characterization of biochar derived from the co-pyrolysis of sewage sludge and cashew pruning residues, as well as the sludge itself, applied to two contrasting soils: Chromic Luvisol and Haplic Planosol. The pXRF technique proved to be precise and practical for quantifying chemical elements without requiring chemical extraction or sample destruction. Multivariate analyses revealed that soil mineralogy was the main factor distinguishing treatment groups, while pyrolysis conferred distinct properties to the biochar compared to the raw sludge. Co-pyrolysis enhanced the concentration of elements in the solid phase and reduced the mobility of potentially toxic elements. Although the applied doses did not significantly alter the chemical composition of the soils, biochar showed potential as a soil conditioner and represents a viable strategy for the safe reuse of sewage sludge through thermal conversion.

KEYWORDS: Correlation matrix; heavy metals; plant residue.

ANÁLISE de pXRF DE SOLOS TROPICAIS TRATADOS COM BIOCARVÃO DE LODO DE ESGOTO

RESUMO: O presente estudo avaliou o uso da espectroscopia de fluorescência de raios X portátil (pXRF) na caracterização química de biocarvão oriundo da copirólise de lodo de esgoto e resíduo vegetal de cajueiro, além do próprio lodo aplicado em dois solos contrastantes: Luvissolo Crômico e Planossolo Háplico. A técnica pXRF demonstrou alta precisão e praticidade na quantificação de elementos, sem necessidade de preparo químico das amostras. As análises multivariadas revelaram que a mineralogia dos solos foi determinante na formação dos grupos, enquanto a pirólise conferiu ao biocarvão propriedades distintas em relação ao lodo. A copirólise concentrou elementos nos resíduos sólidos e reduziu a mobilidade de elementos potencialmente tóxicos. As doses aplicadas não alteraram significativamente a composição química dos solos, mas o biocarvão mostrou-se promissor como condicionante de solo, promovendo o reaproveitamento seguro do lodo de esgoto via conversão térmica.

PALAVRAS-CHAVE: Matriz de correlação; metais pesados; resíduo vegetal.

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INTRODUCTION: Portable X-ray fluorescence spectroscopy (pXRF) is an emerging technical tool for the characterization of solid materials. This technique stands out for being rapid and low-cost, enabling the analysis of the total elemental content of soil samples both in the field and in the laboratory, while allowing the quantification of essential chemical elements, potentially toxic elements, and rare-earth metals (RIBEIRO et al., 2017). Given this, pXRF has significant potential for soil characterization in both field and laboratory settings due to its practicality and accuracy, as well as the fact that it does not require sample deformation or the use of chemical extractors—advantages that can be extended to other solid samples with soil-like properties (RIBEIRO et al., 2017; TEIXEIRA et al., 2019).

Sewage sludge has become an alternative nutrient source for agriculture due to its ease of acquisition. However, its application presents challenges related to chemical composition, particularly the presence of potentially toxic elements (PTEs) such as cadmium, mercury, lead, and arsenic (AHMAD et al., 2022; CHAGAS et al., 2021; MARCIŃCZYK; OLESZCZUK, 2022). Based on this, this study evaluated the application of pXRF for characterizing a sewage sludge and cashew pruning-based biochar, as well as sewage sludge in two distinct soils.

MATERIALS AND METHODS: Data from two greenhouse experiments using two distinct soil types were used. The experiments were conducted from March to May 2024. Samples were collected from Experiment 1, which used an Eutrophic Haplic Planosol, characterized by a pH of 5.10 (without treatments) and high concentrations of iron and aluminum oxides and hydroxides; and from Experiment 2, which used a Chromic Luvisol developed from saprolite, with a pH of 7.15 (without treatments) and high content of 2:1 clay mineral. Composite sampling was performed for each treatment dose by collecting all replicates. The treatments consisted of the application of chemical element sources: biochar (BC), sewage sludge (SS), and mineral fertilizer based on phosphorus (P) recommendations for irrigated maize (FERNANDES, 1993).

The biomass source for biochar co-pyrolysis was sewage sludge obtained from a wastewater treatment plant using a UASB (Upflow Anaerobic Sludge Blanket) reactor operated by the Ceará Water and Sewage Company (Cagece), collected after drying. The second biomass source consisted of dried cashew tree pruning’s (leaves and fine branches), collected in the same dry mass proportion as the sludge, then ground and sieved through a 5 mm mesh. The co-pyrolysis process was carried out in a closed reactor at a 1:1 dry mass ratio under a nitrogensaturated (N_2) atmosphere, with temperature controlled at 500 °C for 1 hour and 37 minutes. Another treatment consisted of applying the same dried sewage sludge directly.

During the setup phase of the experiments, 3.0 kg of soil was weighed per pot. This amount was calculated based on the soil bulk density ($\rho = 1.5$ g cm^{-3}). Accordingly, for the five proposed treatment doses, the amount of biochar applied per hectare was: 0 (mineral fertilizer only), 1111.017, 2222.034, 4444.068, and 8888.136 kg ha^{-1}; and for sewage sludge: 0 (mineral fertilizer only), 1365.625, 2731.25, 5462.50, and 10925.00 kg ha^{-1}, respectively.

X-ray fluorescence (pXRF) analysis was performed using an Olympus XDelta Professional portable X-ray fluorescence spectrometer (pXRF) with a 40 keV beam excitation mode. Three readings were taken per sample, each lasting 30 seconds, for a total of 90 seconds per sample.

Assumptions for variance analysis were verified through Levene's test for homogeneity, Shapiro-Wilk test for normality, t-Student test for outliers, and Durbin-Watson test for residual independence. Subsequently, the data were standardized ($\mu = 0$; $\sigma^2 = 1$) to prevent one variable from overpowering the others. Following standardization, Principal Component Analysis (PCA) and Cluster Analysis were performed using the SAS OnDemand for Academics statistical software (SAS, 2023).

RESULTS AND DISCUSSION: The results of the Principal Component and Cluster Analyses are presented in Figure 1. The Principal Component Analysis (Figure 1A) is represented by components 1 and 2, which were derived from Spearman’s correlation. From this, variances and covariances were calculated, followed by the correlation matrix and, subsequently, the eigenvectors. Component 1 is composed of Ca(0.29) + Mn(0.31) + Co(0.31) + Ti(0.30) + Fe(0.31) + Y(0.29) – K(0.27) – Rb(0.31) – Sr(0.25) – Zr(0.24), and was named “Soil Mineralogy.” Component 2 consists of Cu(0.41) + Zn(0.42) + Cr(0.38) + As(0.39) – V(0.36) – Sr(0.25), and was designated as “Pyrolysis.” The treatments exhibited similar characteristics when analyzed within the same experiment. However, when comparing the two experiments, it becomes clear that the “Soil Mineralogy” component was the defining factor due to the contrasting developmental characteristics of the soils involved (OLIVEIRA et al., 2009).

In quadrant I, the variables Ca, Co, and Fe are highly correlated with the “Soil Mineralogy” component and show high variability due to the size of the mean vector. The variables Cr and Cu are correlated with the “Pyrolysis” component and show low variability because the mean vector is smaller in size. This quadrant is diametrically opposed to quadrant III, which consists of the variables Zr and Sr, highly correlated with “Soil Mineralogy,” strongly correlated with each other, and presenting a large mean vector. Quadrant II consists of the variables Zn and As, which are highly correlated with “Pyrolysis” and have low variability due to the smaller size of the mean vector. The variables Pb, K, and Rb are highly correlated with “Soil Mineralogy” and show high variability due to the size of the vector. This quadrant is diametrically opposed to quadrant IV. In quadrant IV, the variables Y, Mn, and Ti show high variability and are highly correlated with “Soil Mineralogy”; the variable V is proportionally opposed to Th.

The treatments were well characterized according to the component analysis, which makes it possible to discern their characteristics. The main feature that explains the difference between treatments is strongly correlated with “Soil Mineralogy,” separating Luvisol in quadrants I and IV from Planosol in quadrant III. BC and SS were highly correlated with “Pyrolysis” in quadrant II. It is worth noting that the mean vector of BC was larger due to its greater variability compared to SS.

The “Pyrolysis” component is strongly correlated with the sources applied to both soils, biochar from co-pyrolysis of sludge and pruning residues, and sewage sludge alone. Nevertheless, the average vector for BC is greater than that for SS, indicating a stronger association and greater significance for the “Pyrolysis” component. The thermal conversion process of biomass—in this case, sewage sludge and cashew pruning residues—concentrates chemical elements in the ash that constitutes biochar, drastically reducing the contamination potential of potentially toxic elements originally present in the sewage sludge, which are incorporated into the biochar after co-pyrolysis (KUJAWSKA; WOJTAŚ; CHARMAS, 2024; MOHAMED et al., 2022).

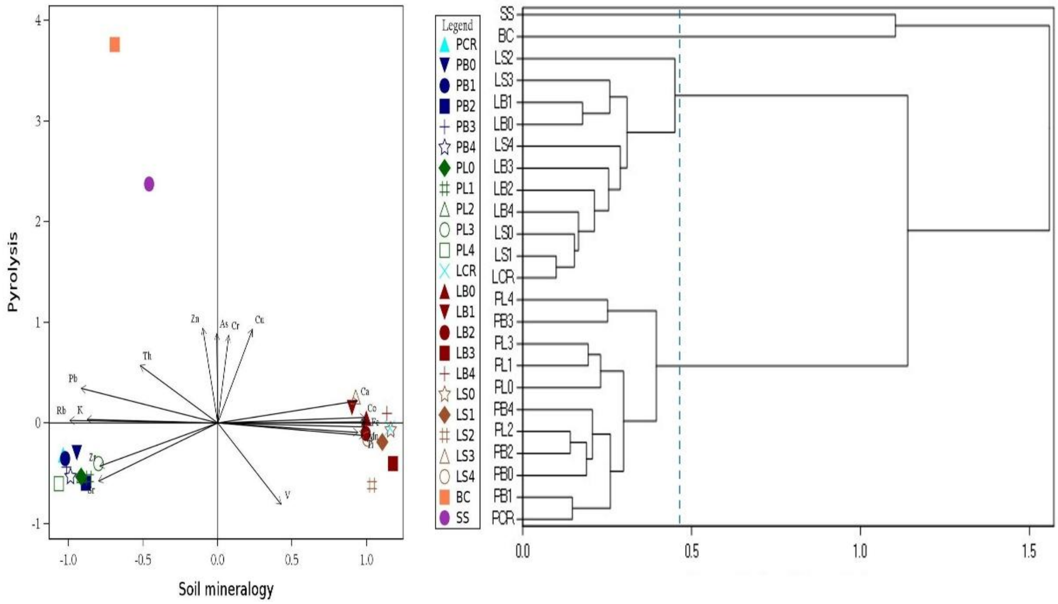

Figure 1. Principal Component Analysis and Cluster Analysis for biochar, sewage sludge, Planosol, and Luvisol.

Cluster analysis grouped the treatment variables into distinct groups in the 0.5 distance, forming four clusters as shown by the dashed lines in Figure 1B. The first cluster is composed of the experiment using the Eutrophic Haplic Planosol, constituting the first group and reinforcing the findings discussed earlier. Similarly, the second experiment with the Chromic Luvisol formed the second group. In this case, the soil type was the determining factor in separating these two groups. Although both soils received the same treatments, the distinguishing characteristics that led to their separation into different groups are related to their genesis and, consequently, their chemical composition—regardless of the addition of biochar and sewage sludge (KUMMER et al., 2010). The treatments using chemical element sources—biochar (BC) and sewage sludge (SS)—formed separate groups. Despite having a similar chemical composition, due to the common biomass origin (sewage sludge), the pyrolysis process alters the characteristics of the biochar, resulting in two distinct groups (FACHINI; DE FIGUEIREDO, 2022).

CONCLUSIONS: The pXRF technique enables precise and non-destructive analysis of soil, sewage sludge, and biochar samples. The amounts of biochar and sewage sludge applied were not sufficient to alter the chemical composition of either soil. Biochar produced through co-pyrolysis of sewage sludge and cashew pruning residues presents a viable alternative for enhancing the use of sewage sludge through thermal conversion as a soil conditioner.

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