

# PhD School on Agriculture, Environment and Bioenergy

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(XL cycle, 2024-27)

## Project draft

### 1. Field of interest

*Indicare il/i settore/i scientifico disciplinari: AGR-13; AGR-12; AGR-10*

### 2. Project title

Biobased fertilizers from Hydrothermal Carbonization Technology: effects of hydrochar on microbioma and biological and chemical soil characteristics

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**co-tutor/s:** Barbara Scaglia

### 4. Relevance of the topic and state of the art:

The circular economy model aims to reduce the input and consumption of natural resources; increase the sharing of energy and renewable and recyclable resources; reduce emissions, waste and residuals; and keep the economic value of products, components and materials. In this way, the production of bio-based fertilizers is advocated as a solution for both waste management and nutrient source for agriculture providing. The study on the technologies of biobased fertilizers production should be integrated with the study on soil and plant growth effects (Bona et al., 2023). Soils are explicitly mentioned in the Farm to Fork strategy and in the Zero pollution action plan (European Commission, 2019) but are indirectly relevant for achieving climate neutrality in 2050, preserving and restoring ecosystems and biodiversity. Sustainable soil management has become a top priority topic for guarantee the sustenance of agricultural production, the safeguarding of quality of water, biodiversity, climate and numerous services ecosystems. The recent “European Green Deal” approved at the end of 2019 posed ambitious goals to be achieved by 2030, including a 20% reduction in fertilizers of synthesis and a 50% reduction in the use of pesticides. Biomasses, residual from different waste (agro-industrial waste) are considered an abundant as renewable resource that can be converted into solid, liquid and gaseous form and fertilizers using biochemical physical -chemistry and thermochemistry technologies (Chew and Doshi 2011). In this context, a possibility of particular interest can be the so-called hydrothermal conversion (HTC) process that seems to be more cost-effective in comparison to conventional process of thermal drying (Wang et al., 2018). During the HTC process, the biomass is transformed into a lignite-like product. The products of HTC can be distinguished in three components: a solid fraction (HC), a liquid mix, composed by water and oil, and gas as CO<sub>2</sub> (Wang et al., 2018). HC is a product rich in organic carbon useful as amendant and for soil remediation (Wang et al., 2018; Kambo and Dutta, 2015). Hydrochar derived from the HTC process, demonstrates superior performance compared to the raw biomass being used for the carbon sequestration, soil improvement, bioenergy production e remediation of wastewater pollution. Liquid product resulting from the HTC process (liquor) is biodegradable due to its high content of organic matter and nutrients. Hydrochar proved to be a high-value carbon-rich material after undergoing a treatment that

reduced the content of hydrogen and oxygen. The environmental benefits resulting are mainly: i) adapting to climate change - saving use of non-renewable resources, ii) climate change mitigation - Saving GHG emissions by reducing the input of external chemical fertilizers, iii) actively contribute to a more sustainable management of different types of organic waste.

## **5. Layout of the project (draft)**

### **5.1. Materials & Methods:**

The experimental activity will aim to test the production of hydrochar from three different high-water content wastes. The tests are aimed to define the properties of the hydrochar in relation to the nutrient and organic matter content. Successively, the hydrochar(s) obtained will be tested for the recovery of N and P as struvite at lab scale. The hydrochar and struvite produced will be characterized as regard the main fertilizing and amendment properties. The hydrochar obtained from each feedstock will be treated by acid solutions, to enhance phosphorus solubilization in the liquid phase. The struvite precipitation process will be carried out by the addition of a source of Mg ( $Mg(OH)_2$  or  $MgCl_2$ ) and/or ammonium ( $NH_4Cl$ ) and NaOH to the liquid fraction, containing most of the initial hydrochar phosphorus. The hydrochar will then be characterized regarding the main chemical parameters, N, P and TOC content. The amendment properties of the hydrochar produced pre-acid leaching and struvite precipitation will be assessed by biological stability and phytotoxicity assay. After each laboratory test, the precipitated crystals will be separated from the aqueous solution by filtration and dried. In order to perform the mineralogical identification of precipitated constituents (i.e. struvite and other phosphates), the samples will be analyzed by X-ray powder diffraction and by scanning electron microscope (SEM). Successively, the agronomic and environmental properties of the different fertilizers obtained from the HTC will be studied.

The fertilizing properties of struvite will be tested by agronomic trial using pot filled with soil. The plant test chosen is the lettuce, as described for plant growth effect of the hydrochar and hydrochar post-treated. The effect on plant growth will be determined by agronomic test with lettuce adding a soil two different doses of each product considered. After 30 days, the plants will be harvested and, for each pot, the biomass produced will be determined by considering the fresh and dry biomass, and the chlorophyll content. Previously, to assess the best doses to use for agronomic trials, phytotoxicity will be tested by a vegetation test. The effects on the soil of the fertilizers tested will be evaluated through the preparation of mesocosms, small soil systems amended with hydrochar mixed and aged using after the best hydrochar assessed by the activity described previously. The dose of use will be chosen according to the previous agronomic test. The effects on soil respiration will also be assessed by measuring  $CO_2$  emissions during the incubation period. The soil samples obtained after agronomic test will be characterized considering C, N and P content. In addition to the analysis of TOC, Total N, pH, and metals, the analysis of the soil will aim to study in depth the effect on C and P. P-forms present in the matrices will be detected by using  $^{31}P$  NMR and Hedley fractionation protocol (Zangarini et al., 2020; Pepè Sciarria et al., 2023). We will proceed with the identification of the main C-type by performing  $^{13}C$  CPMAS NMR analysis on the different, treated and no treated samples of HC to obtain qualitative information on the composition of the biomasses studied.  $^1H$  NMR analysis will be used to identify the main components and the differences in the relative proportion of various classes of organic compounds from recalcitrant and labile soil organic matter. The soils used for the agronomical test, will be also characterized for both labile and recalcitrant organic matter, to assess the ability of hydrochar to store organic carbon. Furthermore, to evaluate possible effects of hydrochar, negative or positive, on soil microbioma, studies

about an amplicon sequencing survey of the bacterial communities inhabiting the rhizosphere will be carried out. Similarly, the agronomic test of struvite application will be performed to assess the effect on plant growth in comparison to a common phosphate mineral fertilizer. The liquid fraction of HC characterized from a chemical-physical point of view will be used to evaluate the possible use through fertirrigation.

## **5.2. Schedule and major steps (3 years):**

### **1<sup>st</sup> YEAR**

- Activities to study the bibliography and optimal formulation of the experimental design
- Hydrochar production and struvite precipitation production test from different wastes
- Hydrochar and struvite characterization
- Liquid fraction exploitation

### **2<sup>nd</sup> YEAR**

- Plot plant production of hydrochar
- Struvite precipitation
- Hydrochar post-treatment to improve amendment properties
- Agronomic test with struvite

### **3<sup>rd</sup>**

- Effects on soil properties and plant growth of amendment produced
- Liquid fraction exploitation for fertilizing use by fertirrigation
- Writing the thesis and papers

## **6. Available funds (to support research):**

- Tambone and Scaglia “free funds” from external activities (10,000 €)

## **7. Co-Financing (to support the bourse):**

## **8. Literature: (**

1. Bona, D., Bertoldi, D., Borgonovo, G., ...Giannetta, B., Tambone, F. (2023). Evaluating the potential of hydrochar as a soil amendment. *Waste Management*, 159, 75–83
2. Chew and Doshi, 2011. Recent advances in biomass pretreatment – Torrefaction fundamentals and technology. *Renewable and Sustainable Energy Reviews* 15(8), 4212-4222
3. European Commission, 2019. The European Green Deal. COM(2019) 640 final.
4. Kambo, H.S., Dutta, A., 2015. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. *Ren. Sust. En. Rev*, 45, 359-378.
5. Pepè Sciarria, T., Zangarini, S., Tambone, F., ...Puig, S., Adani, F. (2023). Phosphorus recovery from high solid content liquid fraction of digestate using seawater bittern as the magnesium source. *Waste Management*, 155, 252–259
6. Wang, T., Zhai, Y., Zhu, Y., Li, C., Zeng., G., 2018. A review of the Hydrothermal carbonization of biomass waste fo hydrochar formation: process conditions, fundamentals, and physiochemical properties. *Ren. Sust. En. Rev*, 90, 223-247.
7. Zangarini, S., Pepè Sciarria, T., Tambone, F., Adani, F., 2020. Phosphorus removal from livestock effluents: recent technologies and new perspectives on low-cost strategies. *Environmental Science and Pollution Research*, 27, 5730–5743