



New bench scale plant for biosorption

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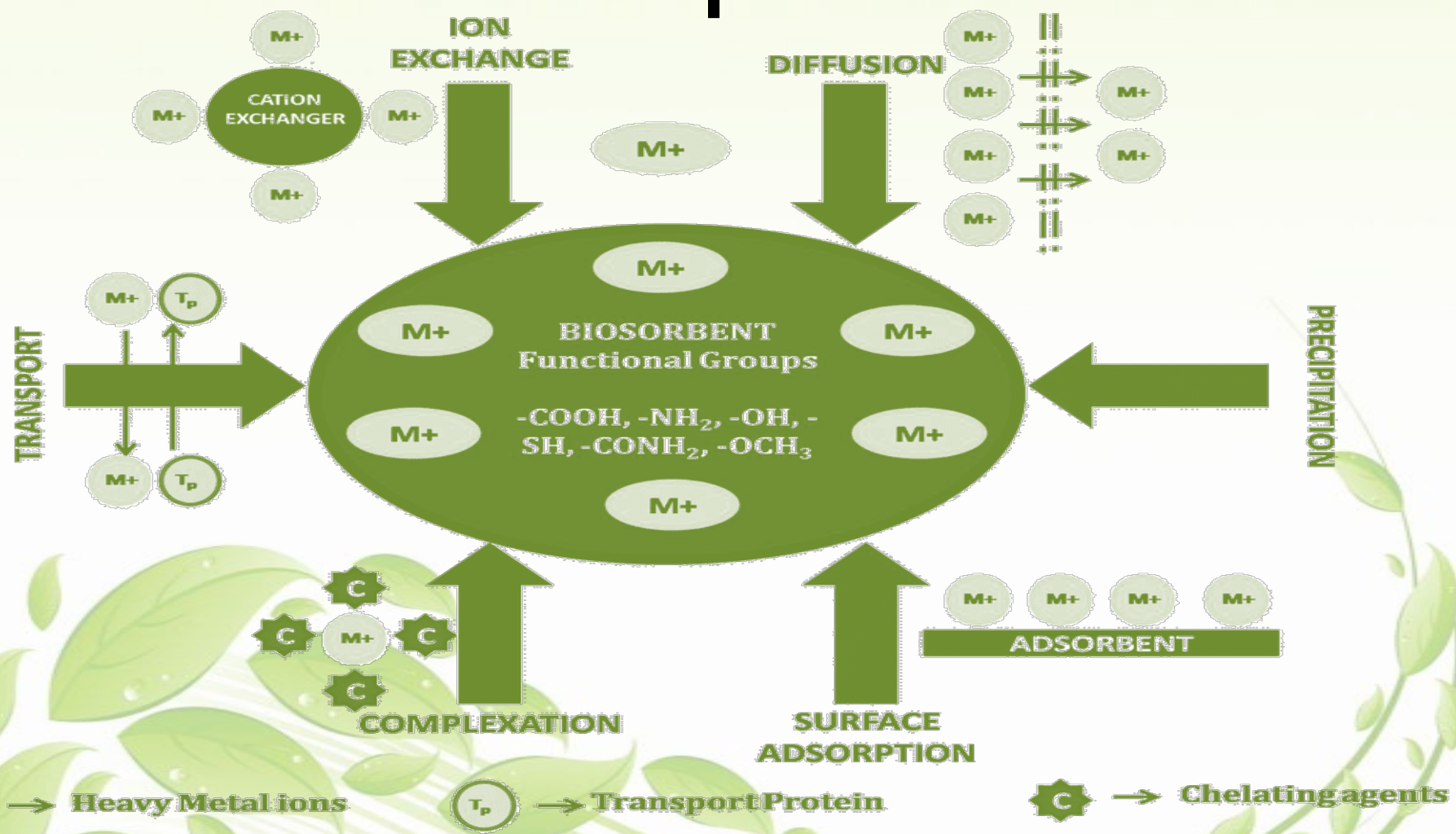
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Biosorption





Biosorption – new trends

Biosorption process

Focus on:
sorbate removal

Focus on:
biosorbent enrichment

Wastewater
treatment
(11 993 papers)

Biological feed
supplements with
micronutrients
(30 papers)

Micronutrients
fertilizer
components
(29 papers)

Potential biosorbents

BIOSORBENTS

Plants

- Leaves
- Seeds



Fungi

- Micromycetes
- Macromycetes



Algae

- Microalgae
- Macroalgae



Animal

- Bones
- Eggshells



Microbes

- Bacteria
- Archea



Waste

- Manure
- Agricultural waste





Micronutrient fertilizer additives

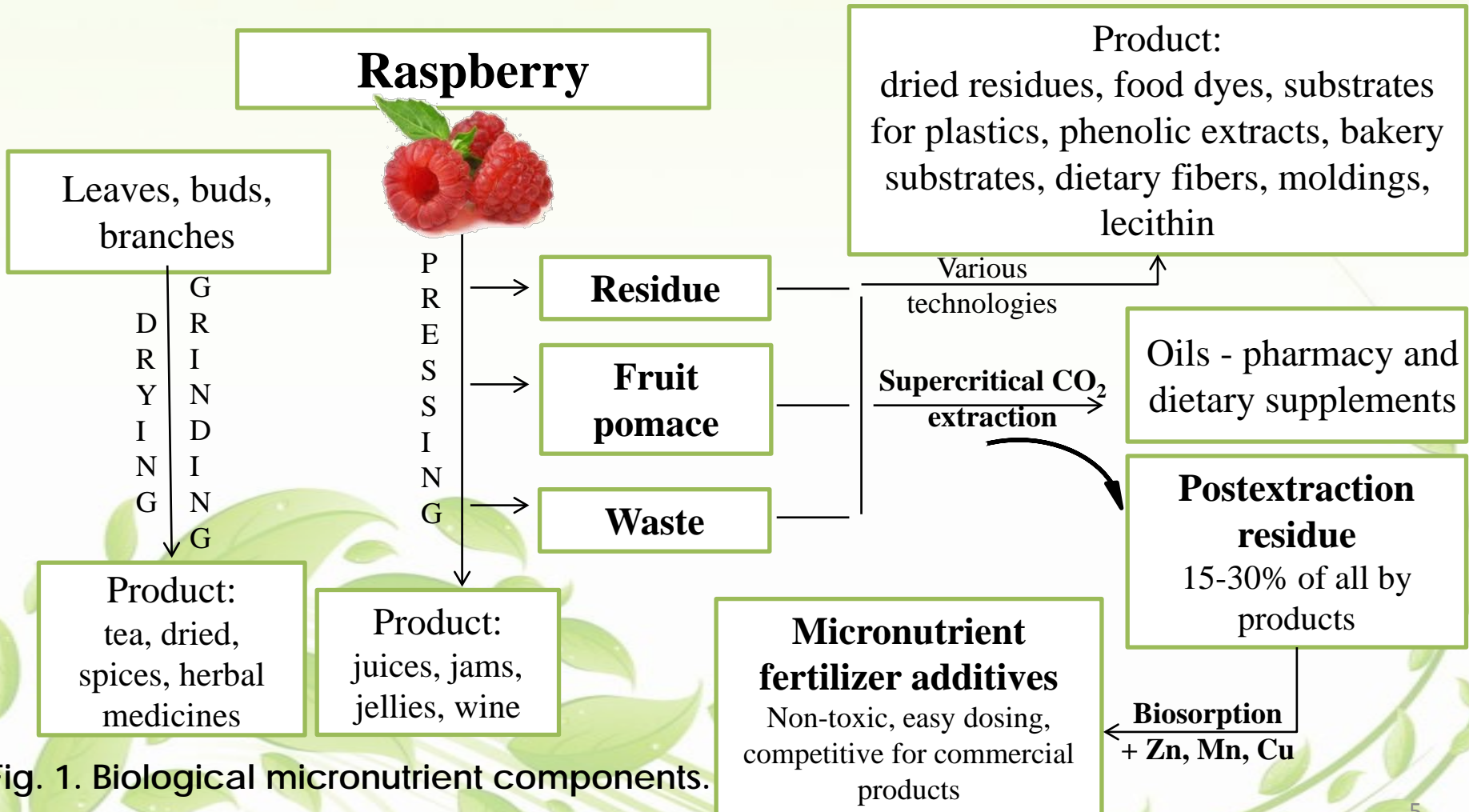
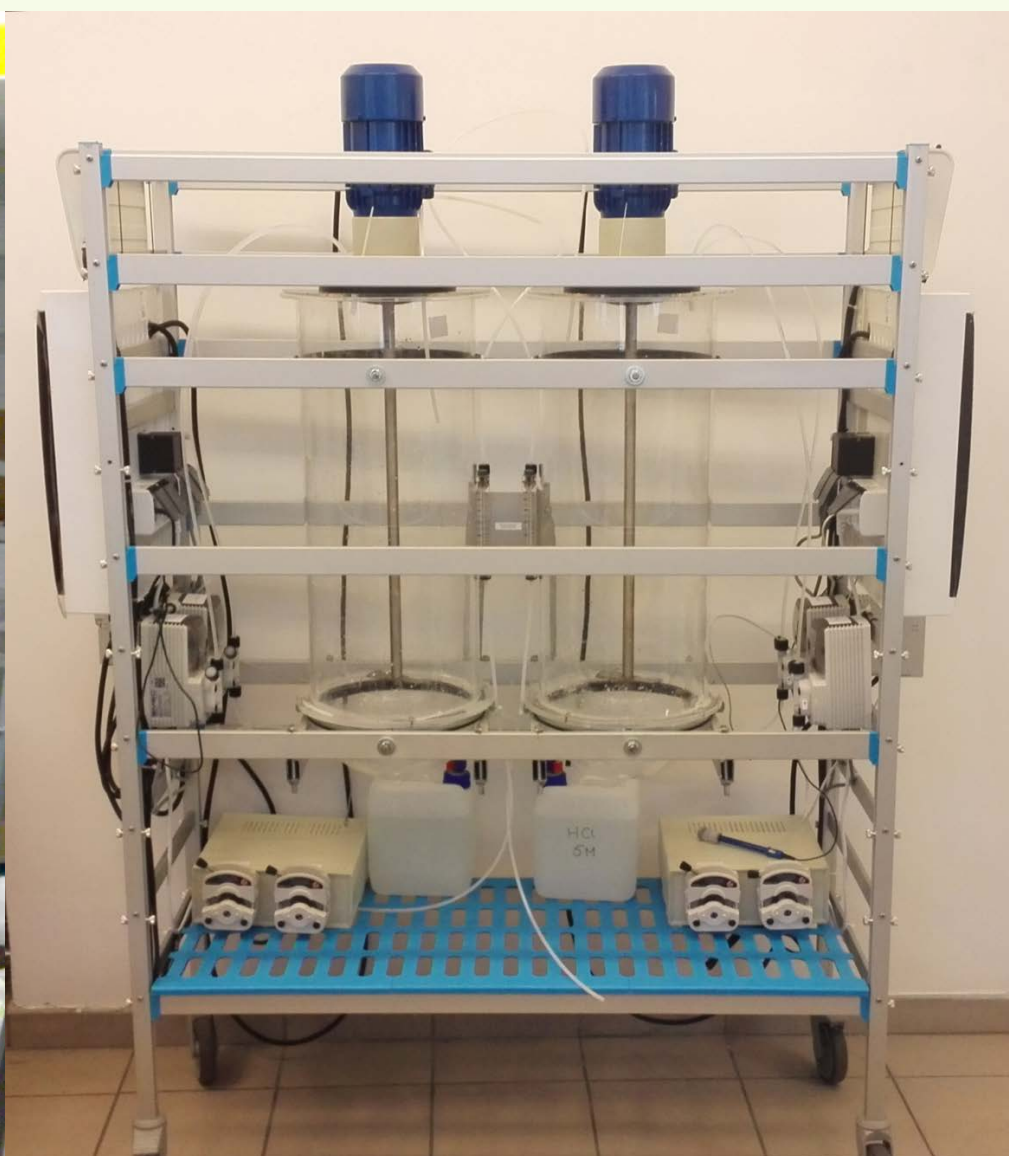
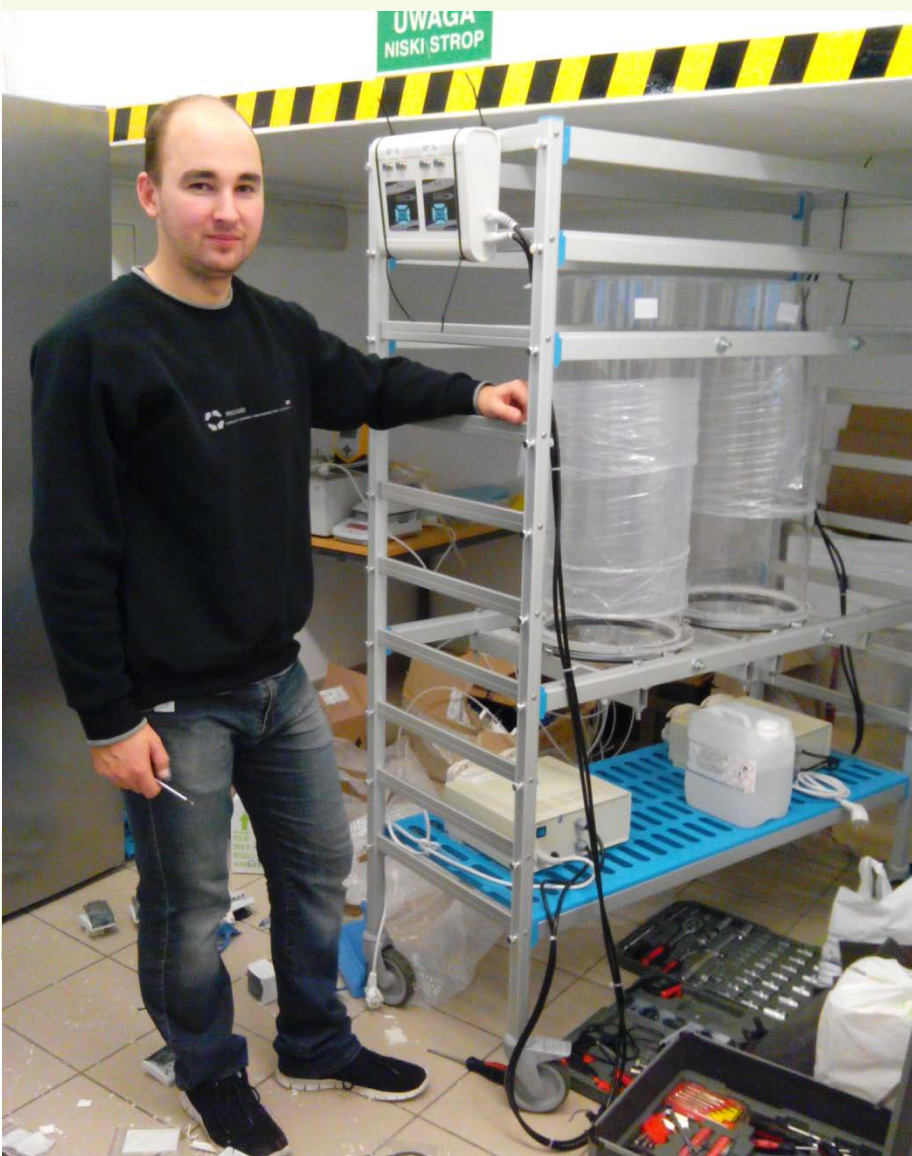


Fig. 1. Biological micronutrient components.



Installation





Installation – stirred tank mode

Fig. 3. Simplified scheme of the process in stirred tank mode – a system of two stirred tank reactors.

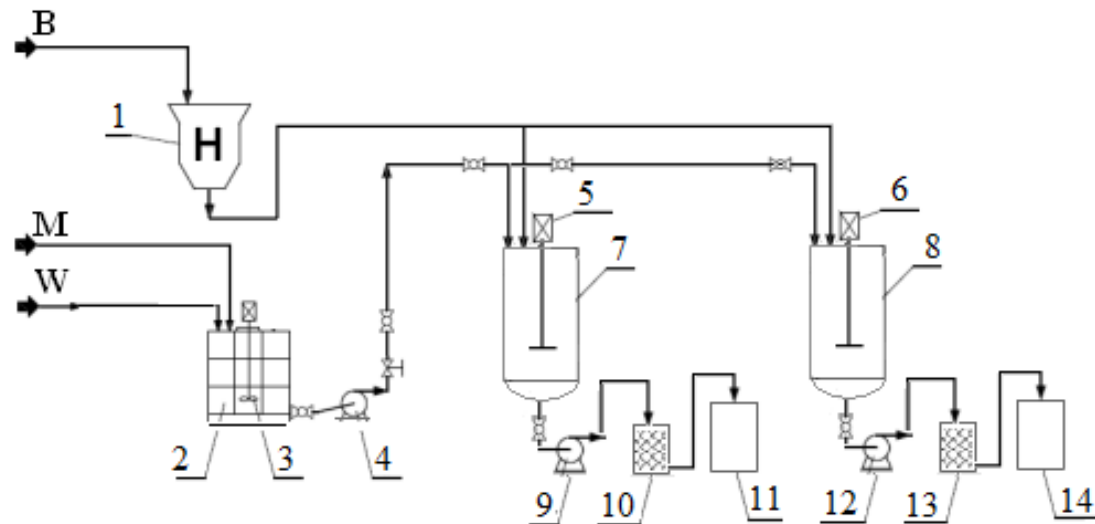
Streams:

B – Biomass,

M – Micronutrients,

W- Deionized water.

Equipment: 1 – Biomass homogenizer; 2 – Micronutrient solution tank; 3, 5, 6 – Stirrers; 4, 9, 12 – Peristaltic pumps; 7, 8 - Stirred tank reactors tank (equipped with pH regulator); 10, 13 – Biomass sedimentators; 11, 14 – Post-process tanks.



Installation – fixed bed mode

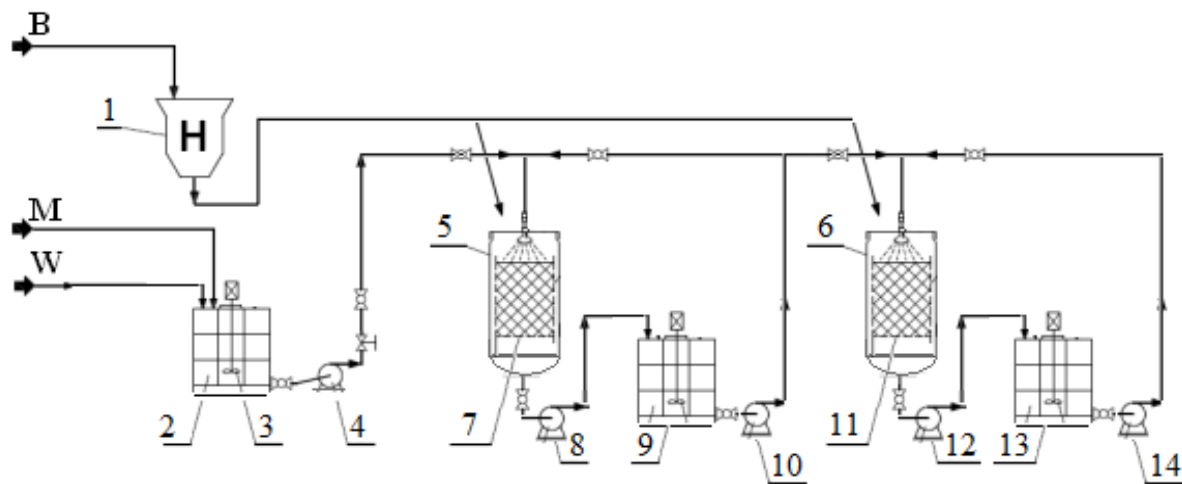


Fig. 4. Simplified scheme of the process in fixed bed mode – a system of two column reactors.

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

Equipment: 1 – Biomass homogenizer; 2 – Micronutrient solution tank; 3 – Stirrer; 4, 8, 10, 12, 14 – Peristaltic pumps; 5, 6 - Reactor tanks; 7, 11 – Sieve; 9, 13 – Recirculated solution tanks (equipped with pH regulator).



Process parameters

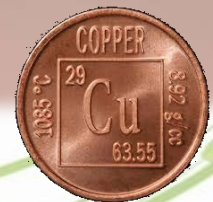
Mode	Stirred tank	Fixed bed
Sorbate	Cu(II) ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	
Sorbate concentration	300 mg/L	
Reactor volume	70L	
Solution volume	50L	200L
pH	5	
Temperature	25°C	
Material losses	10%	
Volumetric flow rate	-	1L/min
Process time	2.5h	6h
Drying	24 h, 50°C	



Final product

R

R + Cu(II)



Results



Daily productivity

- 300–400 g at stirred tank mode
- 10–16 kg at fixed bed mode



Material loses

- 10% in both cases



Estimated 100 kg production costs

- 419\$ at stirred tank mode
- 48.1\$ at fixed bed mode



Multielemental content of product

Element (mg/kg)	R - natural	R + Cu – stirred tank mode	R + Cu – fixed bed mode	
Micronutrients	Cu	<u>8.96±1.79</u>	<u>12611±2522</u> <u>EC=1407</u>	<u>12808±2562</u> <u>EC=1429</u>
	Zn	34.6±6.9	171±34	58.2±11.6
	Mn	75.9±15.2	14±3	13.3±2.660
	Fe	122±24	184±37	77±15.4
	Mo	6.54±1.31	4.41±0.88	0.247±0.049
Macronutrients	P	1551±310	797±159	1839±368
	K	2767±553	156±31 (-94.4%)	140±28 (-94.9%)
	S	1407±281	1370±274 (-2.63%)	925±185 (-34.3%)
	Ca	2502±500	585±117 (-76.6%)	188±38 (-92.5%)
	Mg	1802±360	170±34 (-90.6%)	209±42 (-88.4%)
	Na	472±94	630±126	72.8±14.6
Toxic elements	Cd (5)*	0.83±0.17	0.532±0.106	<0.03
	Ni (60)*	<0.03	<0.03	<0.03
	As (50)*	<0.3	<0.3	10.2±2.0
	Pb (140)*	<0.5	19±4	7.99±1.60
	Cr (100)*	0.117±0.023	0.616±0.123	0.655±0.131

* Act of fertilizer and fertilization, 18 June 2008, approved by Polish Ministry of Agriculture and Rural Development.



Stirred tank mode modelling

Model	Equation	Linear form	Parameters	R ²
Pseudo-1 st order	$\frac{dq_t}{dt} = k_1(q_{eq1} - q_t)$	$\ln(q_{eq} - q_t) = \ln(q_{eq1}) - k_1 \cdot t$	$k_1=0.0235$ (1/min) $q_{-eq1}=12.7$ (mg/g) $q_{ICP-OES}=12.6$ (mg/g)	0.997
Pseudo-2 nd order	$\frac{dq_t}{dt} = k_2(q_{eq2} - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_{eq2}^2} + \frac{1}{q_{eq2}} \cdot t$	$k_2=0.00426$ (g/mg·min) $q_{-eq2}=15.3$ (mg/g)	0.913

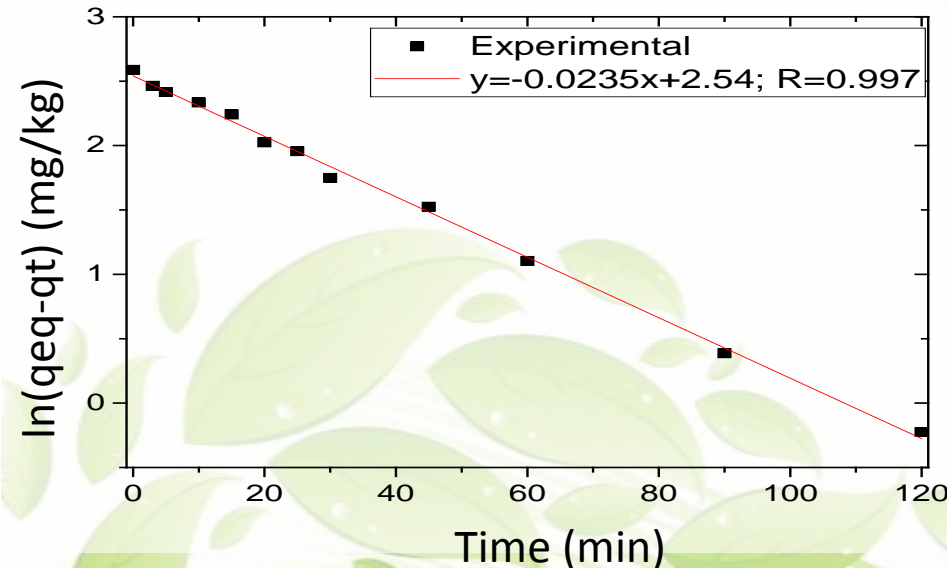


Fig.5. Pseudo-1st order model linear plot.

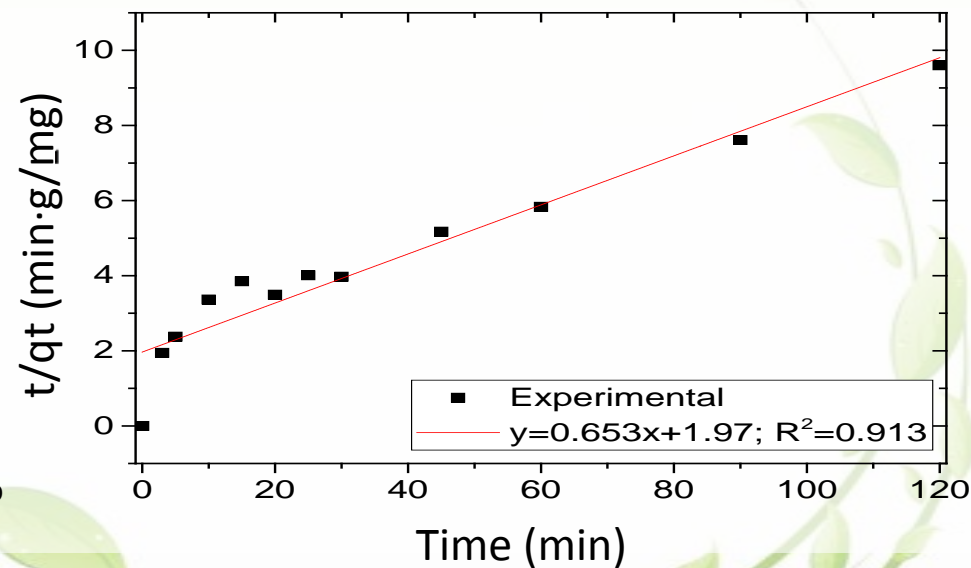


Fig. 6. Pseudo-2nd order model linear plot.



Fixed bed mode modelling

Model	Equation	Linear form	Parameters	R ²
Yoon-Nelson	$\frac{C_t}{C_0 - C_t} = \exp(k_{YN}t - \tau k_{YN})$	$\ln \frac{C_t}{C_0 - C_t} = k_{YN}t - \tau k_{YN}$	$\tau = 105$ (min) $k_{YN} = 0.0078$ (1/min)	0.996
Thomas	$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left[\left(\frac{k_{Th}q_{eq}x}{Q}\right) - k_{Th}C_0t\right]}$	$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{Th}q_{eq}x}{Q} - k_{Th}C_0t$	$k_{Th} = 0.0260$ (mL/min mg) $q_{eq} = 13.5$ (mg/g) $q_{ICP-OES} = 12.8$ (mg/g)	0.996
Walborska	$\partial \frac{\partial c_b}{\partial t} + v \frac{\partial c_b}{\partial H} + \frac{\partial q}{\partial t} = D_{ax} \frac{\partial^2 c_b}{\partial H^2}$	$\ln\left(\frac{c}{C_0}\right) = \frac{\beta_a C_0 t}{q} - \frac{\beta_a H}{v}$	$\beta_a = 0.181$ (1/min) $q = 17.5$ (mg/g)	0.935
Adams-Bohart	$\frac{C_t}{C_0} = \exp\left(k_{AB}C_0t - k_{AB}N_0 \frac{z}{U_0}\right)$	$\ln\left(\frac{C_t}{C_0}\right) = k_{AB}C_0t - k_{AB}N_0 \frac{z}{U_0}$	$N_0 = 17500$ (mg/L) $k_{AB} = 0.0103$ (mL/min mg)	0.935

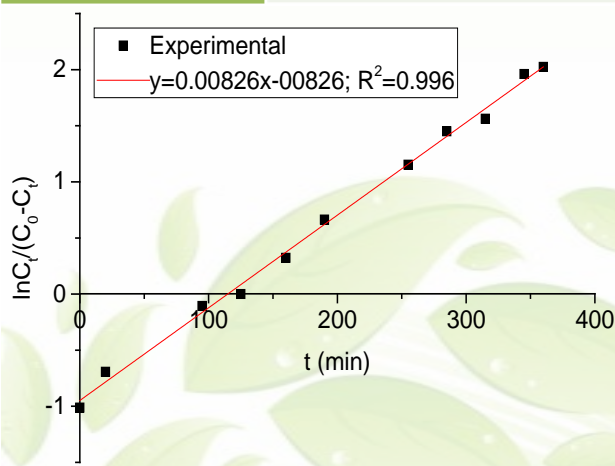


Fig. 7. Yoon-Nelson model linear plot vs. experimental data.

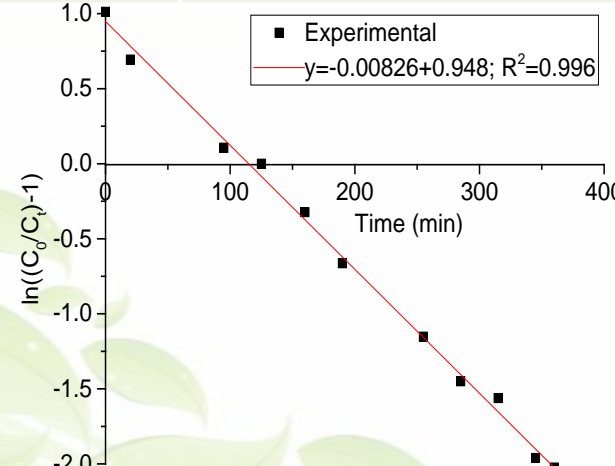


Fig. 8. Thomas model linear plot vs. experimental data.

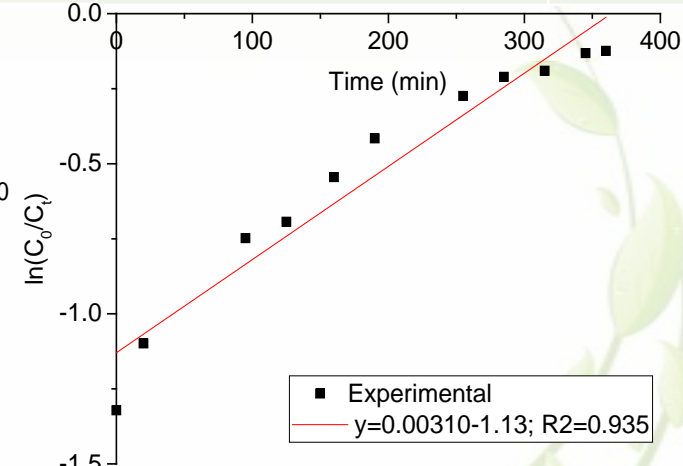


Fig. 9. Adams-Bohart, Walborska model linear plot.



Conclusions



New bench scale installation for biosorption and comparison of two possible process mode was presented with kinetics description



New eco-friendly micronutrient fertilizer additives with copper based on raspberry seeds were produced and multielemental content was determined after sample mineralization



The material losses in the process were about 10% for fixed bed and stirred tank reactors



The cost of the utilization of berries seeds to micronutrient fertilizer components in fixed bed mode was much lower (48.1 \$/100 kg) than in stirred tank mode (419 \$/100 kg)



New installation is an efficient tool in biosorption studies and enables investigation of parameter influence in a wide range



Perspectives



Selection of the process parameters
(and minor modifications of installation)



Vegetation tests of new product
(TF determination and comparison with commercial products)



Scale up to pilot plant scale
(transfer proven solutions)



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Thank you for your attention!

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