

Utilization of alfalfa and goldenrod post-extraction residues as sorbent of plant micronutrients and energy material

A. Dmytryk^{1,*}, M. Samoraj¹, Ł. Tuhy¹, A. Zdunek², P. Rusek², K. Chojnacka¹

¹Department of Advanced Material Technologies, Faculty of Chemistry, Wrocław University of Science and Technology, Wrocław, Smoluchowskiego 25, 50-372, Poland

²Fertilizer Department, New Chemical Syntheses Institute, Puławy, Tysiąclecia Państwa Polskiego 13a, 24-110, Poland

* Corresponding author: email agnieszka.dmytryk@pwr.edu.pl, tel. +48 71 320 63 13, fax +48 71 320 34 69

Abstract

Purpose: The residues of alfalfa and goldenrod after supercritical CO₂ extraction were examined for capability of both carrying micronutrients applicable to crops and energy production, and compared to raw plant materials.

Methods: The enrichment of biomass with plant micronutrients – Cu(II), Mn(II) and Zn(II), was performed *via* laboratory-scale biosorption in a single-metal system and verified by inductively coupled plasma optical emission spectroscopy (multielemental analysis). Also, the temperature-induced decomposition of plant materials was investigated by simultaneous thermogravimetry-differential thermal analysis combined with mass spectrometry under synthetic air.

Results: Biosorption enabled efficient binding of micronutrients to prior- and post-extraction materials of both plant species – increasing the content of Cu(II), Mn(II) and Zn(II) by 54-1700 folds compared to control matrices. Yet, goldenrod was better sorbent. The general affinity sequence for cations was, as follows: Cu(II)>Zn(II)>Mn(II). Under experimental conditions, manganese and copper were preferably accumulated onto post-extraction residues and raw biomass, respectively. As plant matrices were thermally decomposed, prior- and post-extraction materials showed similar weight loss of 92-94%. Two exothermic effects were observed, one of which was stronger for post-extraction residues of a given plant species. The results for alfalfa were generally higher than for goldenrod. Biomass thermal decomposition led to release mainly H₂O and CO₂, and low amount of SO₂.

Conclusion: The usability of residues after supercritical CO₂ extraction as micronutrient bio-component for fertilizer and feedstock for energy production was proved. Utilitarian properties of post-extraction residues might be considered as good enough to replace raw biomass in both applications examined.

Keywords: biomass waste, biosorption, sustainable plant system, renewable energy source, solid biofuels.

1. Introduction

The idea of circular economy – extensively implemented on European Union premises, assumes zero-waste production. Post-extraction materials of natural origin were successfully valorized to valuable products, however mainly as feed additives for livestock [1, 2]. Their application could be much wider, though.

According to Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC [3], at least 20% of energy in each member country will have to be produced using renewable energy sources by 2020. Although, taking average data into

account, the requirement is currently met, there are still countries – like Poland [4], which involve too few renewable sources. Among alternative energy feedstocks, biomass is of particular interest [4, 5]. At the same time, the attention is paid to protect the environmental balance and local species variety by limiting the cultivation of non-native bioenergy crops [6]. Also, the crop cultivation needs high energy input while causing nutrient leaching from soil [7]. While some researchers propose the application of the potential of local perennial grasses and invasive species [5, 6, 8], the use of post-processing residues of plant materials – also those aforementioned, seems to be alternative and reasonable solution.

The intensive agriculture results in impoverishment of micronutrients, hence, their malnutrition which is a global issue [9-11]. Since micronutrient fertilizing is either neglected [12] or performed with inefficient instrumentalities [13] posing environmental risk [14, 15], innovative approach to overcome micronutrient deficiency is required. As micronutrients are highly available to plants when applied with carrier of biological origin, crop treatment with natural waste materials enriched with deficient elements *via* biosorption is worth extensive investigation [16, 17].

The current work focused on applicability of alfalfa (*Medicago sativa*) and goldenrod (*Solidago virgaurea*) residues after supercritical CO₂ extraction to micronutrient bio-component of fertilizers and renewable energy source.

2. Materials and methods

2.1. Biomass enrichment with plant micronutrients

Plant materials (Agricultural Exchange Association “Agrotrader”, Poland) used as carriers for micronutrients underwent supercritical CO₂ extraction in Technology Line within Wrocław Technology Park (Poland). Micronutrients were bound onto both raw biomass and post-extraction residues *via* biosorption under laboratory conditions – in stirred-tank reactor of 3 L working volume. For the current work, Cu(II), Mn(II) and Zn(II) were selected because of playing the crucial role in enzyme-mediated metabolic pathways [18] while remaining deficient in the cultivation area worldwide [19, 20]. In the experiment, a single-metal system was applied – in which 3 g of each plant material were soaking in 0.3 g/L aqueous solution of micronutrients (ZnSO₄·7H₂O, CuSO₄·5H₂O, MnSO₄·H₂O, all analytical grade; Avantor Performance Materials Poland S.A., Poland), pH 5.0 (pH-meter, SevenMulti™, Mettler Toledo, Switzerland), for 1.5 hours at 25°C. The operational conditions were selected based on previous studies [unpublished data]. As the process ended, the separation of solid particles was conducted on sieves and, further, on a filtered press. Recovered materials were dried (SUP 30G, Wamed, Poland) for 24 hours at 50°C and subjected for chemical assessment.

2.2. Multielemental analysis of enriched plant materials

The elemental composition of representative plant material samples – both prior- and post-biosorption, was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES; Vista MPX, Varian Inc., Australia), preceded by microwave-assisted decomposition (Milestone Start D, Milestone S.r.l., Italy).

Besides micronutrients biomass was loaded with, multielemental analysis included: primary nutrients – phosphorus, potassium, secondary nutrients – calcium, magnesium, sodium and sulphur [21] and toxic elements – arsenic, cadmium, chromium, nickel and lead [22]. Among primary nutrients, nitrogen content was also assessed with N/CN analyzer (Vario Macro Cube Analysensysteme, Elementar, Germany). The investigation of alfalfa and goldenrod elemental composition referred to PN-EN ISO/IEC 17025:2005 [23, 24].

Experimental groups subjected for multielemental analysis were hereinafter marked as: B – raw biomass; B+Cu/Mn/Zn – biomass enriched with Cu(II), Mn(II) and Zn(II) ions, respectively; R – post-

extraction residues; R+Cu/Mn/Zn – residues enriched with Cu(II), Mn(II) and Zn(II) ions, respectively.

2.3. Thermogravimetry-differential thermal analysis

Plant materials underwent temperature-induced decomposition, progress and thermal response – with either exothermic or endothermic effect, of which was evaluated by simultaneous thermogravimetry-differential thermal analysis combined with mass spectrometry (TG-DTA-MS; STA 449 F3 Jupiter[®] coupled with QMS 403 C Aëolos[®], Netzsch, Germany). Samples were decomposed in rhodium furnace using Al₂O₃ crucible, under the following conditions: temperature range of 30-1000°C, 20K/min heating rate and synthetic air as reaction gas flowing at 50 mL/min. The assessment involved 50 measuring cycles and, in each of them, the composition of the released gas mixture was scanned at the entire m/z range, i.e. 10-300 amu.

3. Results and discussion

3.1. Biomass enrichment with plant micronutrients via biosorption

Under the conditions of the experiment, biosorption was justified as an efficient method to bind micronutrients to *M. sativa* and *S. virgaurea*, since the content of copper, manganese and zinc in loaded samples surpassed the control groups by 54-1700 folds (Table 1 and 2). In general, the affinity of biosorbents for examined micronutrients was, as follows: Cu(II)>Zn(II)>Mn. Weak accumulation of manganese was particularly noted for raw *M. sativa* biomass providing the result lower by 10 folds than copper and zinc biosorption onto the surface of the same material. In the case of post-extraction residues of alfalfa and raw goldenrod, the capability of binding Mn(II) differed by 68 and 30%, on average, from the affinity for Cu(II) and Zn(II), respectively. Contrariwise, copper was least-favorable micronutrient post-extraction residues were loaded with, as compared with zinc and manganese – 37 and 17% stronger enrichment, respectively.

The selection between raw biomass and post-extraction residues varied for different micronutrients – copper was preferably bound onto the former, while manganese – onto the latter. The affinity sequence was similar for samples of both plant species, yet *S. virgaurea* showed higher biosorption yield (by 10-86%) whether prior- or post-extraction material was considered. Despite differences in sorption properties affected by either biomass origin or processing, each biosorbent might be considered as a micronutrient carrier efficient for plant treatment.

There are few reports on biosorption onto alfalfa and goldenrod. Available works are usually devoted to removal heavy metal ions from aqueous solutions (phytofiltration). Gardea-Torresdey *et al.* [25, 26] and Tiemann [27] verified high *M. sativa* capability of binding Cd(II), Cr(III), Cu(II), Fe(II), Fe(III), Ni(II), Pb(II) and Zn(II) under the following laboratory conditions: packed-bed column, single-metal system, 0.3 mM aqueous solution of each element, pH 5.0, 10 min, 12 cycles. Experiment proved the highest affinity of alfalfa for lead – 43.0-58.9 mg/g, and, at the same time, 6-11-fold lower biosorption capacity for other metal cations (mg/g): Cu(II) – 13.0-19.7, Cr(III) – 7.7-18.2, Zn(II) – 4.9-12.3, Cd(II) – 7.1-8.7, Fe(III) – 4.5, Ni(II) – 2.2-4.1, Fe(II) – 2.9 depending on the species examined. On the other hand, *M. sativa* biomass was efficient biosorbent for Au(III) recovery – 40.1 mg/g, from multi-metal solution at pH 2.0 [27, 28]. As opposed to alfalfa, goldenrod materials are undertested and they have been shown to bind Cr(VI) in the amount of 5.69 mg per g for 4 h-long process at 40°C and pH 2.0 [29]. Comparison of literature data with the obtained biosorption *M. sativa* capacity for Cu(II) and Zn(II) – 11.6-22.0 mg/g and 10.4-18.5 mg/g, respectively, led to the conclusion that conditions proposed in the current paper are, at least, as suitable for metal accumulation as those developed so far. Since enrichment of *S. virgaurea* was even more efficient, it is considered that presented process might be applied to various plant materials of similar kind.

According to “Decree of Ministry of Agriculture and Rural Development of 18 June 2008 on execution of some regulations of act on fertilizers and on fertilizing” [22], micronutrient-loaded biomass cannot be classified as fertilizer due to low potassium content not meeting the legal requirements ($\geq 1\%$ of K_2O in dry mass). Although prior-extraction materials contained 1.7% K_2O , on average, the primary nutrient is replaced by metal cations during ion exchange – reported as the dominant mechanism of biosorption [30]. Since levels of toxic elements was below the limit values determined in the Decree (mg/kg dry mass): $Pb \leq 140$, $Cr \leq 100$, $Ni \leq 60$, $Cd < 5$, obtained products could be permitted for plant treatment. In the previous studies, Cu(II)/Mn(II)/Zn(II)-loaded biomass – when used

in a combination of three materials produced in a single-metal system, has been confirmed as an additive – hereinafter defined as bio-components, for NPK fertilizer under field conditions, and verified against common inorganic form of micronutrients (salts technical grade). Bio-components affected grain yield comparably to inorganic Cu(II), Mn(II) and Zn(II) at the same dose while providing 5-25% higher bioavailability of those micronutrients [16, 17]. Similarity of multielemental composition of led to the conclusion that such approach would be successfully applied for micronutrient-enriched alfalfa- and goldenrod-based matrices, including their post-extraction residues.

3.2. Thermogravimetry-differential thermal analysis

The capability of *M. sativa* and *S. virgaurea* materials for energy production was proved as thermal decomposition resulted in total weight loss by 94 and 92% for raw biomass and post-extraction residues, respectively (Fig. 1 and 2). The half of total biomass weight loss occurred at the range of 120-400°C, except raw goldenrod for which the range was shifted to 180-400°C. As thermal response of matrices analyzed, two exothermic effects were observed at 347-354°C and 511-536°C. Although post-extraction residues responded thermally at lower temperature than raw biomass, they provided stronger the first (by 11%) and the second (by 15%) peak depending on whether alfalfa and goldenrod was considered, respectively. In general, the results for *M. sativa* were higher by 12-28%, as compared to corresponding materials of *S. virgaurea*, yet the second peak was strongest for post-extraction residues of the latter. For each sample, H_2O and CO_2 were main gaseous decomposition products, SO_2 was identified – yet, at a very low amount.

The energy potential of raw biomass of both examined plant families was evaluated by Van Meerbeek *et al.* [5] and Povilaitis *et al.* [8]. *M. sativa* matrix was verified as an alternative to maize – a known bioenergy source, since they showed similar net caloric value about 19 MJ/kg dry mass. The use of alfalfa also provided higher energy output-input ratio – 47, than maize – 20 and 19 for non-fertilized and fertilized plant. It was also estimated that the costs of energy production from alfalfa would be lower by several times compared to calculation for maize [8]. Similar results, however for gross caloric value, was obtained for *S. gigantea* – 19 MJ/kg dry mass. The annual gross energy yield produced by the plant was evaluated as high as about 170 GJ per each ha of the cultivation [5].

4. Conclusion

The research proved that *M. sativa* and *S. virgaurea* residues after supercritical CO_2 extraction as a promising sorbent for plant micronutrients and renewable energy feedstock. While alfalfa matrix was more efficiently enriched with Cu(II), Mn(II) and Zn(II) ions, goldenrod respond for thermal treatment with stronger exothermic effects. Yet, post-extraction residues of both plant species showed utilitarian properties good enough to replace raw biomass in applications examined. Further investigation will include application experiments, such as field trails on wheat and maize, also at lower doses than those recommended for such crops. Due to efficient biosorption, alfalfa and goldenrod materials will be

investigated as feed additives for micronutrient supplementation of laying hens and piglets. In parallel, post-extraction residues will undergo pelleting followed by evaluation of caloric value.

Table 1 Element content in *M. sativa* materials before and after biosorption

	Raw biomass				Post-extraction residues			
	Control (B)	B+Cu	B+Mn	B+Zn	Control (R)	R+Cu	R+Mn	R+Zn
Primary nutrients (mg/kg)								
N	41100±100	40500±300	40700±100	44200±400	40000±300	41700±200	39000±200	43300±300
P	3540±710	3360±670	2780±560	3050±610	3530±710	2990±600	2610±520	2590±520
K	14800±3000	37.6±7.5	88.1±17.6	72.1±14.4	14800±3000	8.78±1.76	17.2±14.4	61.9±12.4
Secondary nutrients (mg/kg)								
Ca	16400±3300	3240±650	6330±1270	5400±1080	16900±3400	1140±230	6050±1210	4280±860
Mg	2090±420	274±55	339±68	357±71	2030±410	50.7±10.1	191±38	102±20
Na	603±121	204±41	398±80	522±104	586±117	119±24	110±22	115±23
S	3420±680	2010±400	2000±400	2330±470	3180±640	2170±430	1970±390	2150±430
Micronutrients (mg/kg)								
Cu	11.1±2.2	18800±3800	11.0±2.2	10.5±2.1	11.0±2.2	13800±2800	19.7±3.9	17.0±3.4
Mn	32.2±6.4	10.1±2.0	1740±350	11.3±2.3	30.4±6.1	18.5±3.7	8440±1690	5.31±1.06
Zn	29.4±5.9	144±29	132±26	15400±3100	28.2±5.6	80.4±16.1	30.8±6.2	10400±2100
Toxic elements (mg/kg)								
As	39.7±7.9	12.2±2.4	10.3±2.1	8.50±1.70	3.30±0.66	4.21±0.84	22.2±4.4	18.9±3.8
Cd	0.289±0.058	0.170±0.034	1.38·10 ⁻² ±2.8·10 ⁻³	0.122±0.024	0.527±0.105	<LOD	0.333±0.067	0.239±0.048
Cr	0.388±0.078	0.788±0.158	0.565±0.113	<LOD	<LOD	1.13±0.23	0.981±0.196	0.129±0.026
Ni	<LOD	8.89±1.78	<LOD	2.91±0.58	3.74±0.75	5.54±1.11	<LOD	<LOD
Pb	10.4±2.1	0.506±0.101	11.8±2.4	3.18±0.64	7.56±1.51	9.52±1.90	19.9±4.0	8.65±1.73

<LOD – below limit of detection

Table 2 Element content in *S. virgaurea* materials before and after biosorption

	Raw biomass				Post-extraction residues			
	Control (B)	B+Cu	B+Mn	B+Zn	Control (R)	R+Cu	R+Mn	R+Zn
Primary nutrients (mg/kg)								
N	14400±100	18200±100	18800±600	18900±800	15500±400	23700±600	21800±200	22200±300
P	2090±420	2320±460	1500±300	1660±330	2140±430	2270±450	2000±400	2090±420
K	13200±2600	82.1±16.4	121±24	105±21	13700±2700	36.3±7.3	202±40	156±31
Secondary nutrients (mg/kg)								
Ca	11000±2200	3200±640	5330±1100	4280±860	11800±2400	1190±240	6760±1400	3600±720
Mg	2580±520	510±102	514±103	598±120	2680±540	282±56	743±149	608±122
Na	397±79	306±61	243±49	270±54	186±37	181±36	209±42	148±30
S	846±169	896±179	886±177	953±191	828±166	1440±290	1070±210	1060±210
Micronutrients (mg/kg)								
Cu	8.92±1.78	22000±4400	9.75±1.95	11.2±2.2	9.60±1.92	11600±2300	11.2±2.2	17.0±3.4
Mn	123±25	72.0±14.4	12700±2500	115±23	135±27	38.2±7.6	14000±2800	139±28
Zn	58.6±11.7	161±32	55.2±11.0	17200±3400	65.9±13.2	71.9±14.4	56.2±11.2	18500±3700

	Toxic elements (mg/kg)							
As	<LOD	24.7±4.9	<LOD	11.0±2.2	22.2±4.4	<LOD	22.5±4.5	12.4±2.5
Cd	0.105±0.021	0.181±0.036	0.299±0.060	<LOD	0.274±0.055	0.228±0.046	0.511±0.102	6.61·10 ⁻² ±1.32·10 ⁻²
Cr	2.39±0.48	2.17±0.43	2.99±0.60	2.08±0.42	1.49±0.30	3.26±0.65	3.15±0.63	3.68±0.74
Ni	2.29±0.46	4.72±0.94	<LOD	<LOD	<LOD	0.366±0.073	1.07±0.21	<LOD
Pb	<LOD	7.10±1.42	10.5±2.1	8.42±1.68	<LOD	3.72±0.74	14.1±2.8	<LOD

<LOD – below limit of detection

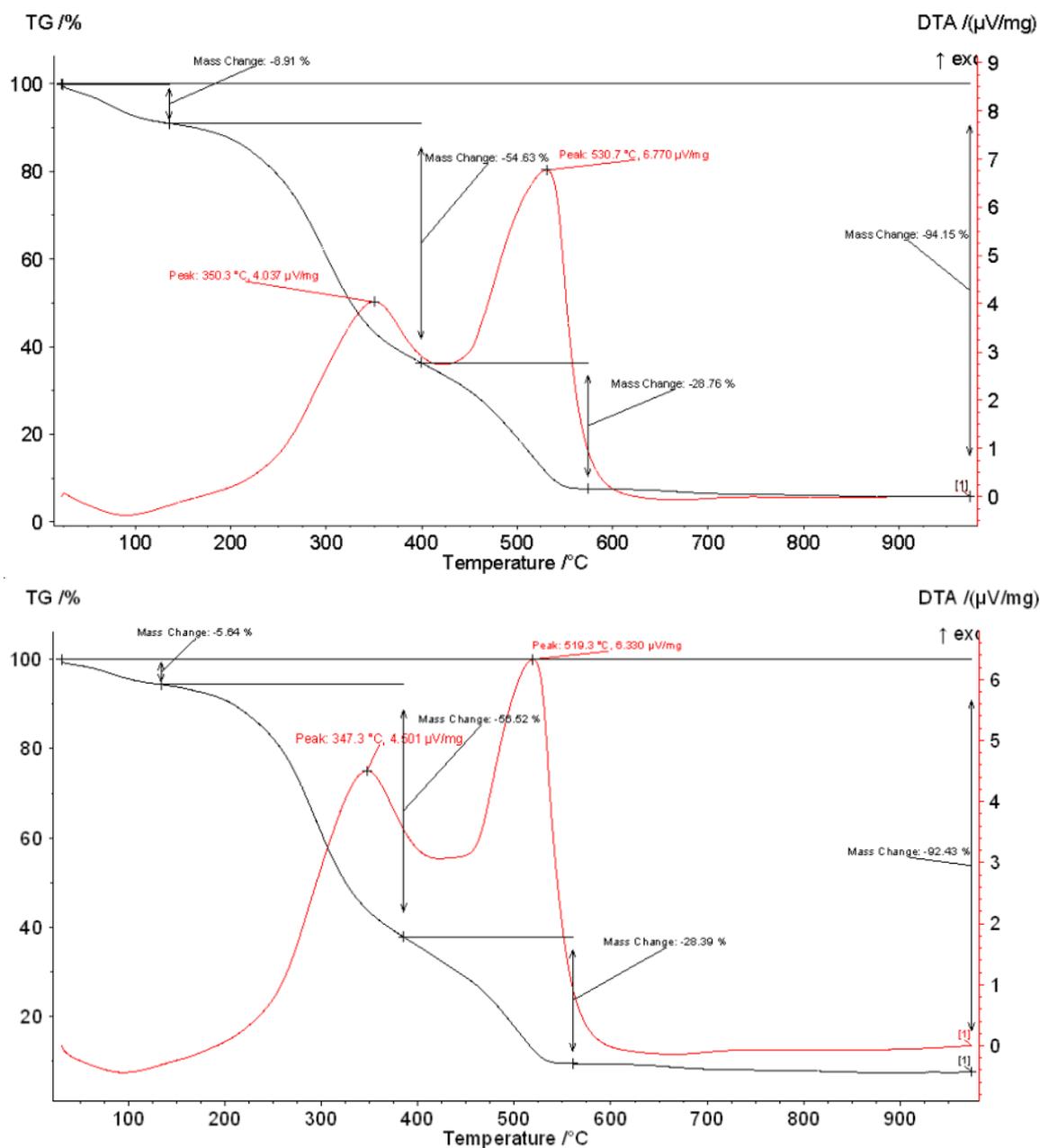


Fig. 1 TG-DTA curves for *M. sativa* raw biomass (top) and post-extraction residues (bottom)

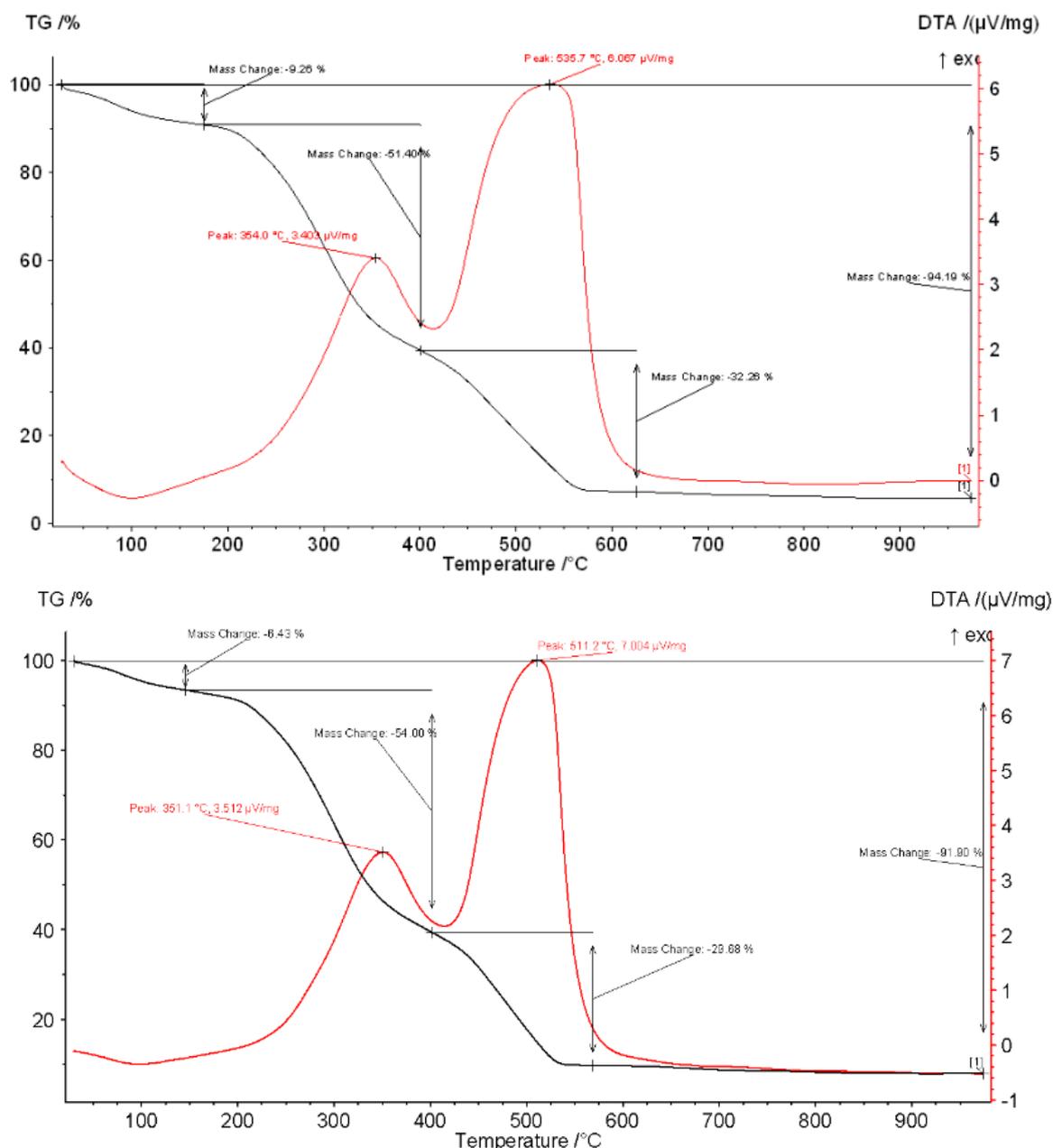


Fig. 2 TG-DTA curves for *S. virgaurea* raw biomass (top) and post-extraction residues (bottom)

Acknowledgement

This project is financed in the framework of grant entitled “Crop plants and natural products as a source of biologically active substances for the manufacture of cosmetics, pharmaceuticals and dietary supplements” (BIOSTRATEG2/298205/9/NCBR/2016) attributed by The National Centre for Research and Development in Poland.

References

- [1] Johnson, M.D., Miller, R.K., Morrill, J., Anderson, D.P., Sawyer, J.E., Wickersham, T.A., Richardson, J.W., Palma, M.A.: 051 Consumer preference for sirloin steaks from post-extraction algal residue (PEAR) fed animals. *J. Anim. Sci.* 94(supplement1), 25–25 (2016).

- [2] Morrill, J.C., Sawyer, J.E., Baber, J.R., Smith, S.B., Miller, R.K., Wickersham, T.A.: 044 Inclusion of post-extraction algal residue in finishing rations of beef steers: Consumer sensory panel ratings and fatty acid composition of ground beef. *J. Anim. Sci.* 94(supplement1), 22–22 (2016).
- [3] Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC (Text with EEA relevance).
- [4] Berent-Kowalska, G., Kacprowska, J., Moskal, I., Jurgaś, A., Kacperczyk, G.: Energy from renewable sources in 2013. Warszawa, Central Statistical Office in Poland (2014) [*in Polish*].
- [5] Van Meerbeek K., Appels L., Dewil R, Calmeyn, A., Lemmens, P., Muys, B., Hermy, M.: Biomass of invasive plant species as a potential feedstock for bioenergy production. *Biofuel. Bioprod. Bior.* 9, 273–282 (2015).
- [6] Raghu, S., Anderson, R.C., Daehler, C.C., Davis, A.S., Wiedenmann, R.N., Simberloff, D., Mack, R.N. Adding biofuels to the invasive species fire? *Science* 313, 1742 (2006).
- [7] Gerin, P.A., Vliegen, F., Jossart, J.M.: Energy and CO₂ balance of maize and grass as energy crops for anaerobic digestion. *Bioresource Technol.* 99, 2620–2627 (2008).
- [8] Povilaitis, V., Šlepetienė, A., Šlepetys, J., Lazauskas, S., Tilvikienė, V., Amalevičiūtė, K., Feizienė, D., Feiza, V., Liaudanskienė, I., Cesevičienė, J., Kadžiulienė, Ž., Kukujevas A.: The productivity and energy potential of alfalfa, fodder galega and maize plants under the conditions of the nemoral zone. *Acta Agr. Scand. B-S P.* 66, 259–266 (2016).
- [9] Gupta, U., Wum, K., Liang, S.: Micronutrients in soils, crops, and livestock. *Earth Sci. Front.* 15, 110–125 (2008).
- [10] Ortiz-Monasterio, J., Palacios-Rojas, N., Meng, E., Pixley, K., Trethowan, R., Pena, R.: Enhancing the mineral and vitamin content of wheat and maize through plant breeding. *J. Cereal Sci.* 46, 293–307 (2007).
- [11] Fageria, N.K., Moraes, M.F., Ferreira, E.P.B., Knupp, A.M. Biofortification of trace elements in food crops for human health. *Commun. Soil Sci. Plan.* 43, 556–570 (2012).
- [12] Li, B., Zhou, D., Cang, L., Zhang, H., Fan, X., Qin, S.: Soil micronutrient availability to crops as affected by long-term inorganic and organic fertilizer applications. *Soil Till. Res.* 96, 166–173 (2007).
- [13] Murakami, T., Nishikiori, T., Nohira, T., Ito, Y.: Electrolytic synthesis of ammonia in molten salts under atmospheric pressure. *J. Am. Chem. Soc.* 125, 334–335 (2003).
- [14] Bucheli-Witschel, M., Egli, T.: Environmental fate and microbial degradation of aminopolycarboxylic acids. *FEMS Microbiol. Rev.* 25, 69–106 (2001).
- [15] European Chemicals Agency (formerly The European Chemicals Bureau, part of the Institute for Health and Consumer Protection in the European Commission's Joint Research Centre): European Union Risk Assessment Report – edetic acid (EDTA). European Union Risk Assessment Report 49. Official Publications of the European Communities, Luxembourg (2004). <http://echa.europa.eu/documents/10162/65615721-ab6d-4f28-b48f-73cf9d8cc529>. Accessed 19 May 2017.
- [16] Tuhy, Ł., Samoraj, M., Witkowska, Z., Chojnacka, K.: Biofortification of maize with micronutrients by *Spirulina*. *Open Chem.* 13, 119–1126 (2015).
- [17] Samoraj, M., Tuhy, Ł., Baśladyńska, S., Chojnacka, K.: Biofortification of maize grains with micronutrients by enriched biomass of blackcurrant seeds. *Open Chem.* 13, 1236–1244 (2015).
- [18] Andreini, C., Bertini, I., Cavallaro, G., Holliday, G.L., Thornton, J.M.: Metal ions in biological catalysis: from enzyme databases to general principles. *J. Biol. Inorg. Chem.* 13, 1205–1218 (2008).

- [19] Graham, R.D.: Micronutrient deficiencies in crops and their global significance. In: Alloway, B.J. (ed.) *Micronutrient Deficiencies in Global Crop Production*, pp. 41–6. Springer Science+Business Media B.V., Dordrecht (2008).
- [20] Sinclair, A.H., Edwards, A.C.: Micronutrient deficiency problems in agricultural crops in Europe. In: Alloway, B.J. (ed.) *Micronutrient Deficiencies in Global Crop Production*, pp. 225–244. Springer Science+Business Media B.V., Dordrecht (2008).
- [21] Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilisers.
- [22] Decree of Ministry of Agriculture and Rural Development of 18 June 2008 on execution of some regulations of act on fertilizers and on fertilizing.
- [23] PN-EN ISO/IEC 17025:2005. General requirements for the competence of testing and calibration laboratories.
- [24] Chojnacka, K.: The application of multielemental analysis in the elaboration of technology of mineral feed additives based on Lemna minor biomass. *Talanta* 70, 966–972 (2006).
- [25] Gardea-Torresdey, J.L., Tiemann, K.J., Gonzalez, J.H., Cano-Aguilera, I., Henning, J.A., Townsend, M.S. Removal of nickel ions from aqueous solution by biomass and silica-immobilized biomass of *Medicago sativa* (alfalfa). *J. Hazard. Mater.* 49, 205–216 (1996).
- [26] Gardea-Torresdey, J.L., Gonzalez, J.H., Tiemann, K.J., Rodriguez, O., Gamez, G. Phytofiltration of hazardous cadmium, chromium, lead and zinc ions by biomass of *Medicago sativa* (Alfalfa). *J. Hazard. Mater.* 57, 29–39 (1998).
- [27] Tiemann, K.J. Study of alfalfa phytofiltration technology to clean heavy metal contaminated waters. Doctoral Dissertation, University of Texas at El Paso, Chemistry Department (1998).
- [28] Gamez, G., Gardea-Torresdey, J.L., Tiemann, K.J., Parsons, J., Dokken, K., Yacaman, M.J. Recovery of gold (III) from multi-elemental solutions by alfalfa biomass. *Adv. Environ. Res.* 7, 563–571 (2003).
- [29] Yu, Z., Zaifu, Y. Modification of *Solidago canadensis* Cellulose and Its Adsorption Property for Cr (VI). *Environmental Protection of Chemical Industry* 1, 022 (2012) [in Chinese].
- [30] Chojnacka, K., Chojnacki, A., Górecka, H.: Biosorption of Cr³⁺, Cd²⁺ and Cu²⁺ ions by blue-green algae *Spirulina* sp.: kinetics, equilibrium and the mechanism of the process. *Chemosphere* 59, 75–84 (2005).