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ORIGINAL PAPER

Valorization of Biomass into Micronutrient Fertilizers

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Abstract Biological waste constitutes a resource that could be valorised into micronutrient fertilizers. Micronutrient fertilizers (berries seeds residues enriched with micronutrients—blackcurrant *Ribes nigrum* L., raspberry *Rubus idaeus* L., strawberry *Fragaria × ananasa*) produced via biosorption were developed. Micronutrient content was investigated by Scanning Electron Microscope with Energy Dispersive X-ray analysis (SEM-EDX) as an alternative method to Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) which is known as costly, time-consuming and sample-destructive method. X-ray mapping of SEM images and ICP-OES analysis showed the differences in the concentration of micronutrients on the materials surface (natural and enriched biomass—from 3 to 24 times). The highest content of micronutrients (ICP-OES) was achieved for enriched blackcurrant [Cu(II)-12.8 mg g^{-1}, Zn(II)-10.8 mg g^{-1}] and strawberry seeds [Mn(II)-5.13 mg g^{-1}]. The highest atomic concentration of micronutrients was found on the surface (SEM-EDX) of enriched strawberry [24.5% for Cu(II), 8.43% for Mn(II) and 11.1% for Zn(II)]. It was shown that increasing content of micronutrient ions in biological material after biosorption was connected with decreased level of the following cations: Ca(II), Mg(II) and K(I) (ion exchange). The uniform distribution of micronutrient ions was observed on SEM micrographs. The structure of the surface, surface topography (steps, bends and broken edges) were also investigated. The content of micronutrients in biomass determined with ICP-OES and SEM-EDX revealed high correlations between these methods for manganese, zinc and copper ions (0.848, 0.739, 0.735, respectively). Described experiments showed that SEM-EDX was an efficient tool and an alternative for ICP-OES.

Keywords Biosorption · ICP-OES · SEM-EDX · Berries seeds

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Introduction

Micronutrient cations [Cu(II), Mn(II), Zn(II)] can be bound to the biomass via biosorption. Ion exchange is supposed to be one of the main mechanisms responsible for the process. Biomass possesses some functional, usually negatively charged sites on its surface. Biosorption is a property of certain types of inactive and dead biomass to bind and concentrate metal ions from even very dilute aqueous solutions. Among the mostly often used biosorbents, plant waste biomass [1], algae [2], fungi [3] and bacteria [4] should be mentioned. Micronutrient cations are bound to the surface of the biomass in the equilibrium process. Reversed process (desorption) occurs when biomass is added to soil. Micronutrient ions can be transferred to the soil solution from where they can be taken up by plants.

In this work, surface of new biosorbents was investigated for the presence and distribution of micronutrients before and after biosorption. The biomass of post-extraction residues was enriched with Cu(II), Mn(II) and Zn(II) ions in stirred tank reactor. The content of elements in the enriched biomass was examined by Inductively Coupled Plasma Optical Emission Spectroscopy which is commonly used in biosorption studies [2, 5]. The surface characterization and metal ions adsorption properties of biomass were studied using Scanning Electron Microscopy with an Energy

Dispersive X-ray analytical system. SEM-EDX is not commonly used technique in biosorption and biosorbent studies. In literature this technique was used to investigate such biosorbents as: sawdust of silver fir [1], ponkan peel [6], *Morus alba* L. fruit peel [7], macroalgae *Enteromorpha* sp. [2], *Sargassum* sp. [8] neem leaf [9], *Saccharomyces cerevisiae* [3] while there is no information about its application in the investigation of chemical composition of berries seeds. Since the last 5 years, there were 8592 published articles about biosorption studies, SEM-EDX technique was used only in 92 (about 1%). This technique was used in current research to determine the content of elements on the surface of natural and metal-loaded material.

In this study, biosorption was conducted on berries seeds residues—blackcurrant *Ribes nigrum* L., raspberry *Rubus idaeus* L., strawberry *Fragaria × ananasa*. In the food industry most of this type of fruits are processed to juice [10], the rest of fruits is used mainly in production of jams, jellies and cordials [11]. Seeds are usually discarded as a useless byproduct. During processing, pomace is obtained. The berry press residue is principally composed of seeds—about 25% of dry mass of pomaces [12]. Seeds are a valuable raw material, because contain a wide variety of compounds such as etheric oils and fatty acids [11, 13, 14], nutrients necessary in animal feeding [15, 16], cutin [17, 18], lignans [19], polyphenols [20], lipids and lipoproteins [21] and have antioxidative properties [22]. These compounds can be extracted and used as food supplements [23] and in cosmetic industry [24, 25]. Berries seed oils have also pharmaceutical potential [26]. After oils extraction from berries seeds, post-extraction residue is obtained. Recent studies showed that these residues are a good biosorbent [27]. Biomass enriched with microelement ions by biosorption could be used in agriculture as the component of fertilizers which will be non-toxic to plants and biodegradable [27, 28]. As it was previously shown [27], post-extraction residues have good biosorption properties—contain many functional groups on the surface (such as carboxyl group) [21, 29]. Because of the chemical composition, press residue could also have an important role as a source of insoluble fiber for industrial applications [10]. Biosorption capacity of berries seed residues was evaluated as 5–20 mg g^{-1} (for Zn, Mn, Cu ions) [27].

Materials and Methods

For the experiments, post-extraction residues after supercritical CO_2 extraction conducted on blackcurrant (*Ribes nigrum* L.), raspberry (*Rubus idaeus* L.) and strawberry (*Fragaria × ananasa*) seeds, delivered by New Chemical Syntheses Institute (Puławy, Poland) were used. The biosorption of Zn(II), Cu(II) and Mn(II) by biological material was conducted instirred reactor separately for each micronutrient for 2 h. The concentration of Zn(II) ($ZnSO_4 \cdot 7H_2O$, POCH, Poland), Cu(II) ($CuSO_4 \cdot 5H_2O$, POCH, Poland) and Mn(II) ($MnSO_4 \cdot 1H_2O$, POCH, Poland) in the solution was about 300 mg/L for each process, pH was 5. The biosorption process was conducted at 25 °C. In each process 40 g of biosorbent was used. Final product was dried at 50 °C for 24 h. The content of elements in the enriched biomass was examined by ICP–OES after mineralization, surface was analyzed by SEM-EDX technique after gold coating of samples.

SEM-EDX Analysis

The surface was analyzed by SEM microscope. The measurements of samples topography have been prepared and an analysis of the elements present on the sample surface were made with Energy Dispersive X-ray analytical system (Energy Dispersive X-ray Spectrometer—EDX) coupled with SEM microscope (Phenom ProX, The Netherlands). Before SEM-EDX analysis, all samples were coated with the layer of gold 20 nm (± 2%). Coating was done on the coater Leica EM ACE200 with plasma. The layer thickness was measured using a quartz microbalance (QSG). During experiment, several data were collected: pictures of the surface of natural and enriched seed residues, maps of the micronutrients distribution on the cell wall of dry biomass, their concentration on the surface of biosorbents before and after biosorption and samples topography. For this purpose, the mapping area and five points on the sample surface was selected. For each point the spectrum was generated by using EDX module. This gave the percentage of the individual element among of all detected elements. All results of analysis for each sample were averaged.

ICP-OES Analysis

Each material was digested with nitric acid (69%, Suprapur, Merck, USA) in Teflon bombs in microwave system Milestone Start D (USA). Parameters of the mineralization process were matched to assure complete digestion of samples. The concentration of elements in digested biomass was determined by 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) 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%).

Result and Discussion

Among analytical methods useful in the quantitative description of biosorption, ICP-OES was shown as the most widely used. While ICP-OES was described as a costly and probe-destructive method, the application of SEM-EDX in the description of metal-loaded material surface affinity constitutes a subject of interest. The growing number of possible applications of biosorption makes the alternative analytical methods for quantitative description of the process an important issue. There is a lot of papers describing the use of SEM-EDX for adsorption of metal ions to the surface of artificial material while only few studies were focused on the application of electron microscopy in biosorption studies.

X-ray mapping of SEM images and ICP-OES analysis showed the differences in the concentration of micronutrients on the surface of enriched biomass in comparison with raw materials. Independently on the type of the biomass, the uniform distribution of particular metal ions was observed on SEM micrographs (Fig. 1). The structure on the surface of the berries seeds was investigated with the use of SEM before and after biosorption. The surface of the sorbent contains steps, bends and broken edges which makes the material a good sorbent. Also some additional destructions in the surface of the biomass when compared with non-loaded material can be observed. It can suggest that the binding of metal ions can lead to the deterioration of the structure which confirmed previous observations on *Enteromorpha* sp. [2]. Multielemental analysis of the biomass carried out with the use of SEM-EDX (Table 1) and ICP-OES (Table 2) showed that increasing content of micronutrient ions in biological material after biosorption was connected with decreased level of abundant cations such as K^{+}, Na^{+} Ca^{2+}, Mg^{2+} in native biomass. The highest decrease was obtained for raspberry seeds—9.55 times for potassium content, 4.27 times for calcium and 5.3 times in case of manganese content. It was due to the ion exchange—the main identified mechanism of biosorption [30] which was confirmed in this study. In case of SEM-EDX analysis (Table 1), the highest micronutrient enrichment was obtained for strawberry seeds—15.5 times for copper ions, 6.42 times for zinc ions and 42.1 times in case of manganese ions.

In case of ICP-OES analysis (Table 2), the highest micronutrient enrichment was obtained for blackcurrant seeds—1040 times for copper ions, 328 times for zinc ions and 105 times in case of manganese ions. These results suggest that more micronutrients were bound to the surface of raspberry seeds (SEM-EDX), while the highest content of micronutrients was obtained for blackcurrant seeds (ICP-OES). High content of micronutrient ions determined by SEM-EDX analysis of the enriched biomass showed favourable binding of metal ions to the surface of the biomass which was confirmed in the previous studies [31].

For Cu enrichment (strawberry, blackcurrant and raspberry respectively), the following levels of biomass enrichment in microelements were obtained using the ICP-OES method, times: 710, 1040, 1400 and SEM-EDX: 15.5, 3.3, 3.8. In the case of Mn, respectively: ICP-OES: 60, 105, 33, SEM-EDX: 42, 24, 1.6. In the case of zinc: 115, 328, 138, and SEM-EDX: 6.4, 2.1, 3.3. These measures are different from each other because of the units. In case of ICP-OES the unit was mg kg^{-1} in whole volume and for SEM-EDX, % atomic surface. During the biosorption process, the ions of K, Mg, and Ca were desorbed, and the ions of the microelements were bound to negatively charged functional groups present on the surface of the cells. This phenomenon is visible clearly in both analytical methods. Figure 2 provides two comparative graphs of the microelement content of biomass determined by two methods.

SEM-EDX was shown to be an efficient tool for the determination of micro- and macronutrient content in enriched biomass. The content of micronutrient in different types of biomass determined with both analytical techniques—ICP-OES and SEM-EDX revealed high correlations between these two methods (Table 3). High values of correlation coefficients were found for manganese, zinc and copper ions (0.848, 0.739, 0.735, respectively) (Table 2). Good agreement of obtained results was also observed when statistical analysis for all micronutrients was carried out ($R = 0.734$) (Table 3).

There were statistically significant correlations between elements determined by ICP-OES and SEM-EDX for individual micronutrients and for all micronutrients simultaneously (correlation coefficient 0.74–0.85). There are therefore premises to validate this method of microelement determination in biomass enriched with biosorption. This will be a great simplification and will generate lower costs in determining the composition of the obtained product, since the analytical results will be received immediately and in a non-destructive manner.

The form-nature of metals in the final product are mainly complexes with carboxyl groups, which are present on (cellulosic type) biomass surface. Biologically bound metal ions are more bioavailable than in inorganic form (oxide hydroxides, salts, etc.), which can be easily dissolved during application. SEM-EDX and ICP-OES were performed in order to investigate the mechanism of metal ions biosorption. Experiments were carried out on three different types of the biomass of berries seeds and hence obtained results suggest that the application of SEM-EDX in biosorption studies was useful and can be used for broader group of biological materials. High correlations between these two methods were also described in literature [32], who examined multielement content of sea sediments.

Taking into account the semi-quantitative nature of the SEM-EDX method, this technique can be useful only after

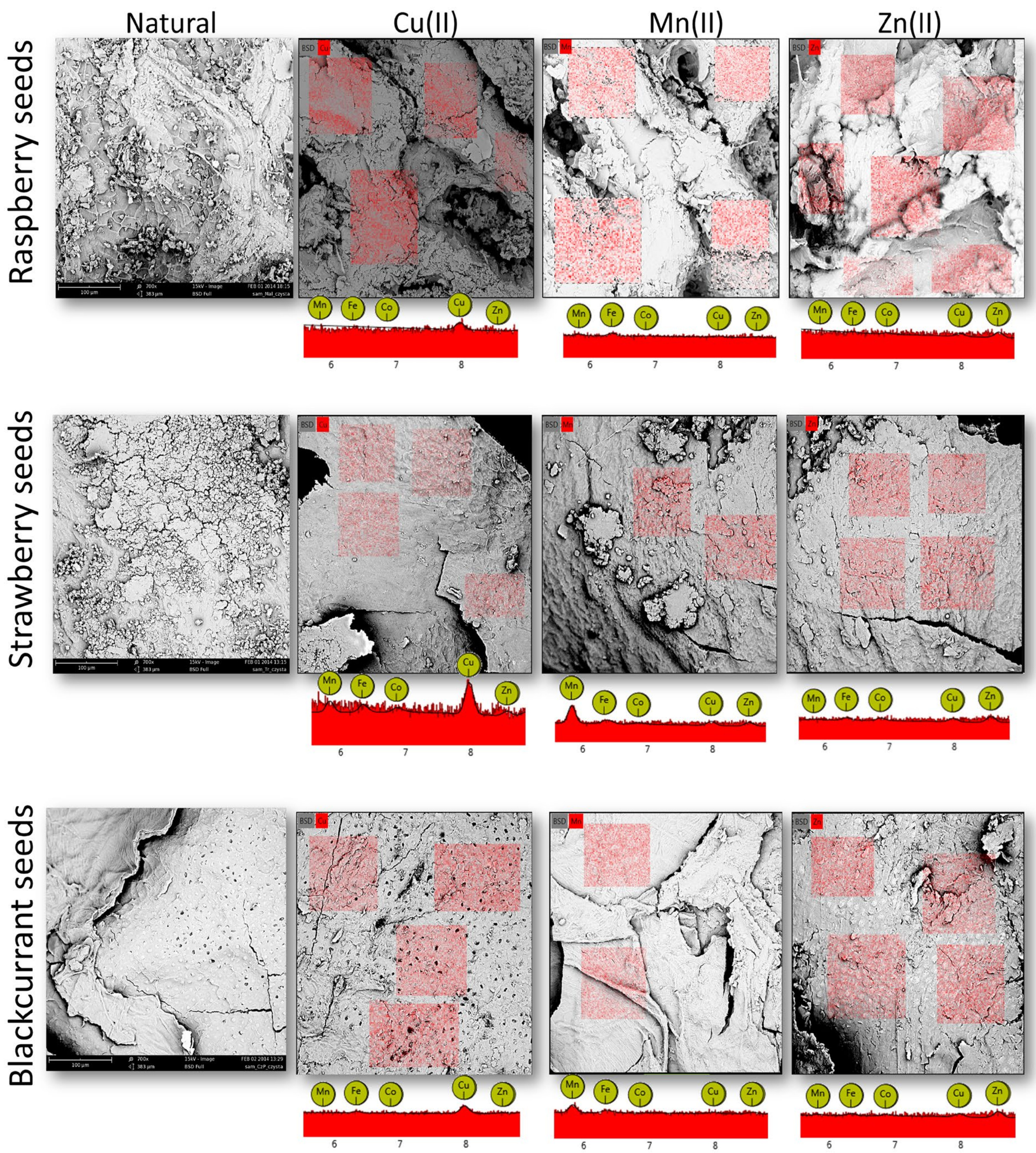

Fig. 1 SEM-EDX surface analysis and micronutrient mapping (for metal loaded materials)

applying a correlation test with the ICP-OES for a given matrix. There is also an significantly higher detection limit of SEM-EDX, which makes the method particularly useful in determining the composition of enriched biomass, ie of the finished fertilizer product. It is important to note that as long as the result of ICP-OES gives the total content of the element in the material, SEM-EDX only shows the composition of the surface. However, the latter measure seems more reliable, because biosorption is a phenomenon occurring on the surface of cells and not in its entire volume.

The development of cheaper analytical techniques validated for a given application is one of the most important challenges of contemporary industrial analytics. Advanced instrumentation techniques such as ICP-OES are expensive and time-consuming, because they require preparation for samples for analysis. In some cases, and especially in the counter product quality, it is necessary to obtain results on

Table 1 Multielemental content of the biomass—EDX, n = 6

Material	Cu		Mn		Zn		P		K		S		Ca		Mg		Na	
	C[a]	SD	C[a]	SD	C[a]	SD	C[a]	SD	C[a]	SD	C[a]	SD	C[a]	SD	C[a]	SD	C[a]	SD
Strawberry																		
Natural	1.58	1.54	0.2	0	1.73	2.5	9.85	0.56	2.08	0.32	4	0.45	0.9	0.12	5.93	0.36	3.6	0.8
+ Cu	24.5	1.9	2.93	0.78	3.6	4.2	3.8	0.62	1.93	1.71	2.28	0.78	2.8	0.67	1.85	1.25	2.93	2.38
+ Mn	2.93	6.35	8.43	0.38	4.7	7.34	8.78	1.27	1.25	0.67	3.95	2.3	0.35	0.49	2.65	1.38	3.65	2.13
+ Zn	5.38	2.41	0.32	1.41	11.1	3.26	8.1	1.65	0.63	0.91	4.35	2.85	0.57	0.26	3.88	2.21	4.78	2.75
Blackcurrant																		
Natural	3.1	0.9	0.1	0.2	4.45	2.36	5.18	0.9	0.45	0.31	2.83	0.81	3.05	2.7	3.68	1.2	4.2	0.77
+ Cu	10.3	2.3	0.12	0.16	7.78	1.14	5.86	1.18	0.08	0.18	2.86	0.72	1.36	0.8	4.8	0.22	0.54	0.78
+ Mn	2.1	1.7	2.4	0.67	2.58	2.23	4.85	0.62	0.15	0.21	2.98	0.56	1.38	2.93	3	1.39	3.85	1.73
+ Zn	4.18	1.73	0.68	0.78	9.53	2.74	6.83	0.37	0.25	0.17	3.68	0.25	9.63	1.09	4.05	1.16	6.23	1.01
Raspberry																		
Natural	2.78	1.24	0.9	0.75	2.75	1.84	5.83	0.78	0.98	0.67	2.95	0.61	1.03	0.72	2.53	0.5	1.83	1.19
+ Cu	10.5	4.81	0.18	0.35	6.65	2.74	5.63	0.62	0.15	0.3	2.98	0.38	0.23	0.45	3.45	0.82	2.08	1.39
+ Mn	1.33	8.39	1.45	0.45	2.38	2.1	5.25	0.38	0.6	0	2.95	0.33	0.23	0	2.65	0.67	4.7	0.67
+ Zn	5.85	1.37	0.23	0.73	9	2.55	3.98	0.19	0	0.69	1.88	0.66	0	0.26	3.53	1.18	5.7	1.78

[a](AC) atomic concentration of elements—% of all detected elements

Table 2 Multielemental content of the biomass—ICP-OES, n = 6

Material	Cu		Mn		Zn		P		K		S		Ca		Mg		Na	
	C[a]	SD	C[a]	SD	C[a]	SD	C[a]	SD	C[a]	SD	C[a]	SD	C[a]	SD	C[a]	SD	C[a]	SD
Strawberry																		
Natural	13.5	1.8	85.8	11.2	43.6	5.7	2780	556	3350	670	2200	440	5590	1120	2460	492	615	92
+ Cu	9580	1920	25.6	3.3	151	20	1300	260	555	83	1450	290	4900	980	791	158	333	50
+ Mn	87.3	11.3	5130	1030	59.1	7.7	1780	356	1720	344	1360	272	5420	1090	505	76	349	52
+ Zn	12.9	1.7	32.8	4.3	5030	1010	1430	286	672	101	1480	296	5120	1030	915	137	674	101
Blackcurrant																		
Natural	12.3	1.6	30.6	4.0	32.9	4.3	3240	648	7730	1550	2060	412	5630	1130	2260	452	<0.05	<0.0125
+ Cu	12,800	2550	29.8	3.9	241	31	3790	758	2010	403	3360	672	5580	1120	2140	428	345	52
+ Mn	36.6	4.8	3210	642	18.2	2.4	1970	394	951	143	1230	246	2610	522	893	134	136	20
+ Zn	11.7	1.5	30.7	4.0	10,800	2160	9710	1942	1950	391	2630	526	6210	1240	1700	340	51	8
Raspberry																		
Natural	8.96	1.16	75.9	9.9	34.6	4.5	1550	310	2770	553	1410	282	2500	500	1800	360	472	71
+ Cu	12,600	2520	14.0	1.8	171	22	797	120	156	23	1370	274	585	88	170	26	630	95
+ Mn	71.5	9.3	2480	496	26.1	3.4	1060	212	295	44	1010	202	1520	304	354	53	787	118
+ Zn	9.09	1.18	18.8	2.4	4780	955	757	114	290	44	1090	218	1120	225	339	51	622	93

[a](mg g^{-1})

an ongoing basis, eg during the production process. For this purpose, it is possible to use the validated SEM-EDX technique with the ICP-OES method. This was investigated in the tests on plants. Utilitarian properties of new preparations, developed in laboratory scale, were investigated also in series of vegetation tests [33–35]. Vegetation tests were performed on garden cress (*Lepidium sativum* L.) in germinator [34] and on white mustard (*Sinapis* L.) in pot trials [35]. Results from both experiments were similar, in comparison to inorganic sources of micronutrients, the highest plant mass was observed for the group treated with new preparations based on biomass of berries seeds. The yield in experimental group was up to 2.5 times higher than in the control group (untreated).

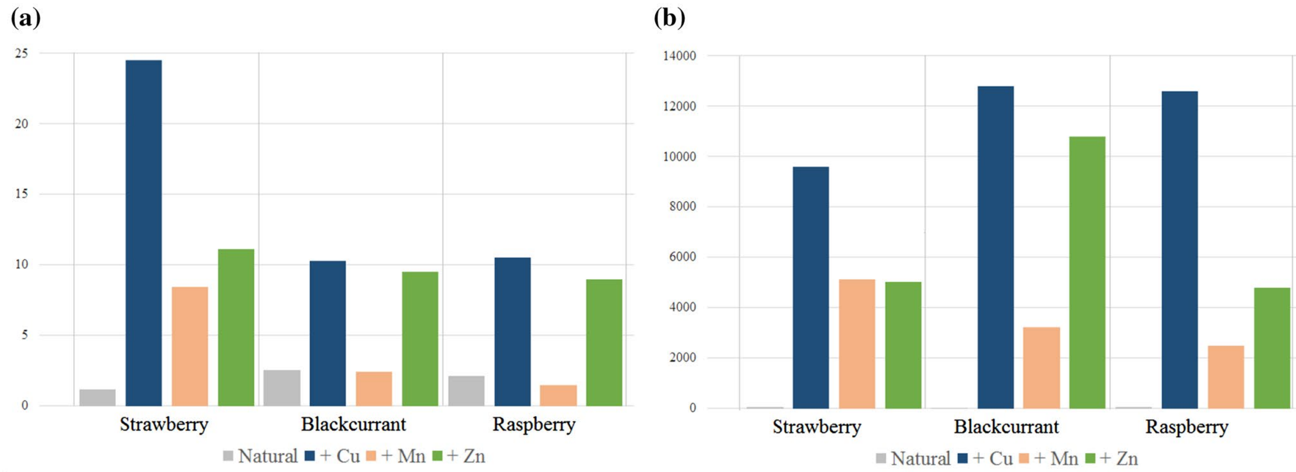

Fig. 2 Micronutrient content in biomass (for natural—mean value) **a** SEM-EDX results, **b** ICP-OES—results

Table 3 Correlation between ICP-OES (mg g^{-1}) and SEM-EDX (atomic concentration of elements—% of all detected elements)

Element	R	Equation
Zn	0.739	Zn-ICP-OES = 787·Zn-EDX − 2560
Cu	0.735	Cu- ICP-OES = 598·Cu-EDX − 781
Mn	0.848	Mn-ICP-OES = 609·Mn-EDX + 29.8
All micronutrients	0.734	ICP-OES = 577·EDX − 657

Conclusion

The concept of new bio-based micronutrient fertilizers was presented in view of feasibility of analytical methods. Biomass can be easily valorized into micronutrient fertilizers. New micronutrient fertilizers are a biotechnological alternative to mineral fertilizers. The use of sustainable resources—a new material, berries seeds, as the biological carrier of fertilizer nutrients contribute to the development of environmental-friendly products. This approach is useful in elaboration of new applications of biosorption, e.g. the design of safer and greener fertilizers.

The comparison of the analytical results obtained for the surface of biosorbents by SEM-EDX and results of multielemental analysis of these materials obtained by ICP-OES was performed in order to investigate the mechanism of metal ions biosorption. New methodology for measuring the surface content of bound micronutrients to the biomass using SEM-EDX was developed. Furthermore, the use of SEM-EDX in comparison with ICP-OES is quick and cost-effective method.

After statistical analysis, correlations between the results were obtained, that confirmed usefulness of SEM-EDX technique for biosorption process analysis. Described experiments showed that SEM-EDX was an efficient tool for qualitative and quantitative description of biosorption process constituting an alternative for widely used but costly ICP-OES. Results suggest that the major part of micronutrients was bound on the surface of biomass. SEM-EDX enabled to determine chemical composition of analyzed material without its destruction giving possibility for the reuse of the sample for further analysis.

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