Valorization of post-extraction biomass residues as carriers of bioavailable micronutrients for plants and livestock

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Abstract:
Purpose: The purpose of the work is to check the possibility of using waste post-extraction biomass residues as carriers of micronutrients for fertilizing and nutritional purposes.
Methods: The waste biomass underwent the biosorption process, the degree of enrichment and the bioavailability of the prepared micronutrient fertilizers and feed additives were determined.
Results: Post-extraction residues, rich in functional groups, have the ability to bind ions of micronutrients. This is related with the property of the biomass to concentrate cations on the surface, due to the presence of anionic functional groups. Such micronutrients provided on biological carrier are easily bioavailable to plants and animals.
Conclusions: Waste biomass can be successfully valorised to feed additives and fertilizers enriched with micronutrients, following the trend of a waste-free economy.

Keywords: biosorption, microelements, fertilizers, feed additives

1. Introduction

Biosorption is a natural capability of biological matter to create reversible bonds with anions and cations on its surface. Biosorption makes use of biomass that is not metabolically active. The process takes place in a way similar to classic sorption. Ion binding may occur in accordance with the physical sorption mechanism, ion exchange or complexation/chelating due to the presence of numerous functional groups on the surface. The most frequently used biosorbents include three groups: microorganisms (bacteria, algae, fungi) and materials of plant or animal origin. Since the method uses industrial (foodstuffs or agriculture) wastes, as well as ubiquitous raw materials that occur in the local environment, the resource is cheap. Additionally, bio-based sorbents are characterized by high sorption capacity [1].

Most biosorption studies are related to the removal of toxic ions or compounds from aqueous solutions [2]. In this field, biosorption has not been implemented yet in the industrial practice, despite the fact that biomass is very effective for concentration of cations. The potential of biomass in its capacity of a sorbent material seems not to be fully exploited; hence it would be valuable to consider other applications for this process. A new alternative for the use of biosorption is the production of value-added products – micronutrient carriers (i.e. feed additives, functional food, fertilizers) for nutritionally significant elements, i.e. Cu^{2+}, Zn^{2+}, and Mn^{2+}

Micronutrients are essential components that must be delivered to living organisms. Their deficiencies are manifested by growth retardation, disorders and diseases. Supplementation of micronutrients takes place mainly in the form of dietary supplements and fertilizers. The main source of microelements in this case are mineral salts and chelates. Biomass having functional groups can also be a carrier of microelements. The enriched biomass constitutes a source of micronutrients for living organisms; the biosorbent developed in this way is nontoxic, has the properties of controlled ion release and good bioavailability of nutrients [3].

Bioavailability can be measured using *in vitro* and *in vivo* tests. In the case of availability to plants, extraction tests (degree of release to the simulating soil solution) and a test for direct uptake of micronutrients by plants. Both parameters could be correlated by transfer factor - determining the degree of concentration of micronutrients in the plant in relation to their content in soil. Bioavailability in animals can be determined by analysing the content of microelements in tissues or animal products (eggs, milk, etc.) in comparison to the control sample [4].

Post-extraction biomass can be a source of functional groups (i.e. carboxyl) which act as chelator, by binding selected microelement ions. The utilization of waste biomass allows the use of sorption potential of functional groups for the production of new materials with desirable properties [5]. Valorization of post-extraction residues is in line with the circular economy concept, minimizes waste generation and enables the recovery of materials for other purposes (Fig. 1.).

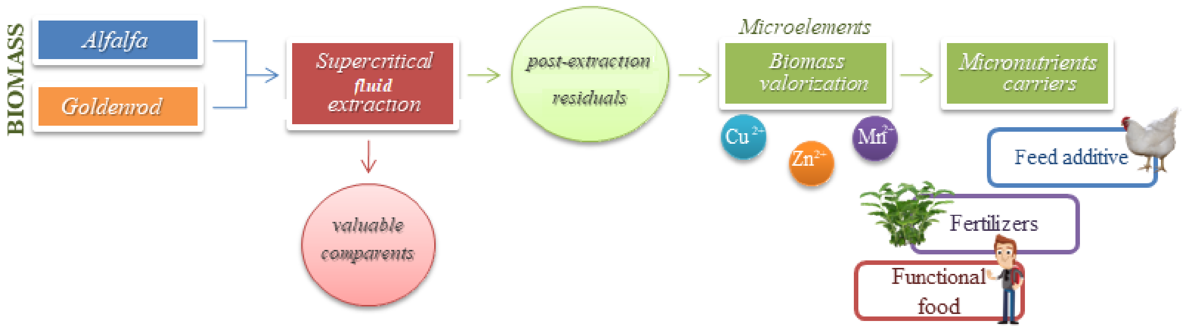

Fig. 1. Valorization of waste biomass as micronutrient carriers

2. Micronutrients carriers – fertilizers

The 21st century economy is heading towards waste-free production. Presented natural materials after supercritical extraction can be valuable products, as biosorbents, feed additives or eco-friendly fertilizers. The growing number of population in the world increases the intensity of agriculture. It results in impoverishment of soils with microelements [6]. Current methods of fertilization are ineffective and create serious environmental difficulties associated with groundwater pollution. This problem requires an innovative approach. The use of residues after the extraction process is a very interesting alternative to commonly used metal sorbents as micronutrient carriers which are are highly available to plants. Functional groups present on the surface of the biomass (carboxyl, hydroxyl and amino groups) favor the binding of metal ions to the biosorbent.

Most of the biosorption work focuses on the removal of heavy metal ions from wastewater. Gamez et al. (2003) [7] presented in their work the possibility of using raw alfalfa as a biomass for accumulating Au(III) ions. Studies related to the sorption of metal ions, such as Pb (II), Cr (III), Zn (II), Ni (II) and Cd (II) were carried out. About 80% metal recovery from the aqueous solution was shown. In this case, the most important element of such a process is wastewater treatment.

The production of biomass-based fertilizers is a new approach to the biosorption process. The use of waste biomass after extraction as carrier of microelements (zinc, copper, manganese ions) is an alternative to traditional chelated fertilizers or technical salts. Chelates are characterized by very high bioavailability, but are expensive. Technical salts are cheap, but microcrystals quickly dissolve in water and are readily released [8]. The general scheme for the production of fertilizers based on post-extraction residues is shown in Fig. 2.

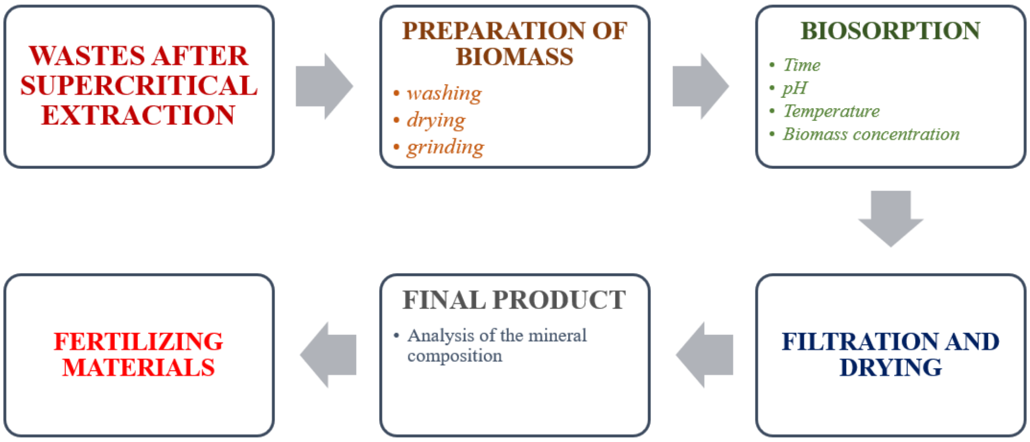

Fig. 2. *The general scheme for the production of fertilizers based on biomass – post-extraction residues*

Samoraj et al. (2017) [5] in their work presented the possibility of using alfalfa and goldenrod after supercritical extraction with carbon dioxide as sorbents of micronutrients. Enrichment of biomass with micronutrient ions of Cu^{2+}, Zn^{2+} and Mn^{2+} was carried out. The sorption capacity of post-extracted materials increased by 54-1700 times compared to raw biomass. In another work, Samoraj et al. (2012) [10] used blackcurrant seeds after the supercritical extraction as a carrier of micronutrients. The enrichment of biomass with Cu^{2+} ions in a fixed bed is presented. The sorption capacity determined by the Walborska model was approx. *17 mg g*$^{-1}$.

Tuhy et al. (2014) [8] also presented in their work fertilizers based on biomass enriched in the biosorption process. Peat, seaweed and bark as well as residues after supercritical extraction of seaweeds were used as the biomass for enrichment. Studies related to the biosorption of the ions were conducted. Germination tests were carried out on *Lepidium sativum*. The results were compared with plants fertilized with traditional fertilizers, inorganic salts. Plants fertilized with enriched biomass showed higher bioavailability of microelements and higher mass compared to the control group.

The presented examples open perspectives for future applications of enriched biomass as carriers of micronutrients. Waste management after supercritical extraction is the part of the circular economy trend through the use of enriched spent biomass directly as fertilizers.

3. Feed additives – towards food biofortification

Due to rising consumers demands, food producers must overcome problems of not only composition, but also bioavailability of their product. In the case of animal production, feed additives are used to achieve expected fortification level. Microelements have essential impact on animal breeding processes and their absence reduces welfare status of inbreeded species [11]. Currently the most common way of microelements supplementation in animals breeding is using inorganic salts or metal oxides [12]. Unfortunately, this form is characterized by low bioavailability of microelements from mineral forms, especially Cu and Zn [13].

To substitute mineral forms of microelements, other sources of nutrients were considered. Biomass naturally contains microelements, but in too low levels to be considered as their proper source. Biosorption process is useful in evaluation of new biomass feed additives. On the other hand organic form of microelements has better bioavailability rate compared to based inorganic types, due to lack of tendency to complex with phytic compounds in the feed [14]. Biomass enrichment by biosorption can be a new trend in feed supplementation and their effects on trace element transfer into animals tissue were acknowledged by several application experiments.

Biomass residues from extraction of essential oils can be valorised via biosorption method. *Spirulina maxima* [15] has good biosorption capabilities [16] due to the presence of functional groups on the surface, such as carboxyl, hydroxyl or amino groups. Feed additives based on *Spirulina* matrix enriched with Cu^{2+} were added to the pig diet [17]. Absorption rate of ions was 30% higher, as compared to the control group (based on inorganic salt) and no negative effects on production factors were detected. *Enteromorpha prolifera* and *Cladophora sp*. were biofortified with several ions (Cu^{2+} | Zn^{2+} | Mn^{2+} | Co^{2+} | Cr^{3+}) and added to laying hens diet as a source of microelements (Michalak et al. 2011). Experiments resulted in higher microelement transfer into eggs content in groups with enriched macroalgae as well as yolk color was improved, compared to the control.

Soybean meal is a waste from oil extraction process, commonly used as livestock feed due to high protein content. In addition, it has a good sorption capacity (43.1 mg/g), so it is an excellent carrier of microelements for the production of feed additives with Cu, Zn, Cr and Fe ions [19]. Obtained feed additive was added to laying hens feed (Cu(II) 0.5 g/kg feed, Fe(II) 2.8 g/kg feed, Zn(II) 4.8 g/kg feed and Cr(III) 0.1 g/kg feed) to ensure microelements transfer factor of eggs. In summary, biofortification effect was achieved, especially in albumen phase. Previous work of this scientific team indicated [20] that biofortified soya feed additives (enriched with Cu^{2+} | Zn^{2+} | Fe^{2+} | and Mn^{2+}) were suitable to substitute mineral salts in goats breeding. In analyzed milk microelements level was higher compared to the control (Cu^{2+}-8.2 %, Mn^{2+}-29.2 %, Zn^{2+}-14.6 %).

Dry yeast are commonly used in laying hens breeding process as feed additives. To check their potential as microelement carriers, experiment with immobilized Zn^{2+} and Se^{2+} ions were performed [21]. Results of *Saccharomyces cerevisiae* enriched with microelements groups had significant improvement in bioavailability compared to the inorganic feed additives (61.1% more compared to the sodium selenite and 35.4% to the and zinc oxide). Dry yeasts are waste from brewing processes and their potential value as feed additive can be greatly improved via biosorption or bioaccumulation method. *Candida utilis* biomass has also capacity to bind Mg^{2+} ions [22].

Moreover, there is plenty of other plant biomass witch high biosorption capacity (Table 1), which could be used as potential carriers of microelements as a replacement for mineral feed additives.

Table.1 Comparison of maximal ions uptake of various biomasses

Biomass	Ion	Maximum metal uptake [$mg \cdot g^{-1}$]
Sugar beet pulp [23]	Cu^{2+} Zn^{2+}	12.39* 9.73*
Eichhornia crassipies [24]	Cu^{2+}	0.323
Irvingia gabonensis [25]	Cu^{2+}	227.27
Portulaca oleracea [26]	Cu^{2+}	85.47
Xanthoria parietina [27]	Zn^{2+}	33.78
Tree leaves [28]	Cu^{2+} Zn^{2+}	31.77* 22.88*
Corncob [29]	Mn^{2+}	6.54
Oil palm fractions [30]	Fe^{3+}	369.32* (for bark)
Sunflower hulls [31]	Cu^{2+}	57.14
Blackcurrant seed [10]	Cu^{2+} Zn^{2+} Mn^{2+}	13.09 6.48 5.88
Moringa oleifera [32]	Cu^{2+}	13.1

*calculated for experiment with best results

4. Conclusions

Post-extraction residues are promising micronutrient carriers that can become fertilizers or feed additives. A high degree of enrichment of the biomass allows to concentrate on the surface of the material a substantial amount of micronutrients which can be released to the soil or to the digestive system of animals. The next step should be research on plants and animal tests related to the bioavailability of microelements from such materials.

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6. References

[1] I. Michalak, A. Witek-Krowiak, K. Chojnacka, and A. Bhatnagar, “Advances in biosorption of microelements – the starting point for the production of new agrochemicals,” *Rev. Inorg. Chem.*, vol. 35, no. 3, 2015.

[2] K. Chojnacka, “Biosorption of Cr 3 + , Cd 2 + and Cu 2 + ions by blue – green algae Spirulina sp .: kinetics , equilibrium and the mechanism of the process,” vol. 59, pp. 75–84, 2005.

[3] Ł. Tuhy, M. Samoraj, Z. Witkowska, and K. Chojnacka, “Biofortification of maize with micronutrients by Spirulina,” *Open Chem.*, vol. 13, no. 1, pp. 1119–1126, 2015.

[4] L. Tuhy, M. Samoraj, and K. Chojnacka, “Evaluation of nutrients bioavailability from fertilizers in in vivo tests,” *Interdiscip. J. Eng. Sci.*, vol. 1, no. 1, pp. 10–13, 2013.

[5] M. Samoraj, Ł. Tuhy, and K. Chojnacka, “Valorization of Biomass into Micronutrient Fertilizers,” *Waste and Biomass Valorization*, vol. 0, no. 0, pp. 1–7, 2017.

[6] D. Davidson and F. X. Gu, “Materials for Sustained and Controlled Release of Nutrients and Molecules To Support Plant Growth,” 2012.

[7] G. Gamez, J. L. Gardea-Torresdey, K. J. Tiemann, J. Parsons, K. Dokken, and M. J. Yacaman, “Recovery of gold(III) from multi-elemental solutions by alfalfa biomass,” *Adv. Environ. Res.*, vol. 7, no. 2, pp. 563–571, 2003.

[8] Ł. Tuhy, M. Samoraj, I. Michalak, and K. Chojnacka, “The Application of Biosorption for Production of Micronutrient Fertilizers Based on Waste Biomass,” *Appl. Biochem. Biotechnol.*, vol. 174, no. 4, pp. 1376–1392, 2014.

[9] M. Samoraj, Ł. Tuhy, and K. Chojnacka, “New bench scale plant for biosorption.”

[10] M. Samoraj, Ł. Tuhy, P. Rusek, E. Rój, and K. Chojnacka, “Pilot plant conversion of blackcurrant seeds into new micronutrient fertilizer biocomponents via biosorption,” *BioResources*, vol. 11, no. 1, pp. 400–413, 2016.

[11] G. F. W. Haenlein and M. Anke, “Mineral and trace element research in goats: A review,” *Small Rumin. Res.*, vol. 95, no. 1, pp. 2–19, 2011.

[12] S. Sobhanirad and A. A. Naserian, “Effects of high dietary zinc concentration and zinc sources on hematology and biochemistry of blood serum in Holstein dairy cows,” *Anim. Feed Sci. Technol.*, vol. 177, no. 3–4, pp. 242–246, 2012.

[13] A. Zielińska, K. Chojnacka, and M. Simonič, “Sustainable production process of biological mineral feed additives,” *Am. J. Appl. Sci.*, vol. 6, no. 6, pp. 1093–1105, 2009.

[14] I. Michalak, K. Chojnacka, and P. Glavič, “The Possibilities of the Application of Feed Additives from Macroalgae in Sustainable Mineral Animal Feeding Izabela Michalak , 1 Katarzyna Chojnacka and 2 Peter Glavič Institute of Inorganic Technology and Mineral Fertilizers , Wrocław University of Tech,” vol. 6, no. 8, pp. 1458–1466, 2009.

[15] P. Spolaore, C. Joannis-Cassan, E. Duran, and A. Isambert, “Commercial applications of microalgae,” *J. Biosci. Bioeng.*, vol. 101, no. 2, pp. 87–96, 2006.

[16] K. Chojnacka, A. Chojnacki, and H. Górecka, “Trace element removal by Spirulina sp. from copper smelter and refinery effluents,” *Hydrometallurgy*, vol. 73, no. 1–2, pp. 147–153, 2004.

[17] A. Saeid, K. Chojnacka, M. Korczyński, D. Korniewicz, and Z. Dobrzański, “Biomass of Spirulina maxima enriched by biosorption process as a new feed supplement for swine,” *J. Appl. Phycol.*, vol. 25, no. 2, pp. 667–675, 2013.

[18] I. Michalak *et al.*, “Effect of macroalgae enriched with microelements on egg quality parameters and mineral content of eggs, eggshell, blood, feathers and droppings,” *J. Anim. Physiol. Anim. Nutr. (Berl).*, vol. 95, no. 3, pp. 374–387, 2011.

[19] Z. Witkowska *et al.*, “Biofortification of hens’ eggs with microelements by innovative bio-based dietary supplement,” *J. Anim. Physiol. Anim. Nutr. (Berl).*, no. October 2018, pp. 485–492, 2019.

[20] Z. Witkowska *et al.*, “Biofortification of milk and cheese with microelements by dietary feed bio-preparations,” *J. Food Sci. Technol.*, vol. 52, no. 10, pp. 6484–6492, 2015.

[21] Z. Dobrzański, J. Dorota, O. Sebastian, and H. Górecka, “ELECTRONIC OF POLISH AGRICULTURAL Volume 6 Issue 2 Series ANIMAL BIOAVAILABILITY OF SELENIUM AND ZINC SUPPLIED TO THE FEED FOR LAYING HENS IN,” pp. 0–5, 2003.

[22] S. Błażejak, M. Chojnacka, W. Duszkiewicz-Reinhard, and M. Gniewosz, “WP Ł YW pH NA ZDOLNO ŚĆ WI Ą ZANIA MAGNEZU PRZEZ DRO Ż D Ż E PASZOWE,” 2005.

[23] Z. Reddad, C. Gerente, Y. Andres, and P. Le Cloirec, “Adsorption of several metal ions onto a low-cost biosorbent: Kinetic and equilibrium studies,” *Environ. Sci. Technol.*, vol. 36, no. 9, pp. 2067–2073, 2002.

[24] A. N. Módenes, F. R. Espinoza-Quiñones, D. E. G. Trigueros, F. L. Lavarda, A. Colombo, and N. D. Mora, “Kinetic and equilibrium adsorption of Cu(II) and Cd(II) ions on Eichhornia crassipes in single

and binary systems," *Chem. Eng. J.*, vol. 168, no. 1, pp. 44–51, 2011.

[25] A. Inyinbor, F. Adekola, and G. Olatunji, "Multifunctional Group Biomass in Biosorption of Cu2+ from Aqueous Solution: Kinetics and Isotherm Studies," *Pakistan J. Anal. Environ. Chem.*, vol. 18, no. 2, pp. 94–104, 2017.

[26] A. Dubey and A. Mishra, "A Novel Plant-Based Biosorbent for Removal of Copper (II) from Aqueous Solutions: Biosorption of Copper (II) by Dried Plant Biomass," *J. Renew. Mater.*, vol. 5, no. 1, pp. 54–61, 2016.

[27] Z. Bingul, H. Gurbuz, A. Aslan, and S. Ercisli, "Biosorption of zinc (II) from aqueous solutions by nonliving lichen biomass of xanthoria parietina (L.) Th. Fr," *Environ. Eng. Manag. J.*, vol. 15, no. 12, pp. 2733–2740, 2016.

[28] J. M. Lezcano, F. González, A. Ballester, M. L. Blázquez, J. A. Muñoz, and C. García-Balboa, "Biosorption of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) using different residual biomass," *Chem. Ecol.*, vol. 26, no. 1, pp. 1–17, 2010.

[29] A. I. Adeogun, A. E. Ofudje, M. Idowu, and S. O. Kareem, "Equilibrium, kinetic, and thermodynamic studies of the biosorption of Mn(II) ions from aqueous solution by raw and acid-treated corncob biomass," *BioResources*, vol. 6, no. 4, pp. 4117–4134, 2011.

[30] S. Khosravihaftkhany, N. Morad, T. T. Teng, A. Z. Abdullah, and I. Norli, "Biosorption of Pb(II) and Fe(III) from aqueous solutions using oil palm biomasses as adsorbents," *Water. Air. Soil Pollut.*, vol. 224, no. 3, 2013.

[31] A. Witek-Krowiak, "Analysis of temperature-dependent biosorption of Cu2+ ions on sunflower hulls: Kinetics, equilibrium and mechanism of the process," *Chem. Eng. J.*, vol. 192, pp. 13–20, 2012.

[32] B. Garcia-Fayos, J. M. Arnal, J. Piris, and M. Sancho, "Valorization of Moringa oleifera seed husk as biosorbent: isotherm and kinetics studies to remove cadmium and copper from aqueous solutions," *Desalin. Water Treat.*, vol. 57, no. 48–49, pp. 23382–23396, Oct. 2016.