Innovative micronutrient fertilizers by biosorption for organic farming

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A healthier and more sustainable EU food system is the cornerstone of the European Green Deal (Haines & Scheelbeek, 2020). The European Commission (EC) has developed the strategy "Farm to Fork", where the key areas are: ensuring healthy, affordable, and sustainable food, combating climate change, protecting the environment and preserving biodiversity, fair profits in the food chain, supporting organic farming (*Farm to Fork Strategy*, 2021). In connection with the European Green Deal guidelines, by 2030, 25% of agricultural land will be used for organic farming. It means an increased demand for fertilizers for organic crop production (*A European Green Deal | European Commission*, 2021).

Commercially available soil fertilizers for organic farming are low in micronutrients, which have to be supplemented by foliar fertilization (Anand et al., 2019). Before a foliar application is possible, it takes several weeks, during which the plant may suffer from a micronutrient deficiency as soils are often deficient in these nutrients (Korzeniowska et al., 2015).

As part of the work, fertilizers with higher micronutrients with slowed release were developed (micronutrients bound to biomass act similarly to chelates). It is possible to provide plants with low doses of micronutrients for a longer time - during the first, crucial stages of development. Proper nutrition of plants reduces their sensitivity to stress, including biotic stress (Bostock et al., 2014). It is crucial for organic farming, where pesticides application is limited (Norton et al., 2009). This study aimed to develop new organic-mineral fertilizers for organic farming containing biomass-associated micronutrients (Cu, Fe, Mn, Zn) and the technology to produce these fertilizers using biosorption.

Secondary cellulosic materials were used in this study, including biomass from supercritical CO_2 extraction process of e.g., raspberry, strawberry, blackcurrant seeds (Samoraj et al., 2019) which so far are not used for fertilizer purposes on a commercial scale. Good sorption properties of these materials have been demonstrated (Samoraj et al., 2019). Additionally, supercritical conditions reduce the risk of microbial contamination of the materials. The residue size after berries seed extraction is similar to that of microgranulate. This means that, at the same mass as conventional pellets, enriched seeds have a larger nutrient release surface area, which allows for a more uniform distribution of nutrients in the plant rhizosphere.

Laboratory scale technology was developed to enrich biomass with Zn, Mn and Cu using a biosorption process to obtain an organic-mineral fertilizer. The ability of the sorbents to bind micronutrient ions in the range of 4-15 mg/kg d.m., evenly on the surface, mainly with the participation of carboxyl and amino (less frequently phosphoryl and hydroxyl) groups, was demonstrated(Samoraj et al., 2019). The biosorption mechanism was based on ion exchange - micronutrient ions were replaced mainly by K^+ and Mg^{2+} (less frequently by Na^+ and Ca^{2+}). Strong correlations between the total content of microelements in the biomass and their content on the surface were confirmed (correlations between the results obtained using XRF, SEM-EDX, ICP-OES methods). The level of contaminants in the studied biomasses met the criteria of fertilizer products. Gradual leaching of micronutrients in successive extraction steps was proved. The share of bioavailable fraction was almost 100% for each studied system, and the exchangeable fraction - 30-86%, depending on the sorbent. The smallest amount of ions was determined in the leachable fraction - 10-15% - reflecting the tendency for micro-nutrients to leach from the system into groundwater.

The bioavailability of micronutrients was evaluated in germination tests on garden cress (according to ISTA guidelines) (Samoraj et al., 2014) and pot trials on white mustard (Samoraj et al., 2015). Higher transfer rates were demonstrated for micronutrients bound to berries biomass than inorganic salts and a commercial chelate. Providing micronutrients to plants in a biomass-bound form with a higher degree of biofortification, with increasing doses. Plant quantitative and qualitative parameters were also improved.

In field trials on maize (Samoraj et al., 2015), the use of enriched blackcurrant seeds at rates, kg/ha: 386 (2.5 kg/ha Zn), 170 (1 kg/ha Mn), and 36 (0.5 kg/ha Cu) resulted in better yield and higher content of applied micronutrients in grain (10% biofortification), compared to the commercial product. Fertilization of raspberry bushes with raspberry seeds enriched in Zn, Mn, and Cu at higher than nominal doses (150 and 200%) provided higher micronutrient content in leaves and fruits (11.5% biofortification) compared to the commercial product. No toxic effects of the new fertilizers on crops were noted. When tested on raspberry fruits, micronutrients were available to plants throughout the fruiting period. The preliminary economic analysis confirmed the competitiveness of the new products against micronutrient chelates.

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