# New bench scale plant for biosorption

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**Abstract**

In the last 20 years, biosorption was developed as an efficient tool in wastewater treatment of heavy metal ions or in organic pollutants removal. The new application of this process is the production of micronutrient fertilizers. For manufacture of new biosorption-based preparations with micronutrients, it was necessary to scale up the process from laboratory to bench scale. For this reason, a new plant was designed and built.

New bench scale plant for biosorption is equipped with two independent reactors (70 L) which can operate in a stirred tank or fixed bed batch mode. Reactors may also be connected in parallel or serial mode. First trials of installation show that the daily productivity for micronutrient fertilizer components was about 300–400 g at stirred tank mode and about 10–16 kg at fixed bed mode, while in both cases material loses were relatively low (<10%).

The aim of this work is to present new bench scale plant for biosorptionthat consists an efficient installation in biosorption studies. The investigation of the effect of process parameters(in a wide range) on indicators is possible. There are many advantages as compared with smalllaboratory scale, which has been used, so far.

**Abbreviations**

$\beta a$ – Walborska kinetic coefficient of the external mass transfer (1/min),

$C_0$ – initial solution concentration (mg/L),

$c_b$ – solute concentration in the bulk solution (mmol/L),

$C_t$ – effluent solution concentration (mg/L),

$D_{ax}$ – axial diffusion coefficient ($m^2$/h),

EC – enrichment coefficient,

H – bed depth (m),

$k_1$ – the rate constant of first order sorption (1/min),

$k_2$ – the rate constant of second order sorption (1/min),

$k_{AB}$ – Adam Bohart a kinetic constant (L/mg·min),

$k_{Th}$ – Thomas model constant(mL/min·mg),

$k_{YN}$ – Yoon-Nelson rate constant (1/min),

$N_0$ – saturation concentration (mg/L),

q – biosorption capacity (mg/g),

Q – influent flow rate (mL/min),

$q_e$ – biosorption capacity (predicted) (mg/g),

$q_{eq}$ – amount of solute sorbed at equilibrium (mg/g),

$q_t$– amount of solute sorbed on the surface of the sorbent at any time t (mg/g),

τ –time required for 50% adsorbate breakthrough (min),

TF – transfer factor,

$U_0$– linear velocity of influent solution (cm/min),

v –migration rate of the solute through the fixed bed (m/min),

x – mass of adsorbent (g),

Z – bed depth of column (cm).

## 1. Introduction

Biosorption process is based on adsorption and ion exchange (mainly) where metabolically inactive biological matter is used as a biosorbent. During the process, biomass is enriched with metal ions(or molecules)which are present in aqueous solution (Chojnacka 2010). Chemical composition of biomass surface promotes binding of metal ions. Functional groups present on the surface, such as carboxyl, hydroxyl and amino groups (Zafar et al., 2015)participate in the formation of biomass-metal ion interactions and bonds. For example, biomass of berries seeds is characterized by a variety of organic compounds such as cellulose and lignin which improves affinity to metal ions binding (Putra et al., 2014). Different biosorbents are used by researchers such as: plant biomass (Chojnacka 2010), micro- (Tao et al., 2014) and macroalgae (Zhang et al., 2015), fungi (Aytaret al., 2014)and agricultural wastes(Yuvarajaet al., 2014), which have individual affinity towards different metal ions.In the last 20 years, biosorption was developed as an efficient tool in wastewater treatment of heavy metal ions (Das et al., 2008) or in organic pollutants removal (Aksu 2001). The new application of this process is the production of micronutrient fertilizers (Tuhy et al., 2014).

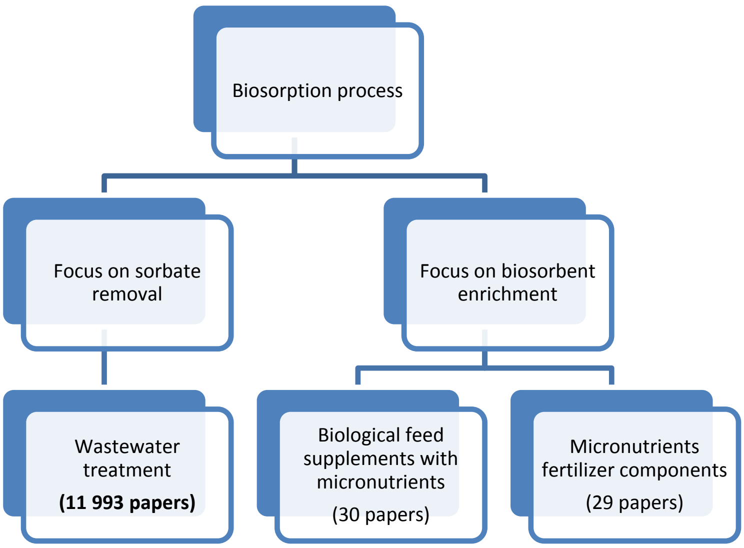


Fig.1. Biosorption trends (webofknowledge.com)in last 10 years.

Since last 10 years, the development of biosorption (Fig.1.) as a wastewater treatment process was continued. But last studies show that this process has greater potential and might be used in production of biological feed supplements and micronutrient fertilizer components.

*Wastewater Treatment*

The greater application of biosorption is the removal and retrieval of contents dissolved insewage or wastewater. In this application,pollutants such as heavy metal ions and some organic compounds may be removed(Voleskyand Holan1995, Klimenko et al., 2002, Crini 2006, Das et al., 2008).Ranaand co-workers (2014) studied the removal of metal ions from wastewater with the use of sugarcane bagasse. In other works,chestnut burs(Kim et al., 2015)and tree bark (Şen et al., 2015) as an efficient material for the purification of wastewater from heavy metal ions was proposed.

*Biological Feed Supplements with Micronutrients*

Biosorption was reported as an effective process for the production of micronutrient feed supplements (supplements for livestock).Several types of biomasses were tested –soybean (Witkowska et al., 2014), micro- (Saeid et al., 2013)and macroalgae (Michalak et al., 2011). In described experiments, the biomass was enriched with essential micronutrients in animal nutrition and used as dietary feed supplements. The biofortification of milk, meat, eggs, cheese with micronutrients was observed(Witkowska et al., 2015).

*Fertilizer Components with Micronutrients*

The production of biological fertilizer components with micronutrients is another approach towardsbiosorption.Waste biomass enriched with micronutrients essential in plants cultivation such as zinc, copper, manganese constituted an alternative to traditional micronutrient fertilizer. New formulations were found to havecomparable bioavailability of nutrients to chelate and salt based fertilizers and led to the biofortification of plant with micrnutrients (Michalak et al., 2013, Tuhy et al., 2014).

*Bisorption installations*

The small laboratory research on biosorption is carried out mainly in stirred tank (batch reactorsmainly)(Khouniet al., 2012, Singh et al., 2012), in larger scale in fixed bed reactors with specially designed shelves and chutes of the columns (column reactors) (Cheknaneet al., 2012, Rubilaret al., 2012).In simple biosorption studies, suspension of biomass is shaked in 250 mL Erlenmeyer flasks (Aksu

2001). In other studies, the experimental system, that produces a countercurrent circulation by a series of four completely mixed identical batch reactors was shown. In this small laboratory scale installation (each reactor had a total volume of 1L) the treated effluent is in contact with fresh biosorbent, thereby minimizing residual metal ions concentration in the solution (Aksu 2001).Chen and co-workers conducted studies with the use of corn stalk as a biosorbent in fix bed column (Chen et al., 2012). In the experiment,the influence of metal ions concentration, solution pH, bed depths and flow rates were examined. In other research, the removal of nickel ions in batch reactor by tomato leaf powder was described. Additionally, data were modeled with kinetic equations(Gutha et al., 2014).

Very complex installation for biosorption is BeePS - Biosorbent Pilot System (BV-SORBEX 2015).“BeePS” is a partially automated, self-standing pilot-scale. Two basically different options of BeePS were developed. The first is a contact system that is based on the use of two sorption fixed bed columns operating in a standard alternating uptake/regeneration mode. The second type is based on a design which allows continuous purification of an unqualified incoming stream.

About 85% of papers available on Web of Science database deals withbiosorption conducted inerlenmayer flask and small stirred tank reactors, the rest 15% is about biosorption in larger scale, mainlyfixed bed (column reactor).

Biosorption in industrial application makes use of mainly vertical or horizontal cylinders connected to each other, similarly as cascades. Depending on the behaviour of the bed in the column, there occurs: sorption in the movable bed or sorption in the fluidized bed. A movable bed of biosorbent is applied to make the functioning of columns more effective on an industrial scale (Michalak et al., 2013).

Besideof the process mode, the selection of appropriate conditions is crucial. Batch reactor experiments constitute a source of basic process information, continuous studies enable to find out the importance of technological parameters andscale up technology(Chojnacka et al., 2014).Also production of application batch for field trials of micronutrient fertilizers via biosorption is possible.

The aim of this work is to present a new bench scale plant for biosorption designed and built in Department of Advanced Material Technologies of Wrocław University of Technology which is an efficient tool in biosorption investigation. Examination of the process parameters in a wide range, is possible. For manufacture of new biosorption-based preparations with micronutrients, it was necessary to scale up process from laboratory to bench scale.

## 2. Material and methods

### *2.1. Biosorbent*

For the experiments, post-extraction residues after supercritical $CO_2$ extraction conducted on raspberry seeds, delivered by New Chemical Syntheses Institute (Puławy, Poland) were used. About 7 kg of biosorbent was subjected for biosorption in fixed bed and about 0.15 kg for biosorption in stirred tank.

### *2.2. Sorbate*

Cu(II) ions were delivered from inorganic salt form - $CuSO_4 \cdot 5H_2O$ (POCH, Poland) dissolved in deionized water (<10 µS/cm). The using of the tap water is not recommended because of the presence of interfering ions (especially Fe ions). Deionized water was stored in a 200L buffer tank. Initial concentration of the metal ions in aqueous solution was 300mg/L. For fixed bed mode about 150L of solution was used, for stirred tank it was 60L.

### *2.3. Bench scale plant for biosorptionprocesss*

Bench scale plant forbiosorption processes (Fig. 2) was designed and constructed in Department of Advanced Material Technologies of Wrocław University of Technology.

Fig. 2. Bench scale plant for biosorption processes

Bench scale plant for biosorption is equipped with measurement and control devices: the buttons for the switch on each device,consumption meter, pH microprocessor controller with acid and base tanks,conductivity meter,microprocessor controller of peristaltic pumps (flow-control devices), process temperature controller, stirrer speed controller, process time meter.

New self-standing bench scale plant is flexible and suitable for testing of a wide range of sorbents as well as different types of sorbate. Devices are mostly automated. Two basically different options of process modes were developed: fixed bed mode and stirred tank mode, also combination of these modes is possible. Two reactors reduce process dead time – while on first biosorption is conducted, on the second optional desorption might be simultaneously carried out.

Regulation of all key process parameters is possible – such as automatic end of process with set time or conductivity, pH control with wide range regulation (4–10), temperature monitoring and regulation (from room temperature to 70 $^{o}$C), flow rate monitoring and correction from 0 to 1 L/min (fine regulation) or from 1 to 5 L/min (coarse regulation). All parameters such as power consumption, pumps parameters, flow rate, temperature, pH and conductivity of solution are presented on control panel. Fast connectors allow for quick changing of reactor work mode.

The biosorption of Cu(II) by biological material was conducted in Bench Scale Plant for biosorption process in fixed bed and stirred tank reactor mode. All process parameters were taken directly from previous small scale experiments(Tuhy et al., 2014).

### *2.3.1. Fixed bed  mode – a system of two column reactors*

In the Figure 3,simplified scheme of the system of two column reactors was presented.

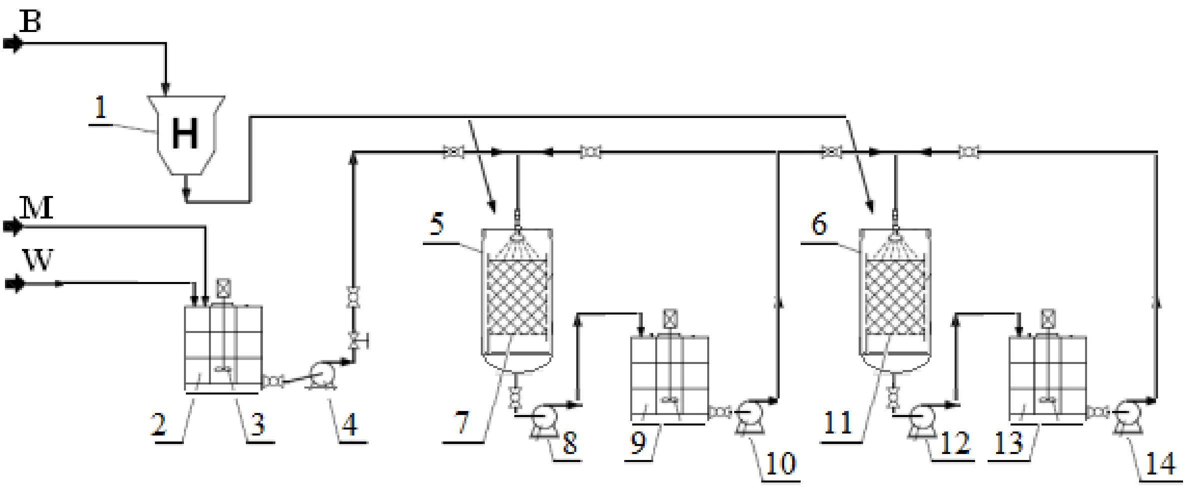


Fig. 3. Simplified scheme of the process in fixed bed mode – a system of two column reactors

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).

The tank (2) is equipped with a pH regulator (inlet pipes for feeding HCl or KOH with membrane pumps and pH controller which adjusts pH value), stirrer (3) and pump (4) which is used for pumping micronutrient solution of proper concentration and pH to reactors (5, 6), where biosorption process is conducted. Eluent from reactor is pumped with a peristaltic pumps (8,12) to a recirculated solution tank (9,13). Returned solution from recirculated solution tank is pumped with a peristaltic pumps (10,14), again to reactor. In this process, no waste streams are generated. After biosorption process, solution of macronutrients (exchanged during process with micronutrients via ion exchange) is obtained, which may be used as fertilizer for foliar application.

The process was conducted for 6 hours in 70L reactor. The concentration of Cu(II) ($CuSO_4 \cdot 5H_2O$, POCH, Poland) in the solution was about 300 mg/L. pH was regulated by pH regulator on 5. The biosorption process was conducted at 25ºC. After the batch, the final product was dried in industrial dryer (Hajnówka, Poland) at 50$^o$C for 24 hours. The content of elements in the enriched biomass was examined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP–OES) after mineralization.

### *2.3.2. Stirred tank mode – a system of two stirred tank reactors*

In the Figure 4 simplified scheme of the system of two stirred tank reactorswas presented.

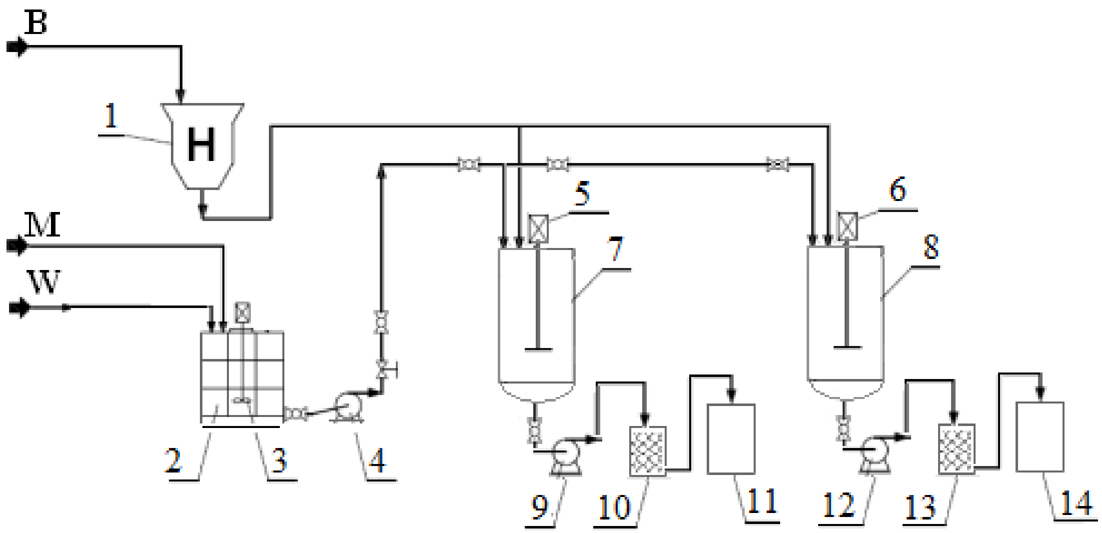


Fig.4. Simplified scheme of the process in stirred tank mode – a system of two stirred tank reactors Streams: B – Biomass, M – Micronutrients, W- Deionized water. Equipment: 1 – Biomass homogenizer; 2 – Micronutrient solution tank; 3, 5, 6 – Stirrers; 4, 9, 12 – Peristaltic pumps; 7, 8- Stirred tank reactors tank (equipped with pH regulator); 10, 13 – Biomass sedimentators; 11, 14 – Post-process tanks.

Stirred tank reactorsareconnectedto a reservoir of micronutrients (2).Micronutrient solutionis pumpedfrom the reservoirvia a peristaltic pump (4)to thereactor (7 or 8). Reactorsare equipped with: stirrer (5,6),whichmay be controlled byinverter,a heaterwhich maintains theprocess temperatureat a constant level, the pH controllerconnected to thepumpsto whichthe acid andbase solution can be supplied. In result, biomass is suspended in the reactorswith micronutrient ions at controlledpH andtemperature.After theprocess, the reactors are emptiedvia a peristaltic pump (9,12)through quicksedimentationfilter to post-process tank (11,14). Similarly like in fixed bed mode,no waste is produced. In this study, the process was conducted for 2.5 hours. The concentration of Cu(II) ($CuSO_4 \cdot 5H_2O$, POCH, Poland) in the solution was about 300 mg/L. pH was adjusted by pH regulator on

5. The biosorption process was conducted at 25ºC. Most of biomass was recovered (about 90%). The content of elements in the enriched biomass was examined by ICP–OES after mineralization.

Bench scale plant installation and production of new fertilizers has been reported for patent protection: “Bench scale system for biosorption of micronutrients” and “Method for producing micronutrient fertilizer components and micronutrient fertilizer components” pat. No P.407673.

***2.4. Multielemental analysis***

Each material (0.5 g) was suspended in nitric acid – 69% m/m (5 ml), spectrally pure (Suprapur, Merck, USA) in teflon bombs. Prepared samples were digested in microwave system Milestone Start D (USA). Parameters of the mineralization process were matched to assure complete digestion of samples. Samples were diluted 10 times with ultrapure water (Millipore Simplicity) to perform multielemental ICP-OES analysis.

Determination of the metal content in natural, metal-loaded biomass and biosorption capacity was examined using optical emission spectrometry (ICP-OES, Varian-Vista MPX, Australia). Samples were supplied with ultrasonic nebulizer CETAC U5000AT+. The analyses were carried out in Laboratory Accredited by Polish Centre of Accreditation (PCA, No. AB696) according to PN-EN ISO/IEC 17025:2005. Quality assurance of the test results was achieved by using Combined Quality Control Standard from ULTRA SCIENTIFIC, USA. All samples were analyzed in three repeats (results of analyses were arithmetic mean, the relative standard deviation was <5%).

***2.5. Modelling***

The biosorption of Cu(II) ions by the biomass of post-extraction residues of raspberry seeds in bench scale plant was conducted in stirred tank and fixed bed mode. For stirred tank, pseudo-1$^{st}$, and pseudo-2$^{nd}$ order kinetic model was used(Ho and  McKay 1998, Ho et al., 1999). For fixed bed mode four the most commonly used kinetic models were investigated – Thomas(Saadi et al., 2013), Yoon-Nelson(Yoon and Nelson 1984), Adams-Bohart(Trgo et al., 2011)and Walborska (Lodeiro et al., 2006).

## 3. Results and discussion

### *3.1. Productivity*

First trials of installation show that the daily productivity for micronutrient fertilizer components was about 300–400 g at stirred tank mode and about 10–16 kg at fixed bed mode, while in both cases material loses were relatively low (<10%).

### *3.2. Multielemental analysis*

Biosorption capacity($q$) of raspberry seeds for Cu(II) ions was evaluated as about 13 mg/g. Multielemental composition of prepared materials was presented in Table 1.

Table 1. Multielemental composition of natural and Cu(II) loaded biomass of raspberry postextraction residues (R).

| Element (mg/kg) | | R - natural | R + Cu – stirred tank mode | R + Cu – fixed bed mode |
|---|---|---|---|---|
| Micronutrients | Cu | 8.96±1.79 | 12611±2522 | 12808±2562 |
| | 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 | 140±28 |
| | S | 1407±281 | 1370±274 | 925±185 |
| | Ca | 2502±500 | 585±117 | 188±38 |
| | Mg | 1802±360 | 170±34 | 209±42 |
| | Na | 472±94 | 630±126 | 72.8±14.6 |
| Otherelements | Al | 57.8±11.6 | 44.2±8.8 | 25.8±5.2 |
| | Se | 7.4±1.5 | 1.14±0.23 | 45.5±9.1 |
| | Si | 130±26 | 170±34 | 90.2±18.0 |
| | V | 1.5±0.3 | 0.894±0.179 | 3.45±0.69 |
| Toxicelemenrs | Cd | 0.83±0.17 | 0.532±0.106 | <0.03 |
| | Ni | <0.03 | <0.03 | <0.03 |
| | As | <0.3 | <0.3 | 10.2±2.0 |
| | Pb | <0.5 | 19±4 | 7.99±1.60 |
| | Cr | 0.117±0.023 | 0.616±0.123 | 0.655±0.131 |

There are large differences between natural and Cu(II)enriched samples. Enrichment Coefficient (EC) (Michalak et al, 2013)for stirred tank mode was 1407, andfor fixed bed was 1429. It was shown that post-extraction residues of raspberry seeds are characterized by good biosorption capacity for Cu(II) ions. Copper ions are essential in plants cultivation – play an important role in photosynthetic electron transport in chloroplasts(Droppa et al., 1987).Raspberry seeds were shown as a source of other micro- and macronutrients important for plants, i.e. phosphorus, potassium, calcium, sulfur, iron etc. Content of toxic elements was below the limit approved by Polish Ministry of Agriculture and Rural Development (Act of fertilizer and fertilization, 2008).

During biosorption, metabolically inactive organic matter is enriched due to adsorption and ion exchange (Chojnacka 2010)with potassium, calcium and magnesium. Basing upon data from Table 1, the content of K, Mg, Ca, Al, S in the enriched with Cu(II) ions biomass ofpost-extraction residues of raspberry seeds decreased by 94.4% , 90.6%, 76.6%, 23.5%, 2.63% for raspberry seeds enriched in stirred tankand 94.9% , 88.4%, 92.5%, 55.4%, 34.3% for raspberry seeds enriched in fixed bed reactor mode, respectively.Enriched biomass is characterized by higher bioavailability of fertilizer micronutrients. Metal ions are releasedin controlled way according to equilibrium dependence and provide lower leaching to groundwater (Tuhy et al., 2014).

### *3.3. Modeling*

#### *3.3.1. Stirred tank mode*

Figures 5 and 6 show a linear plot of pseudo-1$^{st}$and 2$^{nd}$order kinetic models for the biosorption of Cu(II) ions onto post-extraction residues of raspberry seeds. In Table 2 results from model calculations were presented.

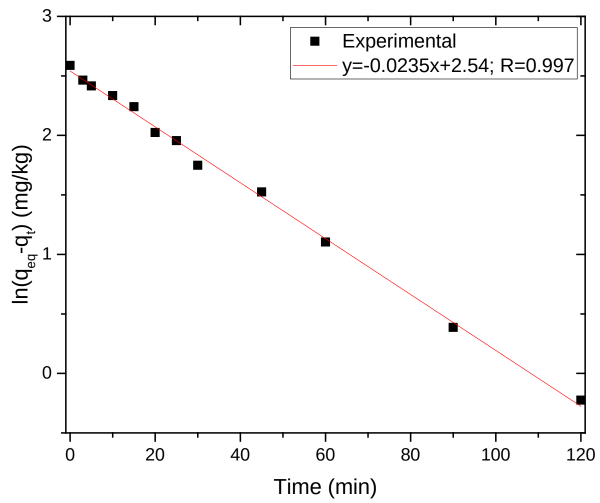


Fig.5. Pseudo-1$^{st}$ order assuming model linear plot.

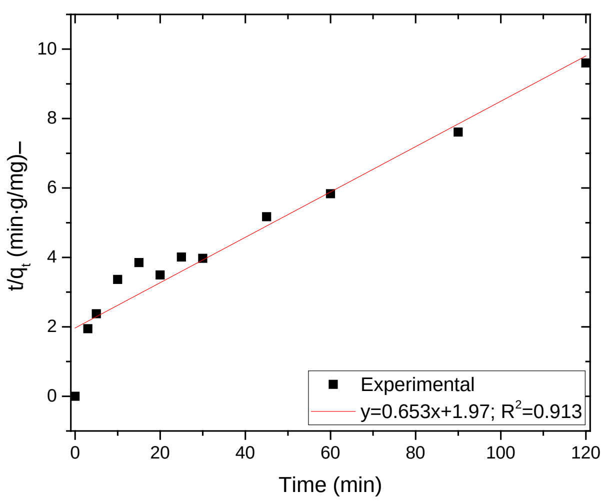


Fig. 6. Pseudo-2$^{nd}$ order assuming model.

Table 2. Model calculations for pseudo-1st and 2nd order kinetics

| ***Model*** | ***Equation*** | ***Linear form*** | ***Parameters*** | ***$R^2$*** |
|---|---|---|---|---|
| Pseudo-1st order(Ho and McKay 1998) | $\frac{dq_t}{dt} = k_1(q_{eq\,1} - q_t)$ | $\ln(q_{eq} - q_t) = \ln(q_{eq\,1}) - k_1 \cdot t$ | $k_1$=0.0235 (1/min) $q_{eq1}$=12.7 (mg/g) | 0.997 |
| Pseudo-2nd order(Ho et al., 1999) | $\frac{dq_t}{dt} = k_2(q_{eq\,2} - q_t)^2$ | $\frac{t}{q_t} = \frac{1}{k_2 \cdot {q_{eq\,2}}^2} + \frac{1}{q_{eq\,2}} \cdot t$ | $k_2$=0.00426 (1/min) $q_{eq2}$=15.3 (mg/g) | 0.913 |

$q_{eq}$ calculated from pseudo-1st and 2nd orderbiosorption model is similar - 12.7 and 15.3 mg/g, respectively. In the experiment about 12.6 mg/g was achieved. The difference between theoretical and experimental data isacceptable.

Both models well describe kinetics of Cu(II) ions biosorptionbypost-extraction residues of raspberry seeds. The pseudo-2nd order equation is based on the sorption capacity on the solid phase and stays in agreement with a chemisorption mechanism being the rate controlling step (Sağ and Yücel 2002).In this study,pseudo-1storder kinetic model provided better fitting to experimental data, similarly to experiments conducted with Cu(II) ions andcoirpith carbon(Namasivayam and Kadirvelu1997), fly ash (Panday et al., 1985)and peanut hull carbon(Periasamy and Namasivayam1996).

#### *3.2.2. Fixed bed mode*

Plots of the linearform of the Yoon-Nelson, Thomas, Adams-Bohart and Walborska models for the biosorption of Cu(II) bypost-extraction residues of raspberry seed are presented in Figures 7-9. In Table 3, results from model fitting are presented.

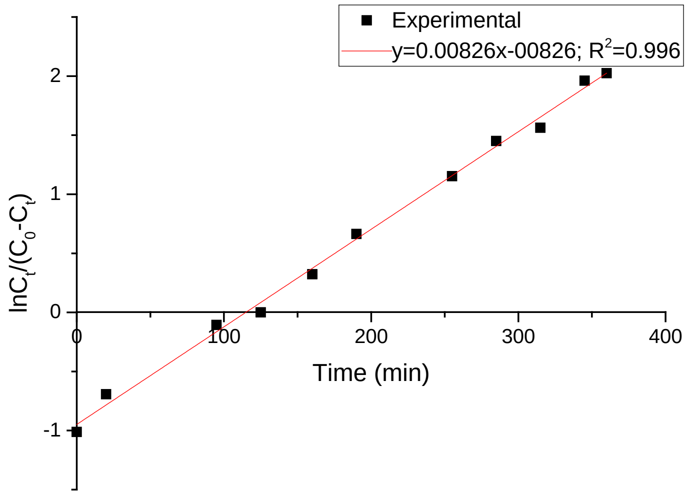


Fig. 7. Yoon-Nelson model linear plot vs. experimental data.

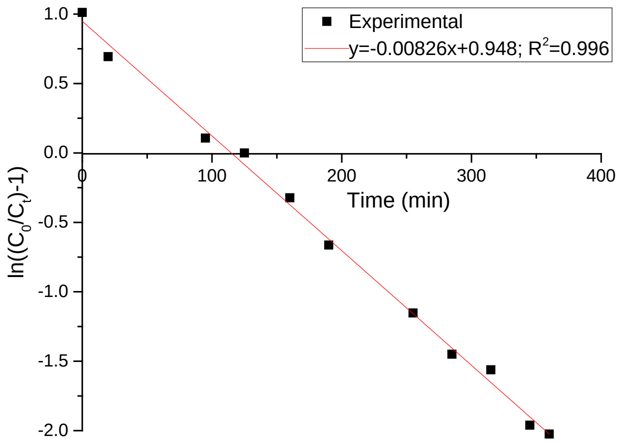


Fig. 8. Thomas model linear plot vs. experimental data.

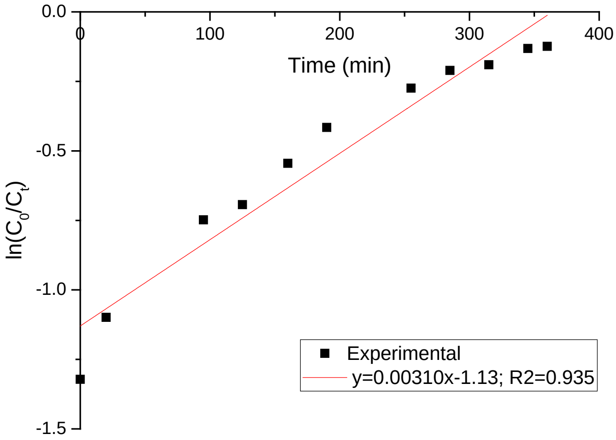


Fig. 9. Adams-Bohard and Walborskamodel linear plot vs. experimental data.

Table 3. Comparison of kinetic models for fixed bed reactor mode.

| ***Model*** | ***Equation*** | ***Linear form*** | ***Parameters*** | ***R²*** |
|---|---|---|---|---|
| Yoon-Nelson(Yoon and Nelson 1984) | $\frac{C_t}{C_0 - C_t} = \exp(k_{YN}t - \tau k_{YN})$ | $ln\frac{C_t}{C_0 - C_t} = k_{YN}t - \tau k_{YN}$ | τ=105 (min)<br>$k_{YN}$= 0.0078 (1/min) | 0.996 |
| Thomas (Saadi et al., 2013) | $\frac{C_t}{C_0} = \frac{1}{1 + \exp\left[\left(\frac{k_{Th}q_e x}{Q}\right) - k_{Th}C_0 t\right]}$ | $ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{Th}q_e x}{Q} - k_{Th}C_0 t$ | $k_{Th}$= 0.0260 (mL/min mg)<br>$q_e$= 13.5 (mg/g) | 0.996 |
| Walborska (Lodeiro et al., 2006) | $\partial\frac{\partial c_b}{\partial t} + v\frac{\partial c_b}{\partial H} + \frac{\partial q}{\partial t} = D_{ax}\frac{\partial^2 c_b}{\partial H^2}$ | $ln\left(\frac{c}{c_0}\right) = \frac{\beta_a c_0 t}{q} - \frac{\beta_a H}{v}$ | $\beta_a$= 0.181 (1/min)<br>q= 17.5 (mg/g) | 0.935 |
| Adams-Bohart(Trgo et al., 2011) | $\frac{C_t}{C_0} = \exp\left(k_{AB}C_0 t - k_{AB}N_0\frac{z}{U_0}\right)$ | $ln\left(\frac{C_t}{C_0}\right) = k_{AB}C_0 - k_{AB}N_0\frac{z}{U_0}$ | $N_0$ = 17500 (mg/L)<br>$k_{AB}$ = 0.0103 (mL/min mg) | 0.935 |

Yoon-Nelson and Thomas model showed good fitting to experimental data (among examined models - Figure 7 and 8). The linear dependence of the Yoon Nelson model corresponds to the same mechanism as the Thomas model. Linear function parameters (a and b) have opposite values and there is no difference in determination coefficients ($R^2$=0.996). Thomas model assumes non-axial dispersion and is often used in modeling fixed bed reactor performance (Saadi et al., 2013). For Walborska and Adam Bohart model fittingobtained determination coefficients were lower than for Yoon-Nelson and Thomas models -$R^2$=0.935. Walborska model bases on equation of mass transfer for the diffusion mechanism (Lodeiro et al., 2006, Trgo et al., 2011). The Adams-Bohart model is the last discussed adsorption model similar to Walborska model. This model assumes that rate of adsorption is proportional to the concentration of the sorbate and the residual capacity of the adsorbent (Lodeiro et al., 2006).

The experimental data determined by sample mineralization and ICP-OES ($q$=12.8 mg/kg) differed from the theoretical data calculated using Thomas model ($q$=13.5 mg/kg).Difference islittle higher than in stirred tank and calculated with pseudo-1st order kinetic model.

Yoon-Nelson model is a simplified model. Lower number of process parameters may be determined, but is more universal and it could be fitted to the description of broad spectrum biomasses in bench scale plant installation.Using Yoon-Nelson and Thomas model it is possible to determinecrucial process parameters for the description of conducted biosorption(Yoon and Nelson 1984, Saadi et al., 2013, Lodeiro et al., 2006, Trgo et al., 2011).

### *3.3. Preliminary economical analysis*

Preliminary economical analysis of the production of biological micronutrient components basing on the biomass of post-extraction residues of raspberry seeds via biosorption in bench scale installation was carried out.

#### *3.3.1. Material costs*

Some companies treat this type of material as a waste and hence it is often offered for free.

#### *3.3.2. Production costs*

The estimated production costs of the enrichment of berries seeds with micronutrient ions via biosorption in bench-scale reactor in stirred tank and column reactors were presented in Table 4.

Table 4. Production costs of the enrichment of berries seeds with micronutrient ions in bench scale reactors (for 100 kg).

| Factor | Inorganic salts | Water consumption | Biomass | Electric energy Process | Electric energy Drying | Total cost |
|---|---|---|---|---|---|---|
| Column reactor | | | | | | |
| Amount | ca. 10,4 kg | ca. 2.6 $m^3$ | ca. 110 kg | ca. 6 kWh | ca. 200 kWh | |
| Cost [$] | ca. 14.5 | ca. 3.0 | - | ca. 1.0 | ca. 29.6 | ca. 48.1 |
| Stirred-tank reactor | | | | | | |
| Amount | ca. 160 kg | ca. 40 $m^3$ | ca. 110 kg | ca. 715 kWh | ca. 200 kWh | |
| Cost [$] | ca. 223 | ca. 46 | - | ca. 120 | ca. 29.6 | ca. 419 |

The material losses in the process were about 10% for fixed bed and stirred tank reactors. The cost of the utilisation of berries seeds to micronutrient fertilizer components in column mode was much lower (48.1 $/100 kg) than in stirred reactor (419 $/100 kg). It was mainly due to higher productivity of the process. In both cases, a large part of production costs was connected with drying of the biomass (29.6 $) and constituted over 50% of total costs for fixed bed reactor mode. One of the methods to reduce costs is to replace tray dryer i.e. with more efficient fluid bed dryer which (according to different soures) allows to reduce drying costs by about 40%.

#### *3.3.3. Depreciation of equipment*

The cost of the bench-scale installation was estimated as 15000 $. The annual depreciation of the installation was assumed at 14%.

### *3.3.4. Total costs*

The productivity of the pilot-plant was 10-16 kg and 300-400 g of micronutrient fertilizer component per day in fixed bed reactor and stirred reactor, respectively. The total cost of the production of new preparation was estimated as 0.72$ (4.43 $ - for stirred reactor). For total cost calculations, labour cost was not taken into account. For stirred-tank mode it is possible to reduce production cost by the use of higher content of biomass suspended in micronutrient solution. In both cases it could be reduced by about 40% with the use of alternative drying method (i.e. the application of fluid drying). As it was observed, production of micronutrient fertilizer supplements in column reactor constitutes much more efficient and economically atractive process. According to the fact that proposed application of berries seeds enriched with micronutrient ions via biosorption is micronutrient fertilization and the dosage of new preparation is about 0.1-0.5% when mixed with NPK fertilizer, the price seems to be reasonable.

## 4. Conclusion

In the present work, the new bench scale plant for biosorption was described. First trials on installation were performed with production of micronutrient fertilizer biocomponents, based on post-extraction residues of raspberry seeds,with Cu(II) in stirred tank and fixed bed reactor mode. It is anew and innovative way of micronutrient fertilizers production. Kinetics description of both processes was performed. It was shown, that the installation is an efficient tool in biosorption studies and enables investigation of parameter influence in a wide range. New self-standing bench scale plant is flexible and suitable for testing of a wide range of parameters, sorbents as well as different types of sorbate. Devices are mostly automated and regulation of all key process parameters is possible– flow regulation, automatic end of process with set time or conductivity, pH control with wide range regulation.Parameters such as power consumption and pumps parameters are presented on control panel, separately for each reactor.Two basically different options of process modes were development: fixed bed mode and stirred tank mode, also combination of these modes are possible - reactors may act as stirred tank and fixed bed reactors in serial or parallel mode. Two reactors reduced process dead time – while on first biosorption is conducted on the second desorption might be simultaneously carried out.

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**References**

Act of fertilizer and fertilization, (2008)Regulation implementing some provisions of the *Fertilizers and Fertilizing Act*. Date of text: *18 June 2008,* Poland

Aksu, Z. (2001) Equilibrium and kinetic modelling of cadmium (II) biosorption by C. vulgaris in a batch system: effect of temperature. *Separation and Purification Technology*, *21*(3), 285-294

Aytar, P., Gedikli, S., Buruk, Y.,Çabuk, A., &Burnak, N. (2014) Lead and nickel biosorption with a fungal biomass isolated from metal mine drainage: Box–Behnken experimental design. *International Journal of Environmental Science and Technology*, *11*(6), 1631-1640

BV SORBEX, (2015) http://www.bvsorbex.net/sxProcess.pdf (access 15.05.2015)

Cheknane, B., Baudu, M., Basly, J. P., Bouras, O., &Zermane, F. (2012) Modeling of basic green 4 dynamic sorption onto granular organo–inorgano pillared clays (GOICs) in column reactor. *Chemical Engineering Journal*, *209,* 7-12

Chen, S., Yue, Q., Gao, B., Li, Q., Xu, X., & Fu, K. (2012) Adsorption of hexavalent chromium from aqueous solution by modified corn stalk: a fixed-bed column study. *Bioresource Technology*, *113,* 114-120

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

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

Crini, G. (2006) Non-conventional low-cost adsorbents for dye removal: a review. *Bioresource Technology*, *97*(9), 1061-1085

Das, N., Vimala, R., &Karthika, P. (2008) Biosorption of heavy metals—an overview. *Indian Journal of Biotechnology*, *7*(2), 159-169

Droppa, M., Masojidek, J., Rózsa, Z., Wolak, A., Horváth, L., Farkas, T., &Horváth, G. (1987) Characteristics of Cu deficiency-induced inhibition of photosynthetic electron transport in spinach chloroplasts. *Biochimica et BiophysicaActa (BBA)-Bioenergetics*, *891*(1), 75-84

Gutha, Y., Munagapati, V.S., Naushad, M., &Abburi, K. (2014) Removal of Ni (II) from aqueous solution by Lycopersicumesculentum (Tomato) leaf powder as a low-cost biosorbent. *Desalination and Water Treatment*, (ahead-of-print), 1-9

Ho, Y. S., & McKay, G. (1998) Kinetic models for the sorption of dye from aqueous solution by wood. *Process Safety and Environmental Protection*, *76*(2), 183-191.

Ho, Y. S., & McKay, G. (1999) Pseudo-second order model for sorption processes. *Process Biochemistry*, *34*(5), 451-465

Khouni, I., Marrot, B., & Amar, R. B. (2012) Treatment of reconstituted textile wastewater containing a reactive dye in an aerobic sequencing batch reactor using a novel bacterial consortium. *Separation and Purification Technology*, *87*, 110-119

Kim, N., Park, M., & Park, D. (2015) A new efficient forest biowaste as biosorbent for removal of cationic heavy metals. *Bioresource Technology*, *175*, 629-632

Klimenko, N. A., Marutovsky, R. M., Pidlisnyuk, V. V., Nevinnaya, L. V., Smolin, S. K., Kohlmann, J., &Radeke, K. H. (2002) Biosorption Processes for Natural and Wastewater Treatment–Part 1: Literature Review. *Engineering in Life Sciences*, *2*(10), 317-324

Lodeiro, P., Herrero, R., & de Vicente, M.E.S. (2007) Thermodynamic and kinetic aspects on the biosorption of cadmium by low cost materials: a review. *EnvironmentalChemistry*, *3*(6), 400-418

Michalak, I., Chojnacka, K., Dobrzański, Z., Górecki, H., Zielińska, A., Korczyński, M., &Opaliński, S. (2011)Effect of macroalgae enriched with microelements on egg quality parameters and mineral content of eggs, eggshell, blood, feathers and droppings. *Journal of Animal Physiology and Animal Nutrition*, *95*(3), 374-387

Michalak, I., Chojnacka, K., &Witek-Krowiak, A. (2013) State of the art for the biosorption process—a review. *Applied Biochemistry and Biotechnology*, *170*(6), 1389-1416

Namasivayam, C.,&Kadirvelu, K. (1997) Agricultural solid wastes for the removal of heavy metals: adsorption of Cu (II) by coirpith carbon. *Chemosphere*, *34*(2), 377-399

Panday, K. K., Prasad, G., & Singh, V. N. (1985) Copper (II) removal from aqueous solutions by fly ash. *Water Research*, *19*(7), 869-873

Periasamy, K., &Namasivayam, C. (1996) Removal of copper (II) by adsorption onto peanut hull carbon from water and copper plating industry wastewater. *Chemosphere*, *32*(4), 769-789

Putra, W. P., Kamari, A., Yusoff, S. N. M., Ishak, C. F., Mohamed, A., Hashim, N., & Isa, I. M. (2014). Biosorption of Cu (II), Pb (II) and Zn (II) Ions from Aqueous Solutions Using Selected Waste Materials: Adsorption and Characterisation Studies. *Journal of Encapsulation and Adsorption Sciences*, 4, 25-35

Rana, K., Shah, M., &Limbachiya, N. (2014) Adsorption Of Copper Cu (2+) Metal Ion From Waste Water Using Sulphuric Acid Treated Sugarcane Bagasse as Adsorbent.*International Journal of Advanced Engineering Research and Science*, *1*(1), 55-59

Rubilar, O., Tortella, G. R., Cuevas, R., Cea, M., Rodríguez-Couto, S., &Diez, M. C. (2012) Adsorptive removal of pentachlorophenol by Anthracophyllum discolor in a fixed-bed column reactor. *Water, Air, & Soil Pollution*, *223*(5), 2463-2472

Saadi, Z., Saadi, R., &Fazaeli, R. (2013) Fixed-bed adsorption dynamics of Pb (II) adsorption from aqueous solution using nanostructured γ-alumina. *Journal of Nanostructure in Chemistry*, *3*(1), 48

Saeid, A., Chojnacka, K., Korczyński, M., Korniewicz, D., &Dobrzański, Z. (2013) Biomass of *Spirulina maxima* enriched by biosorption process as a new feed supplement for swine. *Journal of Applied Phycology*, *25*(2), 667-675

Sağ, Y., &Aktay, Y. (2002) Kinetic studies on sorption of Cr (VI) and Cu (II) ions by chitin, chitosan and Rhizopusarrhizus. *Biochemical Engineering Journal*, *12*(2), 143-153

Şen, A., Pereira, H., Olivella, M. A., &Villaescusa, I. (2015) Heavy metals removal in aqueous environments using bark as a biosorbent. *International Journal of Environmental Science and Technology*, *12*(1), 391-404

Singh, A., Kumar, D., & Gaur, J. P. (2012) Continuous metal removal from solution and industrial effluents using Spirogyra biomass-packed column reactor. *Water Research*, *46*(3), 779-788

Tao, X., Wu, R., Xia, Y., Huang, H., Chai, W., Feng, T., & Zhang, W. (2014)Biotemplated fabrication of Sn@C anode materials based on the unique metal biosorption behavior of microalgae. *ACS Applied Materials & Interfaces*, *6*(5), 3696-3702

Trgo, M., Medvidovic, N. V., &Peric, J. (2011) Application of mathematical empirical models to dynamic removal of lead on natural zeolite clinoptilolite in a fixed bed column. *Indian Journal of Chemical Technology*, *18*(2), 123-131

Tuhy, Ł., Samoraj, M., Michalak, I., & Chojnacka, K. (2014) The application of biosorption for production of micronutrient fertilizers based on waste biomass. *Applied Biochemistry and Biotechnology*, *174*(4), 1376-1392

Witkowska, Z., Chojnacka, K., Korczyński, M., Świniarska, M., Saeid, A., Opaliński, S., &Dobrzański, Z. (2014)Soybean meal enriched with microelements by biosorption–A new biological feed supplement for laying hens. Part I. Performance and egg traits. *Food Chemistry*, *151*, 86-92

Witkowska, Z., Michalak, I., Korczyński, M., Szołtysik, M., Świniarska, M., Dobrzański, Z., & Chojnacka, K. (2015) Biofortification of milk and cheese with microelements by dietary feed bio-preparations. *Journal of Food Science and Technology*, 1-9

Volesky, B., &Holan, Z.R. (1995) Biosorption of heavy metals. *Biotechnology progress*, *11*(3), 235-250

Yoon, Y.H., & Nelson, J.H. (1984) Application of gas adsorption kinetics I. A theoretical model for respirator cartridge service life. *The American Industrial Hygiene Association Journal*, *45*(8), 509-516

Yuvaraja, G., Krishnaiah, N., Subbaiah, M.V., &Krishnaiah, A. (2014) Biosorption of Pb (II) from aqueous solution by Solanummelongena leaf powder as a low-cost biosorbent prepared from agricultural waste. *Colloids and Surfaces B: Biointerfaces*, *114*, 75-81

Zafar, M. N., Aslam, I., Nadeem, R., Munir, S., Rana, U. A., & Khan, S. U. D. (2015) Characterization of chemically modified biosorbents from rice bran for biosorption of Ni (II). *Journal of the Taiwan Institute of Chemical Engineers*, *46*, 82-88

Zhang, D., Ran, Y., Cao, X., Mao, J., Cui, J., & Schmidt-Rohr, K. (2015)Biosorption of nonylphenol by pure algae, field-collected planktons and their fractions. *Environmental Pollution*, *198*, 61-69