# Development of innovative micronutrient fertilizers by biosorption techniques

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The demand for food is predicted to increase by as much as 70% by 2050 (van Dijk et al., 2021). This requires a commensurate increase in agricultural and fertilizer production. Nevertheless, conventional nitrate or ammonium-based fertilizers adversely affect soil fauna, contaminate groundwater supplies, and decrease soil fertility. Recent efforts have been geared towards sustainably producing high-quality, biosecure food and increasing the use of biofertilizers in agriculture. Among the various types of biofertilizers, multicomponent fertilizers based on biomass waste are particularly interesting. Biosorption is a promising technology for producing biofertilizers, wherein the biomass is enriched with essential nutrients of high bioavailability (Samoraj et al., 2022). Micronutrient ions can bind to the surface of the biomass by immersion biosorption, wherein the contacting solution components interact with the functional groups on the biomass surface. The binding capacity is limited by the equilibrium between the bound ions and those remaining in the solution. Another innovative approach is the spraying biosorption technique, which increases the amount of micronutrients attached to the biomass while simultaneously delivering multiple ions without competitiveness in binding to the biomass surface. This is a novel solution that can be employed in the production of micronutrient-enriched fertilizers.

Materials that are a source of nitrogen (>3%) and organic carbon (>45%) such as blackcurrant seeds, blackcurrant residues after supercritical $CO_2$ extraction, and flaxseed were chosen as the most suitable feedstocks for biosorption experimentation. The experiment aimed to produce organic-mineral fertilizers with higher micronutrient concentrations exceeding 1.5%. The immersion method employed a stepwise salt addition technique to generate a multi-ion solution consisting of Cu(II), Mn(II), Zn(II), and Fe(II). Three different micronutrient solutions were developed using the same approach, with concentrations tailored to each specific biomass. Several iterations were performed to fine-tune the final product composition. In contrast, the spray method enriched the biomass with micronutrients by spraying solutions of Cu(II), Fe(II), Mn(II), and Zn(II) with varying concentrations and solid to liquid ratio, followed by drying at 40ºC. Enriched biomasses were analyzed by ICP-OES to determine their final concentration levels. To evaluate the efficacy of the fertilizers, a series of extraction tests were conducted using different media, such as water, neutral ammonium citrate, and potassium nitrate. This was done to assess the leachability of micronutrients from fertilizers. Finally, cucumber cultivation was used to test the fertilizers' potential. The experiment lasted 10 days, after which the biometric parameters of the sprouts were analyzed, including chlorophyll content, stem length, root ball parameters, and fresh weight for each study group. The sprouts were then dried in an oven at 40ºC for 24 hours and submitted for ICP-OES analysis.

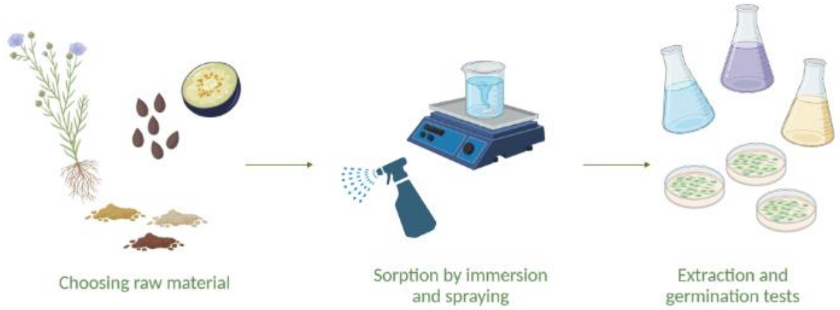


***Figure 1.*** *Representation of procedure (created with Biorender.com)*

The results of a study show that the maximum total micronutrient content achievable through both spray and immersion methods is approximately 2.5%. The nitrogen content ranges from 3.54-3.97%, and the carbon content is 45%. The micronutrients present in the biomass are in bioavailable forms, with a range of 60-100%. The immersion method yields materials with the smallest amount of water-soluble forms of Cu and Fe, which is advantageous in preventing the leaching of these elements into groundwater. However, the water-soluble fractions of Mn and Zn are present in much higher proportions. On the other hand, materials enriched by the spray method contain a higher content of soluble forms, ranging from 30-90%. While the novel technique allows for the introduction of nutrients in desired ratios and quantities, not all ions reach the active sites available on the biomass, which makes their leaching from the surface much easier. Plant-available fractions were mostly higher for materials enriched by the spray sorption method, with zinc being the least available form. In germination tests, the immersion-enriched biomass had better biometric parameters. However, further studies are needed to determine the appropriate ratio of micronutrients using the immersion method. The nutrient transfer to plants varies depending on the element. For copper, the transfer is around 50-60%, for iron, it is 40-50%, for manganese, it ranges from 40-60%, and for zinc, it's 50-70%. Fertilizers produced by immersion biosorption are more bioavailable to plants. Currently, the impregnation method appears more versatile than the immersion method, as the latter requires adjusting the solution's composition to a specific type of biomass. However, formulations produced by the immersion method exhibited greater bioavailability of micronutrients in plant studies. The classical biosorption method resulted in the exchange of a much smaller fraction of micronutrients, while immersion biosorption allows for the complete binding of micronutrient ions to active sites, making their exchange more challenging.

***Table 1.*** *Comparison of different biosorption methods*

| **Immersion biosorption** | | **Spraying biosorption** | |
|---|---|---|---|
| **Pros** | **Cons** | **Pros** | **Cons** |
| • Low leaching of the water-soluble elements into the groundwater supplies<br>• Better bioavailability | • For each different biomass, pH and temperature optimization is required<br>• More time and energy consuming<br>• To collect biomass, filtration or centrifugation is necessary<br>• Unequal ion binding | • Easy-to-apply solution<br>• Low drying cost<br>• Controlled release is possible<br>• Easy to obtain desired quantity and ratio of nutrients | • Not all ions reach the biomass active sites<br>• Higher leaching possibility |

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