

The Use of Biochar and Compost Mixtures as Potential Organic Fertilizers

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Organic wastes have been used in agriculture many years ago, due to its capacity to improve soil quality. The manure was used before the occurrence of chemical fertilizers and treated / untreated sewage sludge, started to be used as a fertilizer a few years ago. The aim of the study is to evaluate the organic matter, organic carbon, organic content and soil composition, after application in greenhouse conditions, of mixtures made from sewage sludge biochar and cattle manure compost. The biochar and compost used in different concentrations, at 5 t/ha and 30 t/ha, application rates, in greenhouse conditions, for a period of 90 days, improved organic matter, organic carbon and organic content from the soil used in experiment. The sewage sludge biochar and the cattle manure compost had similar effects on the parameters determined in the study. Organic and inorganic soil components, identified by the ATR-FTIR method, have not been modified by application of sewage sludge biochar and cattle manure compost.

Keywords: organic waste, soil, greenhouse

The environmental issue are very present in the society development, if we take in consideration the most important sources of pollution and how it interact with actual principle of sustainable development (waste and energy management, water management etc.) [1, 2]. The increase of waste quantity cause environmental degradation, especially for soil, water and air pollution, due to unsustainable waste disposal and management methods [3].

Organic wastes used as a soil fertilizer, has positive effects on organic matter (OM), macro and micro-nutrients in soil, reducing the need for chemical fertilizers [4, 5]. In agriculture, has traditionally used manure as a fertilizer to improve soil properties [6, 7] and to a lesser extent, bio-solids started to be used [7]. Organic matter of soil is a source of nutrients for crops and a decrease in organic matter content indicates a reduction of soil quality [8, 9]. To prevent the depletion of organic matter from intensive agro-ecosystems, many sources of organic matter have been used, such as livestock manure, sludge, various organic byproducts and other wastes [10]. Also, in some cases, it is very important to evaluate the soil composition and how these can influence the crop grow [11, 12].

Loss on ignition is used to estimate organic matter, because it represents a larger fraction of the organic matter present in the soil sample, but can overestimate the organic matter if the soil sample contains a substantial amount of carbonate [13]. Thermal analysis techniques involve combustion or pyrolysis of soil samples, during which the lost mass, the released energy, and the amount of specific gas released are recorded as a function of temperature, providing a value of the thermal stability of the organic matter of the soil (SOM) [14].

The chemical composition of soil organic matter (SOM) can be modified when different types of organic wastes are applied in soil [14]. Soil organic matter includes all non-humic solutes and humus, including organic matter (OM) related to soil minerals and dissolved organic matter (DOM) [15]. Many studies have used infrared spectroscopy

to evaluate structural changes of soil organic matter [16]. Infrared Spectroscopic Techniques (FTIR) are very sensitive to organic and inorganic soil components and are used to characterize soil organic matter (SOM), because this method allow detailed identification of functional groups and molecules [14, 17]. Attenuated total reflection spectroscopy (ATR-FTIR) can be used to identify the main components of the soil, such as carbonates, clay minerals and organic compounds [18].

The aim of the study was to determine organic matter, organic carbon, organic content, organic and inorganic soil components, from soil amended with sewage sludge biochar and cattle manure compost, at 5 t/ha and 30 t/ha application rate, in greenhouse conditions.

Experimental part

Experiment greenhouse description

The soil was collected from a depth of 0-20 cm from the surface of the soil, and passed through a sieve with orifices of 4 mm. The sewage sludge biochar was obtained by the slow pyrolysis process at 500°C and the cattle manure compost was obtained by the passive composting method in static pile [19], for 2 years. The description of the method of obtaining these treated organic wastes is mentioned in the previous articles [20, 21].

The experimental treatments contain: soil control (C); 0% compost-100% biochar (M0-B100); 10% compost -90% biochar (M10-B90); 20% compost-80% biochar (M20-B80); 30% compost-70% biochar (M30-B70); 40% compost-60% biochar (M40-B60); 50% compost-50% biochar (M50-B50); 60% compost -40% biochar (M60-B40); 70% compost-30% biochar (M70-B30); 80% compost-20% biochar (M80-B20); 90% compost-10% biochar (M90-B10); 100% compost -0% biochar (M100-B0). The mixtures made from compost and biochar, in different concentrations, were used for 5 t/ha and 30 t/ha application rates. The quantity of biochar and compost was mixed with 9 kg of soil, resulting in 6 replicates for each experimental variant and each replicate weighing 1.5 kg [22]. In each plastic pot, were sown seeds of barley and two plants were kept for a period of 90 days.

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Soil samples analysis

Soil samples collected with a metallic cylinder were air dried and stored until analysis [23, 24].

Loss on ignition

Soil samples crumbled in mortar, were dried at 105°C for 12 h, after which the soil samples were stored in a desiccator [9]. From each soil sample, 5 g of the sample were calcined at 550°C for 4h [25, 26].

Organic matter

Loss on ignition has become a common method for estimating organic matter, which is then converted to estimate organic carbon [27].

Organic matter (OM) was calculated according to equation (1) [25].

$$OM (\%) = \frac{DW - CW}{DW - W_c} \cdot 100 \quad (1)$$

where: DW is the soil sample weight dried at 105°C plus the crucible weight, CW is the weight of the calcined sample at 550°C plus the crucible weight, W_c is the weight of crucible.

Organic carbon

Estimation of Organic Carbon (OC) from Organic Matter (OM), determined by loss on ignition (LOI) is a simple and inexpensive procedure, but requires the use of a suitable conversion factor [25, 27]. A conversion factor =2, based on the assumption that organic matter contain 50% carbon, would be accurate [27]. Organic carbon (OC) was calculated like in formula (2).

$$OC (\%) = \frac{OM}{2}, \quad (2)$$

where: OM is organic matter, 2 is conversion factor.

Organic content

The organic content was calculated according to the formula (3) [28].

$$Organic\ content (\%) = \left(\frac{Dw - Cw}{Dw} \right) \times 100, \quad (3)$$

where: D_w is dry weight, C_w is combusted weight.

ATR - FTIR analysis

The soil samples were crumbled in mortar, dried in oven at 105 °C and stored in desiccator until the measurements [29]. Experimental data were obtained in the spectral range corresponding to the wavelength of 4000 cm⁻¹ to 550 cm⁻¹ [30]. The spectra were recorded as an average of 32 scans [31], resolution 2 cm⁻¹ [18, 32]. Air spectra on the ATR dry crystal, were used as background for infrared measurement [33, 34]. The soil samples were placed on the ATR crystal with a spatula, and to ensure good contact between the soil sample and the ATR crystal, a controlled pressure was applied [18, 34]. The Origin software was used to process the spectral data [35]. The baseline was corrected, the noise was reduced, and the second derivative of the spectrum was carried out [36].

Results and discussions

Influence of sewage sludge biochar-cattle manure compost mixtures on organic matter

Loss on ignition (LOI) refers to mass loss of solid samples, due to loss of moisture content, carbon and other elements when the soil sample is heated at specific temperatures [37]. Organic matter is composed from carbon, nitrogen, oxygen and hydrogen, but the proportions

of each component can vary depending on the source of the organic matter [28]. Sewage sludge and manure are similar organic wastes in terms of nitrogen (N) and carbon (C) content [38, 39].

Figure 1 shows that the two treated organic waste used in greenhouse conditions contributed to the growth of organic matter in soil. At 5 t/ha, application rate, organic matter increased in all soil samples amended with sewage sludge biochar - cattle manure compost mixtures. The treated organic waste applied at 30 t/ha, significantly increased organic matter compared to the results obtained at the application rate of 5 t/ha. The sewage sludge biochar and cattle manure increased organic matter with approximately 4%, when application rate increased.

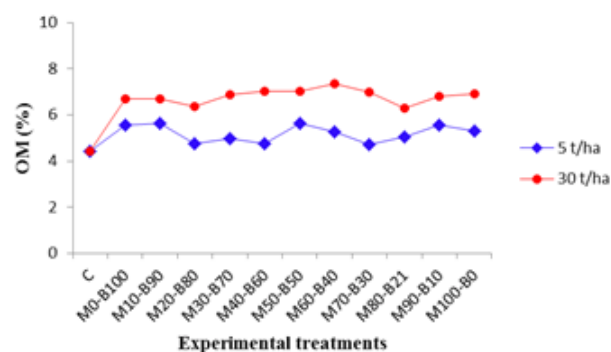


Fig. 1. Effect of biochar and compost on organic matter

Influence of sewage sludge biochar and cattle manure compost on organic carbon

Similar to organic matter, organic carbon has been increasing in line with the increase of application rate of the treated organic wastes. Compared to the control variants, organic carbon increased in all soil samples amended with treated organic waste, in particular at 30 t/ha, application rate. Organic carbon did not vary significantly depending on the different concentrations of sewage sludge biochar and cattle manure compost used in mixtures, as shown in figure 2.

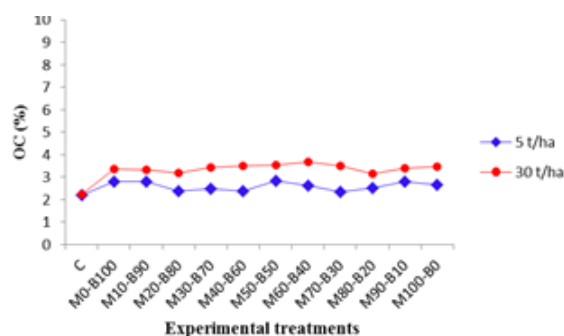


Fig. 2. Effect of biochar and compost on organic carbon

Biochar and manure contain a high amount of organic carbon, which has similar effects on soil nutrients, structure and microbial dynamics in agricultural systems [40].

Influence of sewage sludge biochar-cattle manure compost mixtures on organic content

The term organic content, is used to refer to the organic content as a percentage of the dry weight, determined by the loss on ignition at 550°C [28].

Organic content has increased as a result of the application of organic waste used at different concentrations in mixtures. The organic content has doubled in the experimental treatments with sewage sludge biochar, mixtures of sewage sludge biochar - cattle manure compost in different concentrations and cattle

manure compost, at 30 t/ha application rate. From figure 3, it is noted that even at the application rate of 5 t/ha, the organic content recorded significant values compared to the results determined in the control variants.

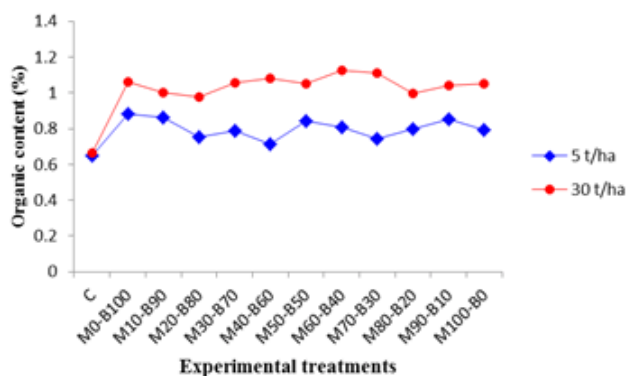


Fig. 3. Effect of biochar and compost on organic content

Influence of sewage sludge biochar - cattle manure compost mixtures on soil components

The identification of soil organic matter (SOM) in the specific peaks, which correspond to the vibrations of functional groups such as carbohydrates, lignin, cellulose, fats/lipids and protein substances, makes infrared spectroscopy suitable to study the structural characteristics and dynamics of soil organic matter (SOM) [41]. Soil organic matter (SOM) is composed by organic and heterogeneous substances, that vary according to structure and chemical complexity, which contributes to plant growth, nutrient bio-availability and absorption of contaminants [42-44].

The spectral graphs presented in figure 4 until figure 14, show that the chemical composition of soil organic matter (SOM) has not changed as a result of the application in soil of compost obtained from cattle manure and of the biochar obtained from sewage sludge at varying quantities. We identified the peaks of the spectra and as can be observed in the ATR-FTIR spectra, a peak at 3694 cm^{-1} was recorded, indicating vibrations of clay, kaolinite and Fe oxides, which are inorganic components [41].

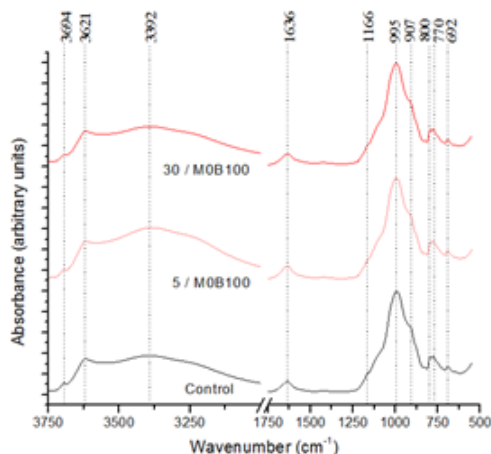


Fig 4. ATR-FTIR spectra of soil amended with M0B100 mixture

The peak 3621 cm^{-1} from the spectral graphs is attributed to inorganic components (vibrations of clay, gibbsite, kaolinite and Fe oxides), and organic components (humidity and oxygen - containing organic matter) [41, 45].

It is important to determine if are changes into the soil organic matter (SOM) composition, as these could reflect changes in the functioning of agro-ecosystems, which in turn can affect the environmental benefits (eg carbon sequestration in soil, retention and release of nutrients), obtained by applying organic waste [14] (fig. 6,7).

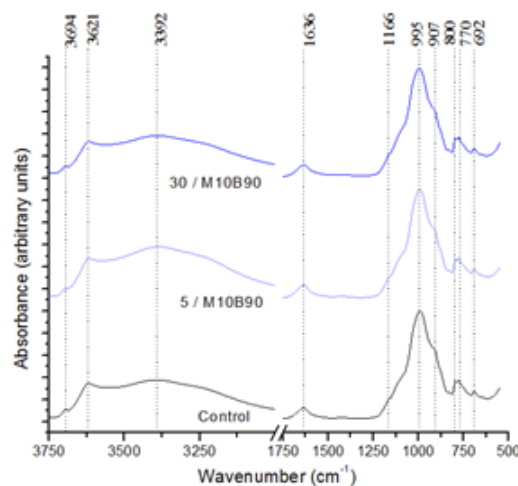


Fig. 5. ATR-FTIR spectra of soil amended with M10B90 mixture

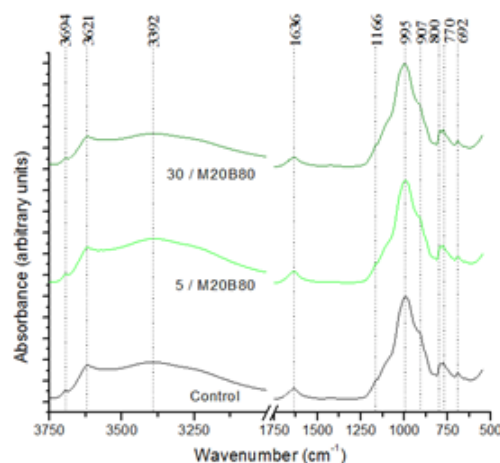


Fig. 6. ATR-FTIR spectra of soil amended with M20B80 mixture

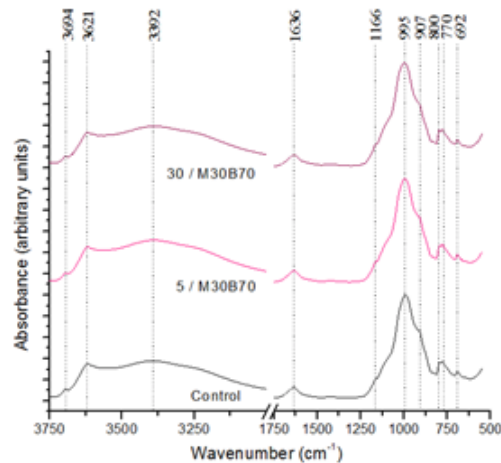


Fig. 7. ATR-FTIR spectra of soil amended with M30B70 mixture

The next peak recorded at 3392 cm^{-1} , indicate the presence only of organic components: O-H and N-H stretching, H-bonded OH [41] (fig. 8).

At the peak 1636 cm^{-1} , are inorganic components (oxygen and nitrogen-containing polar functional group), but also organic components, such as hydrophilic materials of soil organic matter (SOM) [45], amide II of the primary amides, aromatic C = C, C = O (quinones), carboxylates and amides R-O-NO₂ [41] (fig. 9, 10).

At the peak 1166 cm^{-1} , the area is attributed to carbohydrate groups, C-OH of aliphatic alcohols, which are part of the organic component [41, 45] (fig. 11).

The maximum amplitude of the spectra was recorded at 995 cm^{-1} , indicating organic components, namely: aromatic CH out-of-plane bending [45]. Also inorganic

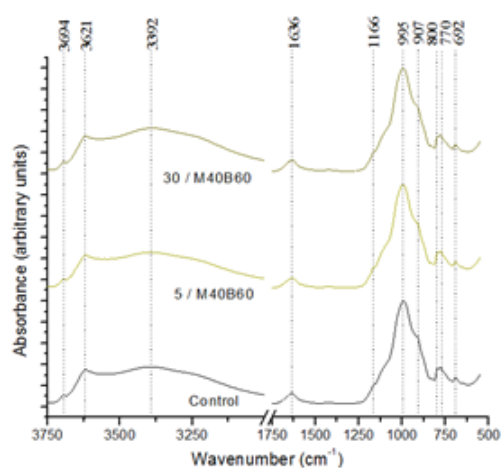


Fig. 8. ATR-FTIR spectra of soil amended with M40B60 mixture

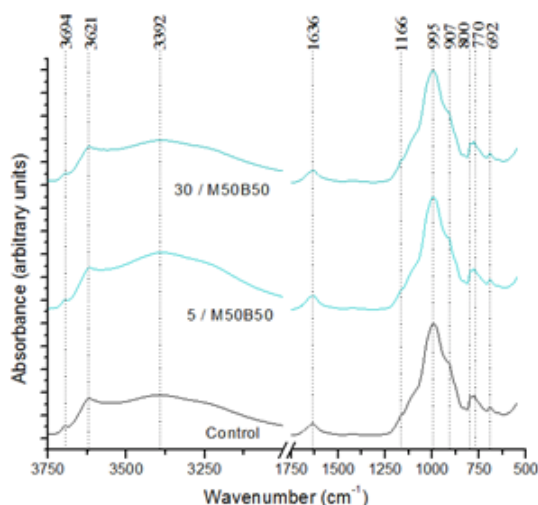


Fig. 9. ATR-FTIR spectra of soil amended with M50B50 mixture

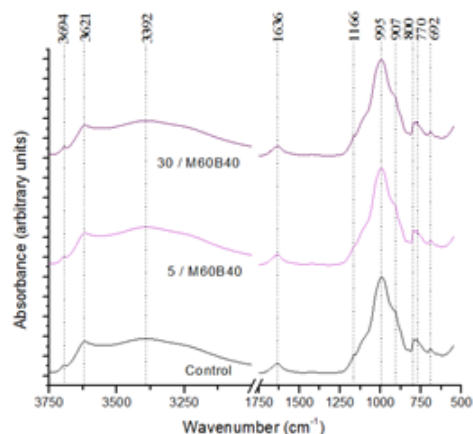


Fig. 10. ATR-FTIR spectra of soil amended with M60B40 mixture

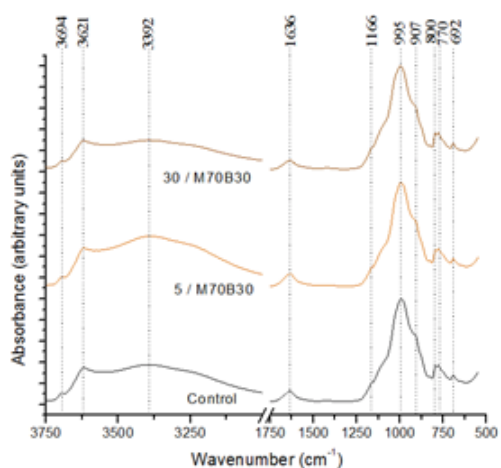


Fig. 11. ATR-FTIR spectra of soil amended with M70B30 mixture

components was identified at 995 cm^{-1} , as Si-OH of alumino-silicate lattice (kaolinite, illite, smectite) [41].

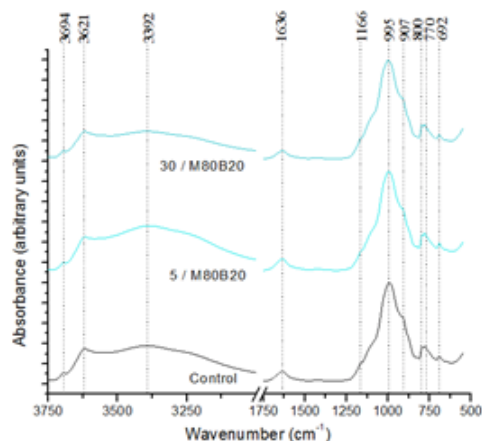


Fig. 12. ATR-FTIR spectra of soil amended with M80B20 mixture

The second peak as intensity, was identified at 907 cm^{-1} , and means the presence of the organic component, like benzoic acid, pyranose ring (carbohydrates), cellulose (ring breathing), $\text{RHC}=\text{CH}_2$, $\text{R}_2\text{C}=\text{CH}_2$ [41, 45].

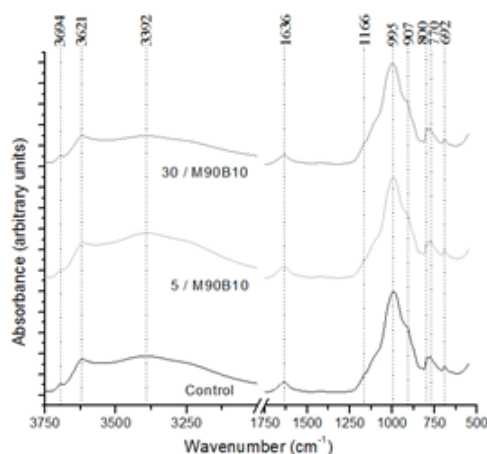


Fig. 13. ATR-FTIR spectra of soil amended with M90B10 mixture

The peaks 800 cm^{-1} and 770 cm^{-1} are caused by inorganic materials: clay and quartz minerals), carbonate and kaolinite, but also by organic components ($\text{R}_2\text{C}=\text{CH}_2$ groups of phenyl) [41, 45]. The authors [46], associated the 692 cm^{-1} band with Si-O symmetrical bending vibration of quartz.

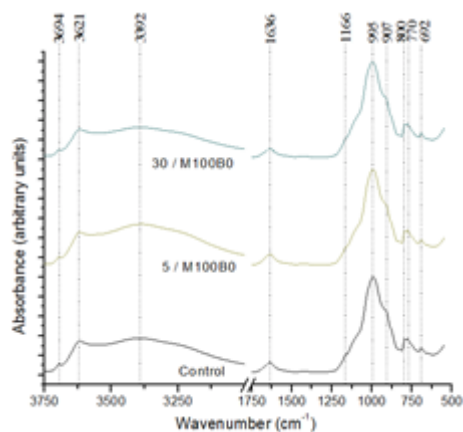


Fig. 14. ATR-FTIR spectra of soil amended with M100B0 mixture

Soil is a mixture of minerals (clays, silt, sand and gravel), water, air and living organisms [47]. The chemical composition of silt and sand is generally dominated by quartz, and the clay fraction is composed mainly by clay minerals (kaolinite, montmorillonite), humic substances and oxides of Al and Fe [47]. Following the interpretation of spectral graphs, the clay prevails in the soil used in the greenhouse experiment.

Little information is available about the effects of manure on the chemical nature of soil organic matter (SOM) [48]. The authors [48], in their study, did not detect any effect of applying cattle manure on soil composition.

Processes and mechanisms, who contribute to the stabilization and destabilization of organic matter in soils amended with biochar, remain largely unknown [49]. Interdependent mechanisms that protect the organic matter in soil by mineralization include: selective conservation and synthesis of resistant structures; the physical separation from decomposers (organisms, soil bacteria, fungi or invertebrates that decompose the organic material), microbial enzymes and O₂ by including it inside macro and micro-aggregates; and inaccessibility of chemical association with mineral surfaces [49].

Conclusions

Due to similar content of nutrients, sewage sludge biochar and the cattle manure compost had similar effects on soil, increasing organic matter, organic carbon and organic content, at both application rates. Changes in the concentrations of biochar and compost in the mixtures did not produce significant oscillations, only the modification of the application rate to 30 t / ha, increased the content of the determinant parameters.

The ATR-FTIR spectra of soil samples amended with biochar-compost mixtures show that organic and inorganic soil components have not been affected by the organic waste type, by the concentrations of biochar and compost, or by the change of application rate.

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