Innovative micronutrient fertilizers by biosorption for organic farming

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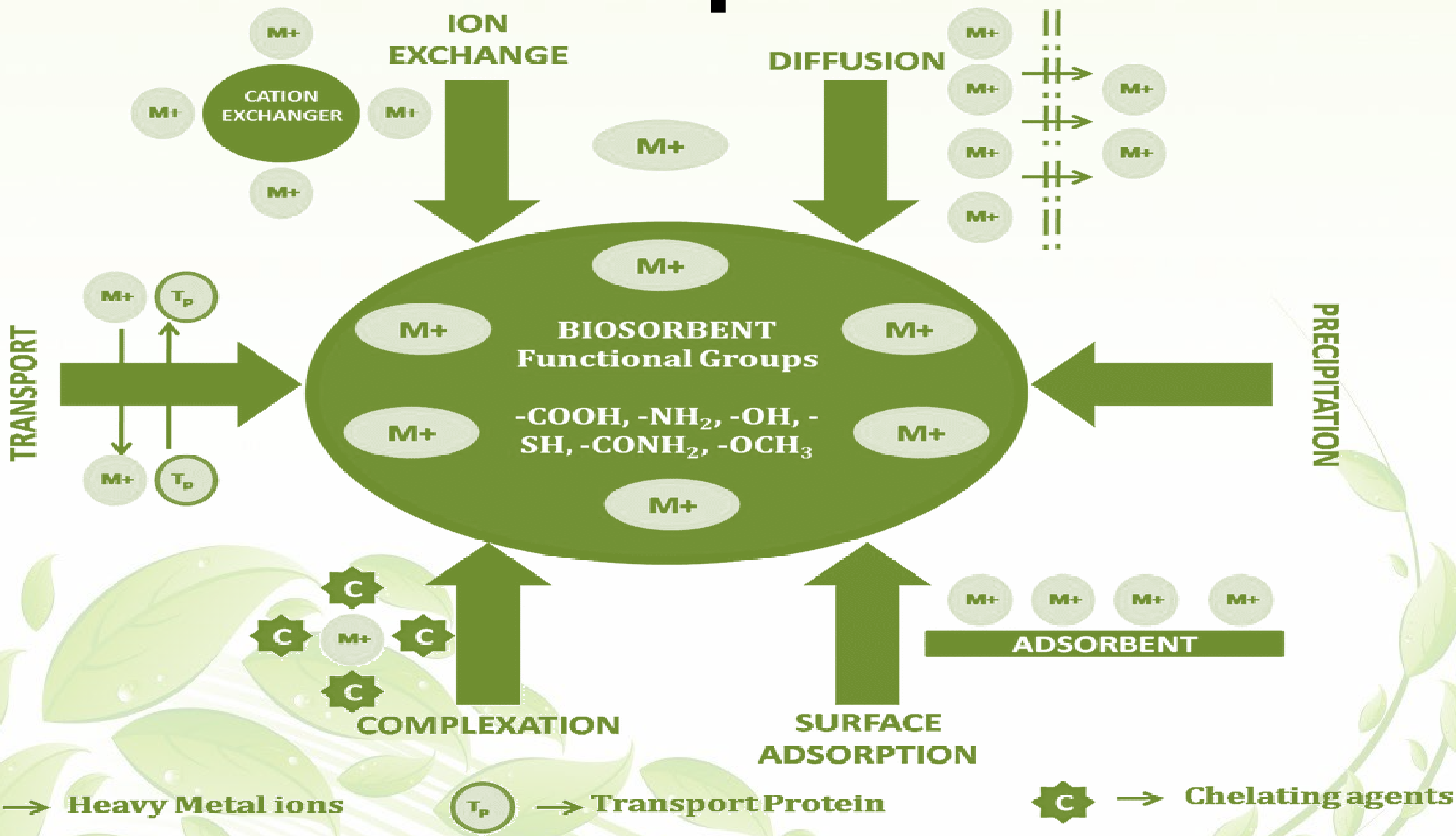
Introduction

- Population growth rate exceeds grain yield by three times, crop area remains the same. The global crisis has made the situation much worse, millions of people are at risk of starvation.
- More than two-thirds of European Union countries are severely deficient in at least one of the micronutrients.
- Today, the main goal is to improve the efficiency of fertilizer ingredients while reducing the environmental impact of their use. The European Green Deal calls for a 25% share of organic farming.
- Micronutrient fertilizers for organic farming will play an increasingly important role.

Biosorption



Gaur, N., Flora, G., Yadav, M., & Tiwari, A. (2014). A review with recent advancements on bioremediation-based abolition of heavy metals. Environmental Science: Processes & Impacts, 16(2), 180-193.

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Biosorption – new trends

Biosorption process

Focus on:
sorbate removal

Focus on:
biosorbent enrichment

Wastewater treatment
(90 600 papers)

Biological feed supplements with micronutrients
(7 040 papers)

Micronutrients fertilizers
(1 640)

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Scholar.google.com –keywoerds: biosorption and wastewater, biosorption and feed supplements, biosorption and valorisation and micronutrient fertilizer

Potential biosorbents

BIOSORBENTS

Plants

- Leaves
- Seeds

Fungi

- Micromycetes
- Macromycetes

Algae

- Microalgae
- Macroalgae

Animal

- Bones
- Eggshells

Microbes

- Bacteria
- Archea

Waste

- Manure
- Agricultural waste

Chojnacka, K. (2010) Biosorption and bioaccumulation–the prospects for practical applications. Environment International, 36(3), 299-307

Micronutrient fertilizers for organic farming

Fruits

Leaves, buds, branches

DRYING / GRINDING

Product: tea, dried, spices, herbal medicines

PRESSING

Product: juices, jams, jellies, wine

Residue

Fruit pomace

Waste

Various technologies

Product: dried residues, food dyes, substrates for plastics, phenolic extracts, bakery substrates, dietary fibers, moldings, lecithin

Supercritical CO_2 extraction

Oils - pharmacy and dietary supplements

Postextraction residue

15-30% of all by products

Biosorption + Zn, Mn, Cu

Micronutrient fertilizers

Non-toxic, easy dosing, competitive for commercial products

Chojnacka, K., Tuhy, Ł., Samoraj, M., Michalak, I., Witek-Krowiak, A. & Górecki, H. (2014) New Biological Fertilizer Components with Micronutrients by Biosorption, Fertilizer Technology: Synthesis, vol. 2, pp 376-409

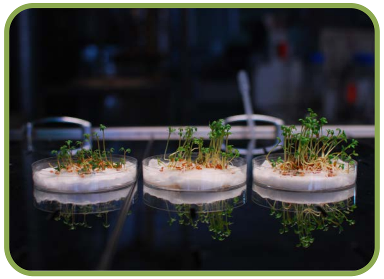
Previous studies

Biosorption of metal ions to the biomass of seeds of berries

2012/05/E/ST8/03055

- Basic research.
- Biosorption in laboratory and bench scale.
- Selection of process parameters for single ions: Zn(II), Mn(II), Cu(II).
- Preliminary utility tests on plants.

Main results



Petri dish tests

- Tests on garden cress according to IRST standard
- Promising results - comparable to commercial chelates products

Pot trials

- Tests on white mustard – up to 2.5x higher dry mass, Zn, Mn and Cu content were higher by 25%, 18% i 38%, respectively

Field trials

- Two-season tests on maize - 10% biofortification
- Tests on raspberries – 12% biofortification

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Current studies

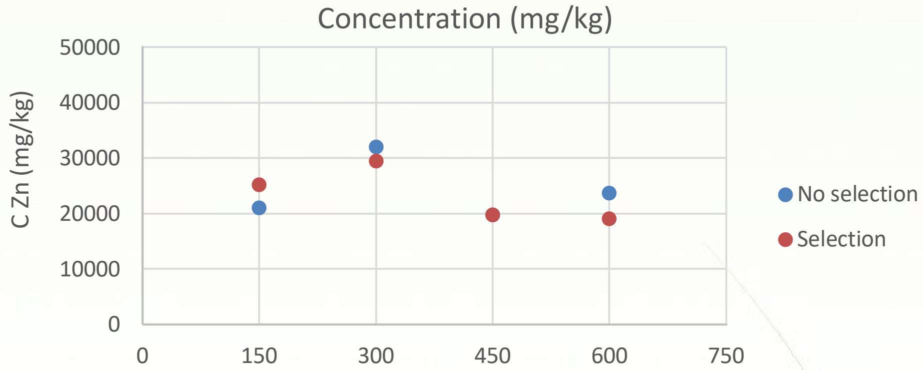
- Implementation project: "Innovative micronutrient fertilizers by biosorption for organic farming" TANGO-V-C/0019/2021-00, WUST and EKOPLON consortium.
- Development of production technology for new biomass-based fertilizers.
- Biosorption carried out in a multi-ion system.
- Use of standardized waste streams as micronutrient solution.
- Scaling up the biosorption process to pilot conditions.

Expected results

- Organo-mineral fertilizers with micronutrients in organic form for food biofortification (Zn, Cu, Fe, Mn).
- Fertilizers dedicated to organic crops: cucumber and/or berries.
- Fertilizer formulation safe for plants and the environment.
- Waste-free technology (micronutrient recovery).

Determination of sorbate concentration and process duration time

- The experiment was conducted until the matrices were fully loaded - i.e. for 9h.
- The volume of the bed was 40 mL.
- Each matrix was prepared in 3 replicates.
- The experiments were conducted using Zn(II) at a concentration of 300 ppm.
- The sorption capacity of the matrices was determined by comparing ICP-OES results for biomass before and after the biosorption process.



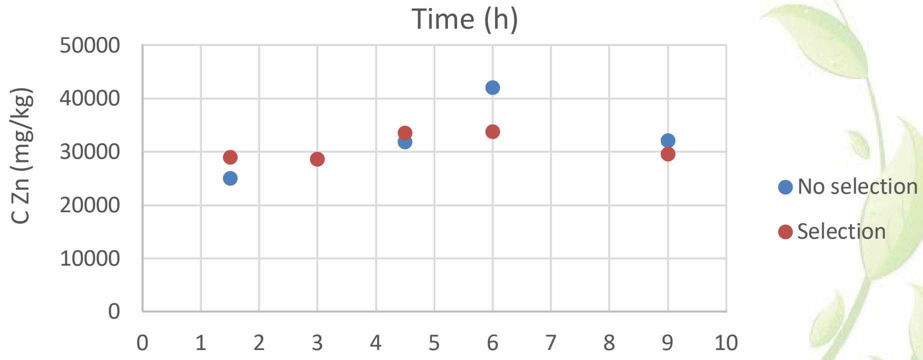


Fig. 1. Sorbate concentration and biosorption time determination.

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Selection of sorbate concentration in a multielemental biosorption

	Content in eniched biomass (ppm)			
Concentration Cu:Mn:Zn (ppm)	Cu	Mn	Zn	Sum
38:300:65	28 635 ± 6 861	14 304 ± 1 474	2 257 ± 103	45 198
75:300:125	32 183 ± 2 253	9 973 ± 981	2 954 ± 295	45 111
150:600:250	34 082 ± 4 876	13 003 ± 3 007	3 763 ± 832	49 648
100:100:100	32 209 ± 6 049	5 355 ± 240	6 399 ± 355	43 965
200:200:200	33 294 ± 3 518	6 263 ± 98	6 526 ± 102	46 084
300:300:300	**36 391 ± 6 840**	**6 562 ± 277**	**6 868 ± 325**	**49 822**

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Final process parameters

Sorbate	Cu(II), Zn(II), Mn(II)
Biosorbents	Blackcurrant seeds, Baltic algae (Fucus)
Sorbate concentration	**300 mg/L**
Reactor volume	**70L**
Micronutrient solution volume	**200L**
pH	**5**
Temperature	**25^{o}C**
Material losses	**10%**
Volumetric flow rate	**1L/min**
Process time	**6h**
Drying	**24 h, 50^{o}C**

Installation

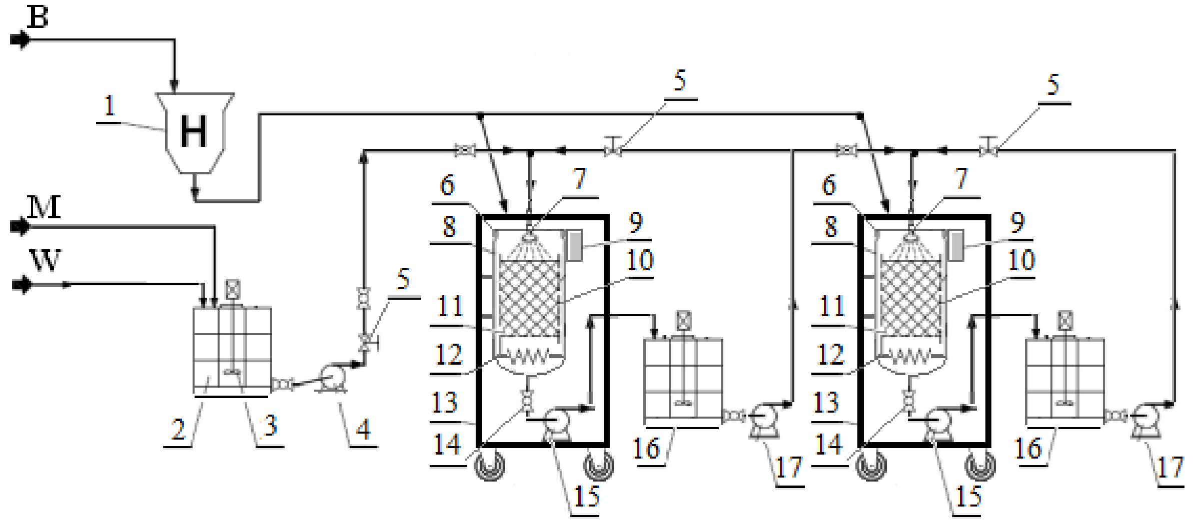

Fig. 4. Simplified scheme of the process in fixed bed mode – a system of two column reactors

Streams: B – Biomass, M – Micronutrients, W- Deionized water.

Main equipment: 1 – Biomass homogenizer; 2 – Micronutrient solution tank; 3 – Stirrer; 4, 15, 17– Peristaltic pumps; 8- Reactor tanks; 10 – Sieve; 16 – Recirculated solution tanks (equipped with pH regulator).

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Multielemental biosorption results

	Baltic algae, raw (mg/kg)	Baltic algae, enriched (mg/kg)	Enrichment coeficient
Cu	17.2 ± 6.0	22 946 ± 1 848	1 302
Mn	417 ± 17	5 684 ± 565	13.6
Zn	71.1 ± 13.6	9 291 ± 1 112	130
	Blackcurrant seeds, raw (mg/kg)	**Blackcurrant seeds, enriched (mg/kg)**	**Enrichment coeficient**
Cu	12.8 ± 0.2	8 415 ± 3 296	**6 584**
Mn	26.1 ± 0.2	2 802 ± 1 029	**107**
Zn	25.6 ± 1.3	8 030 ± 220	**312**

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Multielemental content of product

Macronutrient	Content (%)	Micronutrient	Content (g/kg)
C	45.1	Cu	8.42
N	4.13	Mn	2.80
P_2O_5	1.36	Zn	8.30
K_2O	1.20	Fe	0.256
SO_3	0.840	**Toxic elements***	**Content (mg/kg)**
CaO	0.615	Cd	$3.85 \cdot 10^{-4}$
MgO	0.0965	Ni	$4.63 \cdot 10^{-3}$
Na_2O	0.0310	As	$2.65 \cdot 10^{-5}$
***Below the legal limit**		Pb	$2.42 \cdot 10^{-3}$
		Cr	$6.78 \cdot 10^{-3}$
		Hg	$1.16 \cdot 10^{-5}$

**Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 .*

Final product

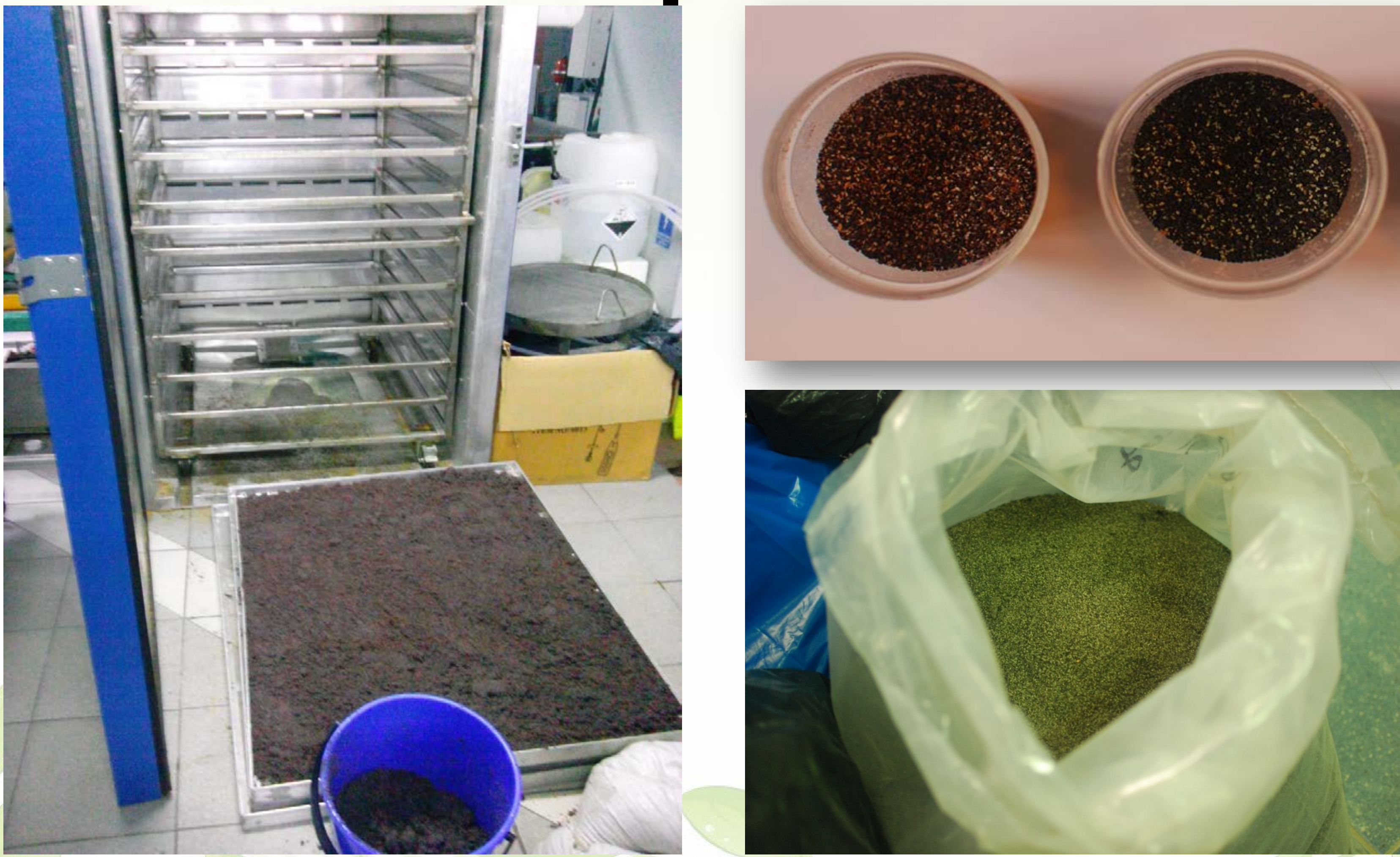

Fig. 9. Final product

Fixed bed modelling

Model	Equation	Linear form		Parameters	R^2
Thomas	$\frac{C_t}{C_0} = \frac{1}{1+\exp\left[\left(\frac{k_{Th} q_e x}{Q}\right) - k_{Th} C_0 t\right]}$	$ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{Th} q_e x}{Q} - k_{Th} C_0 t$	Zn(II)	k_{Th} = 0.0209 (mL/min mg) q_e = 8.66 (mg/g)	**0.914**
			Cu(II)	k_{Th}= 0.0353 (mL/min mg) q_e= 4.05 (mg/g)	**0.948**
			Mn(II)	k_{Th}= 0.0523 (mL/min mg) q_e= 5.52(mg/g)	**0.858**
Nelson-Yoon	$\frac{C_t}{C_0 - C_t} = \exp(k_{YN} t - \tau k_{YN})$	$ln \frac{C_t}{C_0 - C_t} = k_{YN} t - \tau k_{YN}$	Zn(II)	τ=14.8 (min) k_{YN}= 0.0053 (1/min)	**0.914**
			Cu(II)	τ= 12.6 (min) k_{YN}= 0.005 (1/min)	**0.948**
			Mn(II)	τ= 12.9 (min) k_{YN}= 0.097 (1/min)	**0.858**
Wolborska	$\partial \frac{\partial c_b}{\partial t} + v \frac{\partial c_b}{\partial H} + \frac{\partial q}{\partial t} = D_{ax} \frac{\partial^2 c_b}{\partial H^2}$	$ln\left(\frac{c}{c_0}\right) = \frac{\beta_a c_0 t}{q} - \frac{\beta_a H}{v}$	Zn(II)	β_a= 0.0240 (1/min) q= 8.46 (mg/g)	0.833
			Cu(II)	β_a= 0.0253 (1/min) q= 4.72 (mg/g)	0.941
			Mn(II)	β_a= 0.0251 (1/min) q= 6.19 (mg/g)	0.523
Adams-Bohart	$\frac{C_t}{C_0} = \exp\left(k_{AB} C_0 t - k_{AB} N_0 \frac{z}{U_0}\right)$	$ln\left(\frac{C_t}{C_0}\right) = k_{AB} C_0 t - k_{AB} N_0 \frac{z}{U_0}$	Zn(II)	N_0 = 3188 (mg/L) k_{AB} = 0.00751 (mL/min mg)	0.833
			Cu(II)	N_0 = 1991 (mg/L) k_{AB} = 0.0127 (mL/min mg)	0.941
			Mn(II)	N_0 = 1547 (mg/L) k_{AB} = 0.0162 (mL/min mg)	0.523

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Fixed bed modelling

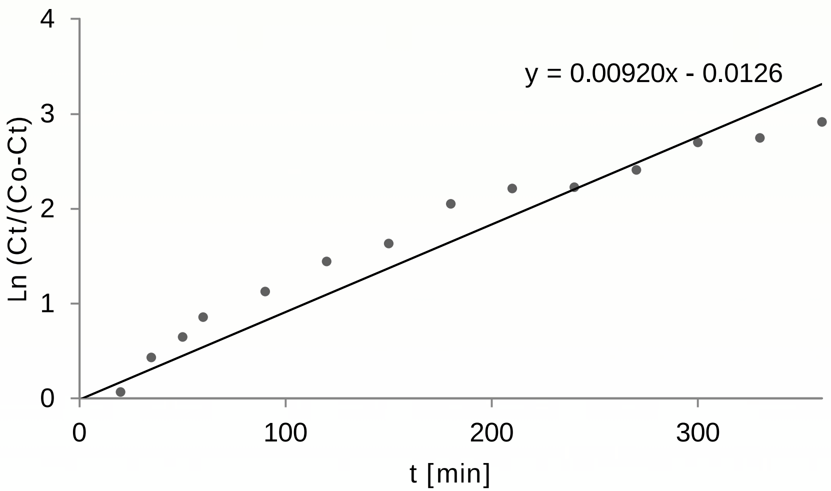

Fig. 5. Linearization of data for post-extraction residues with Zn(II), Nelson-Yoon model.

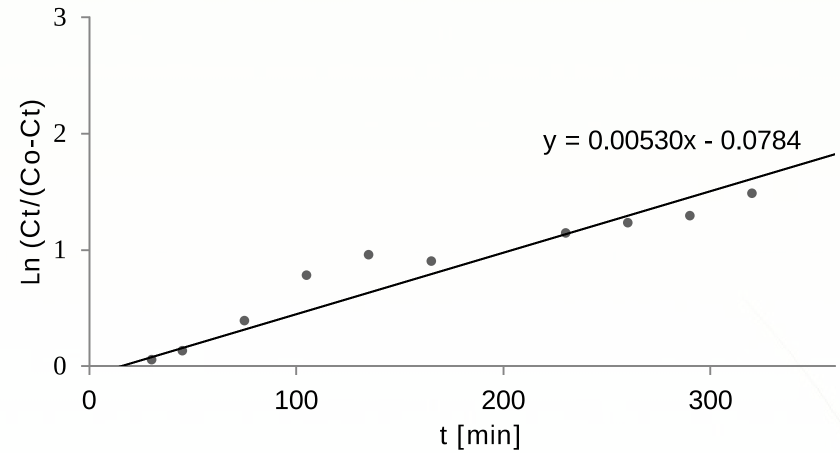

Fig. 6. Linearization of data for post-extraction residues with Mn(II), Nelson-Yoon model.

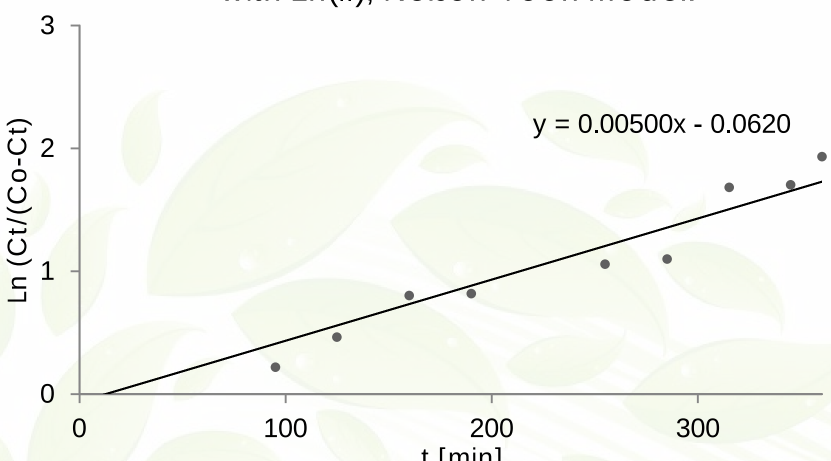

Fig. 7. Linearization of data for post-extraction residues with Cu(II), Nelson-Yoon model.

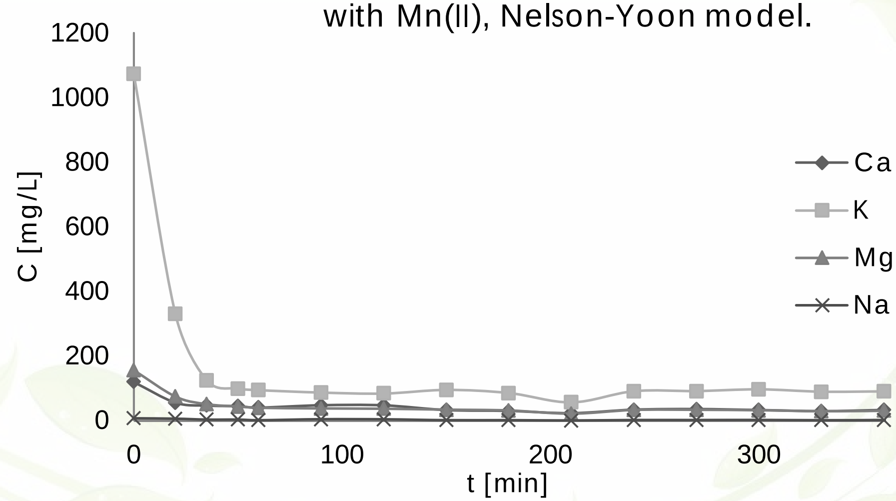

Fig 8. Release of Ca(II), K(I), Mg(II), Na(I) during the process.

Waste streams as micronutrients source - standarization

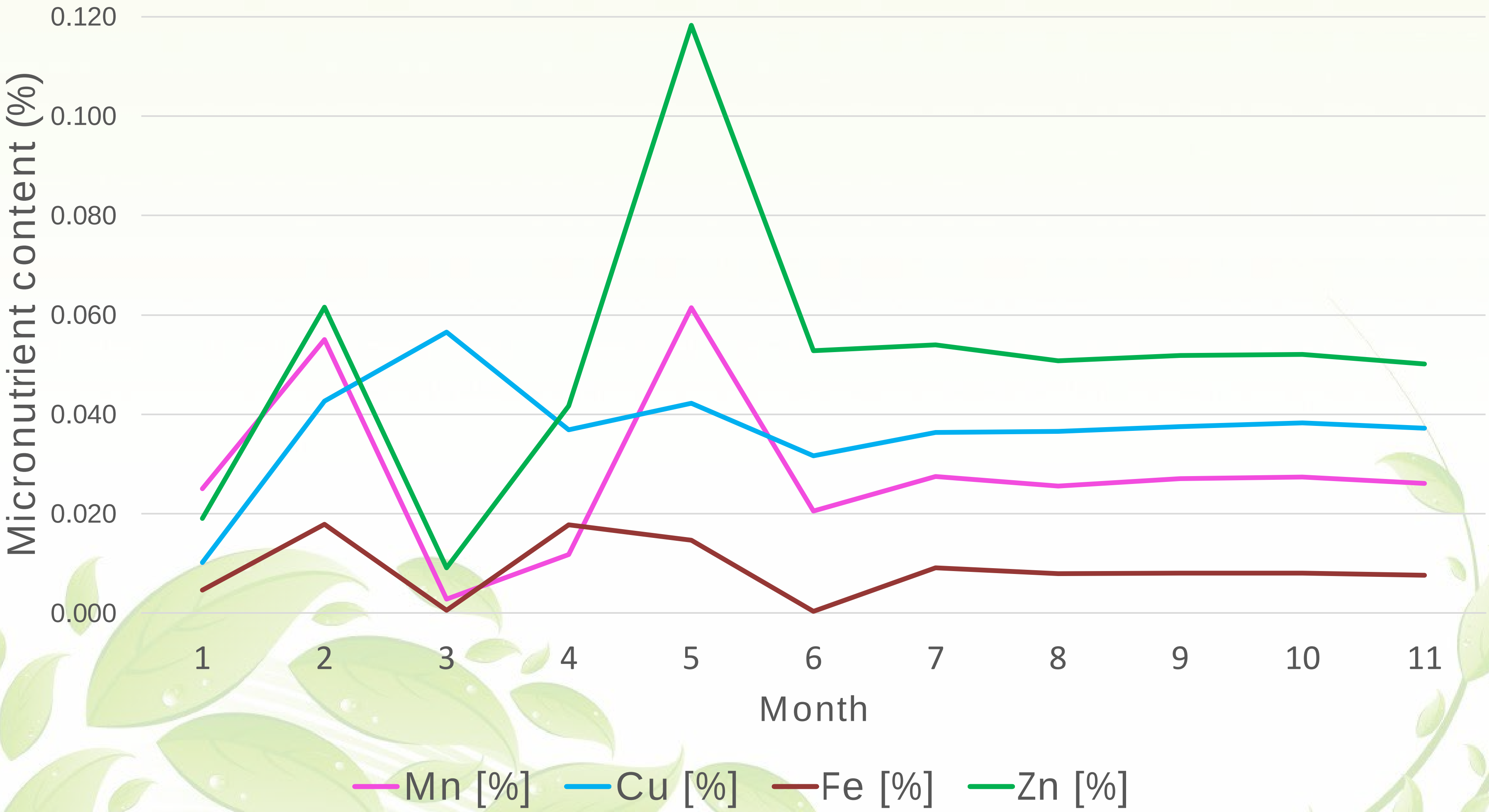

Fig. 2. Sidestream – micronutrients concentration vs. month

Perspectives and next steps

Scale up to pilot plant scale

transfer of verified bench-scale solutions

Selection of the process parameters

minor modifications of installation

Registration of the new product

pot and field trials of the final formulation on selected plant

Suitable for Organic Farming

The work was supported by National Centre for Research and Development, under the TANGO-V-C/0019/2021-00 project, entitled: "Innovative micronutrient fertilizers by biosorption for organic farming".

Thank you for your attention!

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