

OVERVIEW OF TECHNOLOGIES FOR Zn EXTRACTION FROM HYPERACCUMULATING PLANTS: CURRENT STATE OF RESEARCH AND FUTURE DIRECTIONS

G. Jovanović^{1#}, D. Randelović¹, B. Marković¹, M. Sokić¹

¹Institute for Technology of Nuclear and other Mineral Raw Materials, Belgrade, Serbia

Received: September 5, 2022; Accepted: October 10, 2022

Abstract

Phytomining, although predominantly in its early stages on the broader scientific scope of investigation, has garnered interest in metals such as Ni, Au, or rare earth elements (REE). However, Zn pollution from mine wastes, smelters, coal ash and other anthropogenic sources has become an environmental problem. Phytoremediation by hyperaccumulating plants is one of the proposed solutions to mitigate the pollution. Therefore, a need to utilize or dispose Zn hyperaccumulating plants occurred. Since studies of certain hyperaccumulating plant species have been previously conducted in order to extract metal products, similar hydrometallurgical and pyrometallurgical techniques were tried with Zn. The hydrometallurgical route was more focused on producing crude eco catalysts for organic chemistry or separating metal hydroxides by cementation. This was achieved with acid leaching of the ash which was obtained by calcinating the aboveground plant biomass. On the other hand, the pyrometallurgical route was more focused on safe and eco-friendly disposal of combustion products such as ash or biochar, while achieving zero toxic gaseous emissions from biomass pyrolysis. Regardless of the approach further research is needed to investigate the stabilization of metals that remain in the solid fraction during combustion and lowering the metal content in produced gases. So far, none of these technologies have been brought to a semi industrial scale and there is the potential of linking those two approaches together.

Key words: Phytomining; Hyperaccumulators; Metal extraction; Hydrometallurgy; Pyrometallurgy.

1. Introduction

Green remediation technology named “phytomining” or “agromining” describes the usage of plants with the ability of metal hyperaccumulation for the extraction of valuable metals from low-grade ores or metal-rich and polluted soils that otherwise could not be efficiently exploited by conventional metallurgical methods [1]. Although reaching lower prices in the metal market than other elements explored within phytomining technologies (such as nickel, rare earth elements or gold), recovery of Zn becomes more intensively studied due to an increase in Zn pollution from anthropogenic sources (mine wastes, smelters, coal ash, zinc galvanizing, fertilizers etc.). Zn contamination may arise as an important environmental problem, as a very high concentration of in the topsoils of certain areas has already been spotted [2]. In some contaminated surface soils near smelters, the content of Zn exceeds 4%, and deposits of pyrite-rich Zn-Pb mine wastes contain over 1% of Zn [3]. Regular zinc production requires smelting,

which is a high energy-consuming activity, so recently raised energy costs in the world have caused limited Zn production. Consequently, the price of Zn has increased, putting the alternative methods for obtaining zinc into greater focus.

So far, only phytomining of nickel has been commercialized, as technologies for obtaining Ni salts have been initially developed [4, 5] and field-scale trials have proved its economic potential [6]. This paper aims to provide an overview of the current state of the art concerning emerging technologies for Zn extraction from hyperaccumulating plants, highlighting their limitations and outlining future research directions.

Zn is considered to be an essential plant nutrient with a metabolic role, and its average content in plants is around 50-150 ppm [2, 7]. However, certain plant species are able to absorb more than 10,000 ppm of zinc in their aerial parts, and they are known as hyperaccumulators. According to Balafrej et al. [8], total of 28 species with Zn hyperaccumulation ability have been described so far. The majority of them belong to

#Corresponding author: g.jovanovic@itnms.ac.rs

the family *Brassicaceae*, while 12 species belong to the genus *Noccaea*.

Species *Noccaea caerulescens* (J. & C. Presl) F.K. Mayer (syn. *Thlaspi caerulescens* J. Presl & C. Presl) is known as model species for metal hyperaccumulation (Zn, Cd, and Ni) and can extract 2-4% zinc dry weight in its aboveground biomass [9, 10]. On Zn-enriched soils, it can accumulate up to 43,700 ppm of Zn in its tissues [11]. It is also recognized as Cd hyperaccumulator [12]. Similarly, *Sedum plumbizincicola* has been noticed as a perennial Zn and Cd hyperaccumulator plant with significant biomass [13]. *Sedum alfredii* Hance is also a Zn and Cd hyperaccumulator, a Pb accumulator, and a Cu tolerant plant originating from China [14, 15].

Legume species *Anthyllis vulneraria* L. develops metalcolous populations on Zn-polluted sites [16], exhibiting a high accumulation of Zn in roots and shoots. Due to its nitrogen-fixing ability and the existence of symbiotic bacteria, *Mesorhizobium* nodulated subspecies *carpatica* could enhance Zn phytoextraction capabilities [17]. Tree species *Dichapetalum gelonioides* subsp. *Sumatranum* and *Dichapetalum gelonioides* subsp. *pilosum* are so far only known tropical woody Zn-hyperaccumulators [18].

Many hyperaccumulating plants thrive on calamine soils (naturally rich in Zn, Pb, and Cd) as well as on multi-metal polluted sites and therefore possess the ability to accumulate more than one element. This fact influences the technology of biomass treatment prior to single metal recovery.

2. Extracting technology

Extracting metals from hyperaccumulating plant biomass can be conducted by the hydrometallurgical or pyrometallurgical route. The hydrometallurgical route can be performed in two ways: when the leaching agent is applied to the dried biomass, or when the leaching agent is applied to calcined biomass.

Significant studies on Zn hyperaccumulation are exhibited on plants cultivated from the Les Avinières mine site, in Saint Laurent le Minier, Gard, France. The hyperaccumulator plant's biomass was dried and crushed, followed by thermal treatment to destroy the organic matter. The obtained ashes from the site were treated with hydrochloric acid to destroy the remaining organic compounds, finally converting the metallic cations into metal chlorides. Several Zn hyperaccumulating plants originating from Europe were investigated in this area, considering different practical

applications within organic chemistry in mind, since various metal chlorides act as Lewis acids.

2.1. Hydrometallurgical route

Since zinc is not present in nature in its metallic form, its leaching is dependent on the transformation to oxides, carbonates, sulfates and sulfides that are dissolvable in the leaching medium. The main challenge of the hydrometallurgical route is finding the right conditions (time, temperature, and agent) to form the lixiviant that can be further used in different separation techniques of choice.

Losfeld et al. [19] explored an innovative way of producing Lewis acid catalysts by utilizing extracts from Ni(II) hyperaccumulators (*Psychotria douarrei* and *Geissois pruinosa*) and Zn(II) hyperaccumulators (*Thlaspi caerulescens* and *Anthyllis vulneraria*). The harvested biomass was subjected to thermal treatment at 400 °C and the obtained ashes were treated with 1 M hydrochloric acid, upon which the reaction mixture was stirred for 2 h at 60 °C, and filtered on celite. The various mixtures of extracts as Lewis acid catalysts in reaction for the acetylation of anisole, the preparation of 4-methoxy-acetophenone and the benzylation of toluene were used.

It is suggested that when producing Lewis acid catalysis, the purification steps are not mandatory [19]. However, when partial purification is required, it is to select the most active species such as ZnCl₂ or FeCl₃. As a general rule, they conclude that about 2% to 5% of Zn metal is enough to convert 1 mole of substrate in the studied reactions.

Grison et al. [20] focused on the Zn hyperaccumulating species *Anthyllis vulneraria* and investigated the production of an eco-Zn catalyst by studying its impact on the bromination of aromatic substrates. The leaves of *A. vulneraria* were harvested before flowering, and then air-dried and crushed. Again, the obtained solid biomass was calcinated at 400 °C for 5 h and the resulting ash was treated with 1 M hydrochloric acid. The solution of metal chlorides was heated at 60 °C and stirred for 2 h, after which it was filtered on celite, producing the Eco-Zn catalyst. In order to carry out the bromination, the researchers supported the Eco-Zn catalyst by mixing it with montmorillonite K10.

The bromination of aromatic substrates catalyzed by the Eco-Zn catalyst was compared to FeBr₃ and pyridine. The three catalytic systems were studied

through benzene bromination and compared with Sheldon's E factor [21, 22]. The Eco-Zn clearly demonstrated the lowest E-factor compared to classical methods. While using this approach, no further purification was needed and a simple filtration was sufficient to recover the active Eco-Zn. Furthermore, the usage of both conventional catalysts resulted in waste containing toxic compounds. Therefore, the green advantage of using plant-based catalyst is even more pronounced.

During the *Anthyllis vulneraria* cultivation process, a symbiotic interaction between a subspecies of *A. vulneraria* subsp. *carpatica* and a rhizobia-like bacteria, *Rhizobium metallidurans*, has been discovered. This multi-symbiosis phenomenon is especially noted when the microbial biodiversity in the soil is low. Grison et al. [20] concluded that when *A. vulneraria* was inoculated by *R. metallidurans*, the concentration of Zn in shoots increased by 36%.

Losfeld et al. [23] investigated the use of Zn hyperaccumulator *T. caerulea* for the chlorination process of alcohols as green Lucas' reagents. They produced the green Lucas' reagents in two steps. In a first step, the same thermal treatment was applied to *T. caerulea* leaves (400 °C for 5 h) and then the ashes were treated with hydrochloric acid in 1 M and 10 M concentrations. Afterwards, the reaction mixture was stirred for 2 h at 60 °C, and filtered on celite. The resulting solutions were composed of different metal chlorides, and the 10 M solution was chosen. The second step was the conversion of aliphatic alcohols into chloride derivatives. This was done to show that the mixture of metal chlorides demonstrates adequate catalytic properties in the chlorination of alcohols, and again, unlike in conventional processes, there was no advantage in obtaining pure ZnCl₂.

Two classic separation processes were applied and investigated: solid-liquid separation and liquid-liquid extraction, and both methods resulted in partial separation and poor yields. Solid-liquid separation was obtained with pH adjustment for selective precipitation of metal hydroxides and separation by selective precipitation of metal was also considered. Liquid-liquid extraction system was unsuccessful, based on reactive extraction by trioctylamine (TOA) dissolved in toluene and selective complexation with (2-ethylhexyl) phosphoric acid (DEHPA).

Separation by ion exchange was found to be the most effective and rapid process. The acidic solution of the different solvated metal chlorides was treated in

order to remove undesired metal ions with exchange resin. The use of Amberlite IRA 400 resulted in the adsorption of Zn(II) (90% min) on the resin, producing a metal mixture enriched in ZnCl₂. In addition, the green Lucas' reagent could be recycled easily by simple concentration of the aqueous layer at 110 °C.

Escande et al. [24] demonstrated that metallophytes synthesized from two prominent zinc hyperaccumulating plants, *N. caerulea* and *A. vulneraria*, showed potential as a metallo-catalytic platform for the Diels–Alder reactions.

Again, the harvested leaves were air-dried, crushed and calcinated at 400 °C for 5 h, resulting in ash that was added to a 1 M hydrochloric acid solution. The resulting solution of metallic chlorides and oxides was heated at 60 °C and stirred for 2 h reaction mixture, and then filtered on celite. They applied the ion-exchange resin Amberlite IRA 400 to the filtrate to separate the metallic species and obtain fractions enriched in Zn(II) and Ca(II) in order to produce the crude ecological extracts.

The resulting crude plant extract was deposited on montmorillonite K10 as a conventional support, producing an ecological catalyst. This was achieved with the co-grinding methodology by placing montmorillonite K10 in a porcelain mortar and adding the air-dried crude extract to be mixed together.

Furthermore, the Lewis acidity of the crude ecological catalyst was determined by comparing the bands from previous studies that were attributed to pyridine coordinated to Lewis acid sites [25].

The nature of the used Lewis acid catalyst revealed a pronounced effect on the Diels–Alder reaction yield. It was found that the use of the K10-supported ecological catalyst led to the desired organic product in quantitative yield, whereas the application of commercially available ZnCl₂ resulted in only 67% of the same desired product.

Deyris et al. [26] studied the utilization of the two Zn accumulating plant species *Salix "Tordis"* (*Salix schwerinii* × *Salix viminalis*) and *A. halleri* as Lewis acid catalysis in Knoevenagel condensation reaction. The leaves of the respected plants were dried in an oven at 80 °C and then thermally treated in an oven under air flow. The ashing was conducted gradually in two steps: first step from 20 to 350 °C (60 min), and 350 °C (120 min); second step from 350 to 550 °C (60 min), and 550 °C (120 min).

The resulting ash was subjected to a chemical treatment with 6 M HCl, and the leaching solution was heated and stirred at 60 °C for 3 h. The reaction

mixture was filtered through celite, and the resulting yellow filtrate was refluxed for 5 h and then evaporated at 80 °C.

Both ecocatalysts were able to convert aldehydes, but interestingly, the conversion promoted by Eco-S.T. was better than with Eco-A.h. in spite of its lower zinc concentration. Even though the research was focused on zinc salt to act as the active specie as the Lewis acids, surprisingly, the activity of magnesium salt KMgCl_3 showed strong Lewis acid character when compared to K_2ZnCl_4 and MgCl_2 in the conversion of benzaldehyde. These observations were supported by DFT calculations which showed that magnesium is a better Lewis acid when it possesses three chlorine atoms in its first coordination sphere instead of two.

Hazotte et al. [27] studied a novel process to recover cadmium and zinc from a well-known hyperaccumulator plant, *Noccaea caerulescens*. The process was divided into four steps: I - Plant ashing; II - Ash washing to remove potassium (K) and leaching to transfer metals into solution; III - Cd recovery by cementation with Zn powder; IV - Recovery of excess Zn by selective precipitation.

Since ashing is the most sensitive step to avoid Cd volatilization, already observed during calcination of *N. caerulescens* and *Salix viminalis* [28], the *N. caerulescens* plants were calcinated at 620 °C to ashes under strict temperature control. Ash washing has been done twice with deionized water at a pulp density of 20% in order to remove potassium (K), and the ashes were thereupon dried at 100 °C until constant weight. The dried ashes are further leached in 2 M sulfuric acid (H_2SO_4) at a pulp density of 10% at 100 °C on a hotplate, followed by the separation of leachate by vacuum filtration.

Following this leaching process, the metal separation was comprised of two main steps: Cd cementation using Zn powder and the selective precipitation of Zn. Cementation is a simple and effective technique based on the difference in standard redox potentials of metals: ($E^\circ(\text{Cd}^{2+}/\text{Cd}^0) = -0.40 \text{ V}$, $E^\circ(\text{Zn}^{2+}/\text{Zn}^0) = -0.76 \text{ V}$ relative to a standard hydrogen electrode). According to equation (1), it is done by adding Zn powder to a solution containing Cd^{2+} cations, which gives Cd metal and Zn^{2+} cations:



This Cd extraction was achieved by cementation at a Zn:Cd ratio of 2, adjusting the pH of the leachate

solution to 4.5 by adding 1 M NaOH and keeping it at 25 °C for 50 min while magnetically stirring it at 300 rpm. The extraction of Cd was terminated by filtration, and the filtrate was prepared for further Zn extraction by washing the solid residue twice with deionized water.

In order to precipitate the excess of Zn from the solid residue, it was first leached with 7 M HNO_3 to dissolve Cd and Zn. The pH was then increased by addition of 1 M NaOH up to pH of 13.5, to form $\text{Cd}(\text{OH})_2$, while Zn remained in solution as $\text{Zn}(\text{OH})_3^-$ [29, 30]. The same pH treatment was applied to the filtrate after cementation increasing the pH to 13.5 to precipitate $\text{Cd}(\text{OH})_2$ and other hydroxides, and in both cases the solid and liquid phases were separated by vacuum filtration. Then the pH was decreased to 11.0 by adding HNO_3 to precipitate Zn as $\text{Zn}(\text{OH})_2$.

According to Hazotte et al. [27], there were also some other potential applications where cadmium and zinc were used together as (Cd,Zn)S pigments and (Cd,Zn)S thin films in photovoltaic devices. Certain research has shown that the production of eco-green catalysts does not require complete purification of metals [20, 24, 25, 27].

Studying of other Zn hyperaccumulator plant species *Sedum alfredii* and *Sedum plumbizincicola* in terms of Zn extraction was predominantly done in China, since both hyperaccumulators originate from this area.

Yang et al. [31] utilized the Taguchi method in the leaching experiments of *Sedum alfredii*. The hyperaccumulator biomass was first rinsed with deionized water and dried in an oven at 35 °C for around 30 min to get rid of the exterior water, and then grounded. The Taguchi method was applied to the leaching temperature, the leaching agent (molar ratio of NH_4Cl to NH_3), leaching time, and the solid-liquid ratio of the leaching solution.

In these investigations according to the Taguchi method, the leaching temperature had the highest contribution in the experiments. Factor contribution is the amount of improvement obtainable by setting the factor to the desired level. According to the analysis of variance (ANOVA) and in accordance with the Taguchi method, the optimized leaching conditions were obtained as follows: temperature of 60 °C, molar ratio of NH_4Cl to NH_3 of 0.6, leaching time of 2 h, and solid/liquid ratio of 5 to 1.

In that study, a buffer solution of ammonia (NH_3) ammonium chloride (NH_4Cl) was found to be effective

leaching agent for zinc extraction (removing up to 97.79% of Zn) from *S. alfredii*. Heavy metals (zinc, copper, and lead) concentration in leftover biomass was significantly reduced to satisfy the limit set by China legislation related to biosolids disposal.

2.2. Pyrometallurgical route

In phytomining, ashing is commonly used before leaching since it significantly reduces weight and converts the accumulated metals into more suitable forms for leaching. However, the main challenge of the pyrometallurgical route is finding the right conditions that can avoid or at least minimize the volatilization of present metals. Nevertheless, if the metals escape and do not encapsulate, they can still be recovered from condensed gases in the form of bio-oils.

Zhang et al. [32] studied the thermal treatment of Zn hyperaccumulator *Sedum plumbizincicola*, making a distinction between ashing and pyrolysis. The ashing experiment was carried out in a muffle furnace, while the pyrolysis experiment was conducted in a bench-scale chamber-type atmospheric pyrolysis furnace. Both experiments were done at three final temperature settings: 350 °C, 500 °C, and 650 °C with a heating rate of 18 °C per min. The difference between ashing and pyrolysis thermal treatment was that the pyrolysis experiments used a constant pure nitrogen gas flow (1 L per min), ensuring an oxygen-free environment maintained in the furnace chamber. Chemical speciation of samples was then obtained by using a four-step BCR extraction procedure [33]. Upon the increasing the thermal degradation temperature from 350 °C to 650 °C in both ashing and pyrolysis, concentration of Cd and Zn in solid phase had significantly increased, remaining higher in bio-char from pyrolysis process. However, recovery of elements decreased with an increase in temperature in both cases, as zinc and cadmium tend to volatilize during heating processes.

In their summary, the researchers found that ashing could reduce the acid-soluble/exchangeable and reducible fraction of Cd and Zn in *S. plumbizincicola* by about 42% in solid residue, converting 32.5% of cadmium to the oxidisable state and 34.3% of zinc to the residual fraction. However, the pyrolysis could convert a maximum of 80.0% of Cd and 70.3% of Zn from the acid-soluble/exchangeable and reducible fraction in *S. plumbizincicola* to more stable, oxidisable, and residual states. The pyrolysed biochar stability was confirmed by the TCLP test and DTPA extraction. They

concluded that in the treatment of the metal-enriched hyperaccumulator plant, the pyrolysis treatment is superior to ashing in terms of metal encapsulation in the solid residues.

Several research studies have been conducted on the issue of combusting *Sedum plumbizincicola* using a horizontal tube furnace. However, most pyrolysis studies focus on the safe and environmentally friendly disposal of this hyperaccumulator since it is used for phytoextraction on mine waste sites.

Zhong et al. [34] investigated the emission of heavy metals during the thermal disposal of a Zn and Cd hyperaccumulator (*S. plumbizincicola*) biomass, which is produced in the phytoremediation process. They found that it is optimal to maintain the temperature above 700 °C with excess air supply during the thermal disposal of *S. plumbizincicola*. Under reducing conditions, Pb and Cd form heavy metal complex compounds with other metals (Cu, Al, and Ag), while Zn can be found as pure metal, crystalline oxide, sulphide, or it may also form complex compounds with other metals.

Zhong et al. [35] studied the kinetics of the pyrolysis process of *S. plumbizincicola*, the behavior of heavy metals and bio-oil composition. They detected no heavy metals in the gas emitted by pyrolysis, since pyrolysis effectively transferred all metals from the gaseous fractions into the condensed bio-oil. The main components of the pyrolysis oils were acids (at 450 °C) which decreased with increasing pyrolysis temperature. Furthermore, with pyrolysis at 650 °C, the highest yields were obtained for alkenes with low levels of oxygenated compounds in the bio-oil. However, recovery of Zn from the char and Cd from the bio-oil was stated as the further research direction.

2.3. Brief overview

The processes currently developed for recovering metals from biomass include thermal, hydrothermal, or hydrometallurgical processes. To satisfy the demand for "green" technologies, they should be designed as efficiently as possible in terms of chemical reagents, energy, and water usage, in order to maintain a low environmental impact.

To give a clear overview and for easy comparison, the previously studied Zn hyperaccumulator species, the technologies applied to the extraction of Zn, as well as the obtained extraction products, are presented in Table 1.

Table 1 Overview of extraction technologies for various Zn hyperaccumulator species

Hyperaccumulator	Extraction route	Biomass (Temp./°C)	Extraction agent	Extracting Temp./°C	Extracting Product
<i>Anthyllis vulneraria</i>	Hydrometallurgy	Leaf Ash (400)	HCl	60	Lewis acid catalysts
<i>Noccaea caerulescens</i> (syn. <i>Thlaspi caerulescens</i>)	Hydrometallurgy	Leaf Ash (400)	HCl	60	Lewis acid catalysts Lucas' reagents
		Leaf Ash (620)	H ₂ SO ₄	100	Cd(OH) ₂ Zn(OH) ₂
<i>Salix Tordis</i>	Hydrometallurgy	Leaf Ash (350-550)	HCl	60	Lewis acid catalysts
<i>A. halleri</i>	Hydrometallurgy	Leaf Ash (350-550)	HCl	60	Lewis acid catalysts
<i>Sedum alfredii</i>	Hydrometallurgy	Dry plant (35)	NH ₄ Cl/ NH ₃	60	Zn lixiviant
<i>Sedum plumbizincicola</i>	Pyrometallurgy	Dry plant	Heat	350 - 650	Environmentally stable biochar

Therefore, the technology route applied to a specific Zn hyperaccumulator species is more dependent on the end product than the plant itself. However, the pyrometallurgy route is more focused on the disposal of plant biomass by thermal treatment, with the goal of producing environmentally friendly and stable ash or bio-char. Certain Zn hyperaccumulators store a significant concentration of more than one heavy metal (usually Zn, Cd, and Pb) in their biomass. While Zn and Cd can be transferred to aboveground plant parts, thus becoming available for extraction and separation treatments, Pb often remains more concentrated in the plant roots in case the physiological barrier for its transfer to shoots is preserved [2].

When taking into account the hydrometallurgy route, the temperature of leaching extraction depends on the leaching agent employed. If the product is a Lucas reagent (ZnCl₂ + HCl) or various Lewis acid catalysts, the applied leaching agent is hydrochloric acid and the temperature is rather low at 60 °C. This is because the synthesized product does not have to be completely purified metal lixiviant and the applied acid is aggressively reactive. In the case of eco-green Lewis acid catalysts, much research stated that although the studied plant is a Zn hyperaccumulator, the eco catalysts can also include other chlorides that act as Lewis acids, such as FeCl₃ KMgCl₃ etc. These Lewis acid eco catalysts can be used in numerous reactions in organic chemistry such as

Diels–Alder reaction, Knoevenagel condensation reaction, bromination of aromatic substrates, acetylation of anisole, benzylation of toluene and preparation of 4-methoxy-acetophenone etc.

However, when there is a need to separate and purify metals from hyperaccumulators of Cd/Zn, the employed leaching agent is sulfuric acid and the extraction is performed at 100 °C. As a leaching agent, sulfuric acid is commonly used for leaching extraction since it is cheap, readily available, and forms soluble salts that do not interfere with the separation processes of metals from the lixiviant. Under atmospheric conditions, the employed leaching temperatures are between 60 and 100 °C depending on the metal carriers and the need for water vaporization.

Furthermore, the leaf ashes undergo washing before leaching to contribute to the purification process later on, since washing dissolves most K and Ca based salts. Purification is carried out by cementation and sequential filtration, based on the difference in standard redox potentials of metals and pH adjustment.

When the pyrometallurgy route is applied, the raising issues are optimization of different parameters (pyrolysis device, temperature and heating rate, addition of catalyzers, etc.). This is necessary because the concentration of heavy metal contaminants in the solid phase possesses high risk of pollution, since after combustion the plant metals can be retained in bottom ash (solid phase), or fly ash and flue gases (gaseous

fractions). Most studies so far concerning the pyrometallurgical route have focused on volatilization of metals from biomass and preventing secondary pollution, thus enabling safe use of contaminated biomass during the pyrometallurgical process [36, 37]. Nevertheless, they provide crucial insights into combustion and calcination kinetics and mechanisms. Furthermore, on a larger scale, classic commercial firing systems used for biomass combustion are not suited for burning contaminated hyperaccumulator biomass and require redesigning for that unique purpose [38]. Some investigators collected plant bio-oil gained after pyrolysis that has high a concentration of heavy metals, but its study remains a topic for future research [35]. Generally, additional research is needed in terms of stabilizing Zn in the solid fraction and lowering the content of Zn from gases and liquid fractions obtained in the pyrolysis of Zn hyperaccumulating plants.

4. Conclusion

Zinc pollution is increasing worldwide, thus becoming an emerging environmental problem. Simultaneously, the price of Zn is growing on world markets as the current production is highly energy-dependent. Such a situation puts alternative methods for obtaining zinc, such as phytomining, into greater research and practical focus. However, the field of metal phytoextraction is still predominantly in the investigating phase and so far technologies for extracting Zn from plant biomass are still developing, being oriented towards creating green technologies with practical applications and low environmental impact.

Out of 28 currently known hyperaccumulators of Zn, mainly investigations concerning extraction of Zn from biomass have been conducted on *Noccaea caerulescens* and *Sedum plumbizincicola*, due to the high rate of Zn accumulation or ability to develop a significant biomass. Newly discovered woody Zn-hyperaccumulator tropical plants have not been investigated in that sense, which opens the potential for new approaches in studying Zn extraction technologies.

As far as hydrometallurgical studies are concerned, the most prominent ones are those that investigate the production of ecological Lewis catalysts from Zn/Cd hyperaccumulating plants. However, the extraction of purified zinc and cadmium hydroxide by cementation has also been studied. Pyrometallurgical studies are focused more on the safe and eco-friendly disposal of combustion products such as ash or bio-char. So far,

none of them have been brought to a semi-industrial scale, and there is potential for linking those two approaches together.

Regardless of the approach, further research is needed to investigate the stabilization of metals that remain in the solid fraction during combustion and lower the metal content in gaseous products. Overall, integrated approaches, such as bioenergy production coupled with extraction of metals from biomass of hyperaccumulators, can offer more economically viable and environmentally acceptable solutions in the future.

Acknowledgments

This study was financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract number: 451-03-68/2022-14/200023).

5. References

- [1] Dang, P.T., Li, C. (2021) A mini-review of phytomining. *International Journal of Environmental Science and Technology*, 1-14.
- [2] Kabata-Pendias, A. (2011) *Trace elements in soils and plants*. 4th ed. Taylor&Francis, New York, 548.
- [3] Chaney, R.L. (2010) Cadmium and Zinc. In (Hooda, P.S): *Trace element in soils*, Blackwell Publishing Ltd, 409-439.
- [4] Barbaroux, R., Plasari, E., Mercier, G., Simonnot, M-O., Morel, J.L., Blais, J.F. (2012) A new process for nickel ammonium disulfate production from ash of the hyperaccumulating plant *Alyssum murale*. *Sci Total Environ*, 423, 111-119.
- [5] Zhang, X., Laubie, B., Houzelot, V., Plasari, E., Echevarria, G., Simonnot, M-O. (2016) Increasing purity of ammonium nickel sulfate hexahydrate and production sustainability in a nickel phytomining process. *Chem Eng Res Des*, 106, 26-32.
- [6] Simonnot, M., Vaughan, J., Laubie, B. (2021) Processing of Bio-ore to Products. In: (van Der Ent et al. eds) *Agromining: Farming for Metals: Extracting Unconventional Resources Using Plants*, 2nd Edition, Springer Nature Switzerland, 39-51.
- [7] Markert, B. (1992) Establishing of 'Reference Plant' for inorganic characterization of different plant species by chemical fingerprinting. *Water Air & Soil Pollution*, 64, 533-538.
- [8] Balafrej, H., Bogusz, D., Triqui, Z.-E.A., Guedira, A., Bendaou, N., Smouni, A., Fahr, M. (2020)

- Zinc Hyperaccumulation in Plants. A Review. *Plants*, 9, 562
- [9] Foroughi, S., Baker, A.J.M., Roessner, U., Johnson, A.A.T., Bacic, A., Callahan, D.L. (2021) Hyperaccumulation of zinc by *Noccaea caerulescens* results in a cascade of stress responses and changes in the elemental profile. *Metallomics*, 6, 1671–1682.
- [10] Chaney, R.L. (1993) Zinc Phytotoxicity, in *Zinc in Soil and Plants*, Robson, A.D., Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands.
- [11] Peer, W.A., Mahmoudian, M., Freeman, J.L., Lahner, B., Richards, E.L., Reeves, R.D., Murphy, A.S., Salt, D.E. (2006) Assessment of plants from the *Brassicaceae* family as genetic models for the study of nickel and zinc hyperaccumulation. *New Phytologist*, 172, 248–260.
- [12] Tlustoš, P., Břendová, K., Száková, J., Najmanová, J., Koubová, K. (2016) The long-term variation of Cd and Zn hyperaccumulation by *Noccaea* spp and *Arabidopsis halleri* plants in both pot and field conditions. *Int J Phytoremediation*, 18 (2), 110-5.
- [13] Wu, L.H., Liu, Y.J., Zhou, S.B., Guo, F., Guo, X., Baker, A., Smith, J., Luo, Y. (2013) *Sedum plumbizincicola* X.H. Guo et S.B. Zhou ex L.H. Wu (Crassulaceae): a new species from Zhejiang Province, China. *Plant Systematics and Evolution*, 299, 487–498.
- [14] Yang, X., Long, X., Ni, W., Fu, C. (2002) *Sedum alfredii* H: A new Zn hyperaccumulating plant first found in China. *Chinese Scientific Bulletin*, 47, 1634–1637.
- [15] Wu, Y., Santos, S., Vestergård, M., González, A., Ma, L., Feng, Y., Yang, X. (2020) A field study reveals links between hyperaccumulating *Sedum* plants-associated bacterial communities and Cd/Zn uptake and translocation. *Science of The Total Environment*, 805, 150400.
- [16] Escarré, J., Lefèbvre, C., Raboyeau, S. et al. (2010) Heavy metal concentration survey in soils and plants of the les malines mining district (Southern France): implications for soil restoration. *Water Air & Soil Pollution*, 216, 485–504.
- [17] Grison, C.M., Mazel, M., Sellini, A., Escande, V., Biton, J., Grison, C. (2015) The leguminous species *Anthyllis vulneraria* as a Zn-hyperaccumulator and eco-Zn catalyst resources. *Environmental Science and Pollution Research International*, 22 (8), 5667-5676.
- [18] van der Ent, A., Nkrumah, P.N., Aarts, M., Baker, A., Degryse, F., Wawryk, F., Kirby, J. (2021) Isotopic signatures reveal zinc cycling in the natural habitat of hyperaccumulator *Dichapetalum gelonioides* subspecies from Malaysian Borneo. *BMC Plant Biology*, 21, 437.
- [19] Losfeld, G., Blache, P., Escande, V., Grison, C. (2012) Lewis acid catalysts: A potential exploitation for zinc and nickel phytoextraction. *WIT Transactions on Ecology and the Environment*, 162, 563-575.
- [20] Grison, C.M., Mazel, M., Sellini, A. et al. (2015) The leguminous species *Anthyllis vulneraria* as a Zn-hyperaccumulator and eco-Zn catalyst resources. *Environ Sci Pollut Res*, 22, 5667-5676.
- [21] Sheldon, R.A. (2007) The E factor: fifteen years on. *Green Chem* 9:1273.
- [22] Sheldon, R.A. (2008) E factors, green chemistry and catalysis: an odyssey. *Chem Commun* 3352.
- [23] Losfeld, G., Vidal de La Blache, P., Escande, V., Grison, C. (2012) Zinc hyperaccumulating plants as renewable resources for the chlorination process of alcohols, *Green Chemistry Letters and Reviews*, 5 (3), 451-456.
- [24] Escande, V., Olszewski, T.K., Grison, C. (2014) Preparation of ecological catalysts derived from Zn hyperaccumulating plants and their catalytic activity in Diels–Alder reaction, *Comptes Rendus Chimie*, 17 (7-8), 731-737.
- [25] Zaki, M.I., Hasan, M.A., Al-Sagheer, F.A., Pasupulety, L. (2001) In situ FTIR spectra of pyridine adsorbed on SiO₂–Al₂O₃, TiO₂, ZrO₂ and CeO₂: general considerations for the identification of acid sites on surfaces of finely divided metal oxides. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 190 (3), 261-274.
- [26] Deyris, P.A., Bert, V., Diliberto, S., Boulanger, C., Petit, E., Legrand, Y.M. Grison, C. (2018) Biosourced Polymetallic Catalysis: A Surprising and Efficient Means to Promote the Knoevenagel Condensation. *Front. Chem.* 6, 48.
- [27] Hazotte, C., Laubie, B., Rees, F., Morel, J.L., Simonnot, M.O. (2017) A novel process to recover cadmium and zinc from the hyperaccumulator plant *Noccaea caerulescens*. *Hydrometallurgy*, 174.
- [28] Keller, C., Ludwig, C., Davoli, F., Wochele, J. (2005) Thermal treatment of metalenriched biomass produced from heavy metal

- phytoextraction. Environ. Sci. Technol., 39 (9), 3359-3367.
- [29] Moradkhani, D., Rasouli, M., Behnian, D., Arjmandfar, H. Ashtari, P. (2012) Selective zinc alkaline leaching optimization and cadmium sponge recovery by electrowinning from cold filter cake (CFC) residue. Hydrometallurgy, 115, 84-92.
- [30] Shriver, D.F., Atkins, P.W., (2001) Chimie inorganique. Traduction of Inorganic Chemistry, 3rd Edition, De Boeck Université, Bruxelles.
- [31] Yang, J.G., Peng, C.H., Tang, C.B., Tang, M.T., Zhou, K.C. (2009) Zinc removal from hyperaccumulator *Sedum alfredii* Hance biomass. Transactions of Nonferrous Metals Society of China, 19 (5), 1353-1359.
- [32] Zhang, J., Wu, S., Xu, J., Liang, P., Wang, M., Naidu, R., Liu, Y., Bon Man, Y., Wong, M.H., Wu, S. (2021) Comparison of ashing and pyrolysis treatment on cadmium/zinc hyperaccumulator plant: Effects on bioavailability and metal speciation in solid residues and risk assessment. Environmental Pollution, 272, 116039.
- [33] Rauret, G., Lopez-Sanchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, P. (1999) Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. Journal of Environmental Monitoring 1 (1), 57-61.
- [34] Zhong, D.X., Zhong, Z.P., Wu, L.H., Xue, H., Song, Z.W., Luo, Y.M. (2015) Thermal characteristics and fate of heavy metals during thermal treatment of *Sedum plumbizincicola*, a zinc and cadmium hyperaccumulator. Fuel Processing Technology, 131, 125-132.
- [35] Zhong, D., Zhong, Z., Wu, L., Ding, K., Luo, Y., Christie, P. (2016) Pyrolysis of *Sedum plumbizincicola*, a zinc and cadmium hyperaccumulator: pyrolysis kinetics, heavy metal behaviour and bio-oil production. Clean Technologies and Environmental Policy, 18 (7), 2315-2323.
- [36] Nzihou, A., Stanmore, B. (2013) The fate of heavy metals during combustion and gasification of contaminated biomass—a brief review. Journal of hazardous materials, 256, 56-66.
- [37] Song, U., Park, H. (2017) Importance of biomass management acts and policies after phytoremediation. Journal of Ecology and Environment, 41, 1715.
- [38] Kovacs, H., Szemmelveisz, K. (2017) Disposal options for polluted plants grown on heavy metal contaminated brownfield lands—a review. Chemosphere, 166, 8-20.

PREGLED TEHNOLOGIJA ZA EKSTRAKCIJU Zn IZ BILJAKA HIPERAKUMULATORA: TRENUTNA ISTRAŽIVANJA I BUDUĆI PRAVCI

G. Jovanović^{1#}, D. Randelović¹, B. Marković¹, M. Sokić¹

¹Institute for Technology of Nuclear and other Mineral Raw Materials, Belgrade, Serbia

Primljen: 5. septembar 2022.; Prihvaćen: 10. oktobar 2022.

Izvod

Iako u ranoj fazi istraživanja fitorudarenje je podstaklo interesovanje u ispitivanju metala poput Ni, Au i retkih zemalja (REE). Međutim zagađenje cinkom iz rudničkog otpada, topionica, letećeg pepela i drugih antropogenih izvora postalo je ekološki problem. Fitoremedijacija hiperakumulirajućim biljkama pokazala se kao jedno od rešenja za smanjenje tog zagađenja. Stoga se pojavila i potreba za korišćenjem ili odlaganjem biljaka-hiperakumulatora cinka. Pošto su ranije sprovedena ispitivanja određenih hiperakumulatora za ekstrakciju metala, slični hidrometalurški i pirometalurški postupci ispitani su i za Zn. Hidrometalurški pravac ispitivanja fokusiran je na proizvodnju grubih eko katalizatora za potrebe organske hemije ili separaciju metalnih hidroksida cementacijom. Ovo je postignuto kiselim luženjem pepela dobijenog sagorevanjem nadzemne biomase. S druge strane, pirometalurški pravac više je fokusiran na bezbedno i ekološki prihvatljivo odlaganje proizvoda sagorevanja poput pepela i biočadi, uz postizanje nulte emisije toksičnih gasova pri pirolizi biomase. Bez obzira na pristup, potrebna su dalja istraživanja kako bi se ispitala stabilizacija metala koji zaostaju u čvrstoj frakciji tokom sagorevanja kao i smanjenje sadržaja metala u emitovanim gasovima. Do sada nijedna od ovih tehnologija nije dovedena do poluindustrijskih razmera u ispitivanjima, mada postoji potencijal u povezivanju ova dva pristupa.

Ključne reči: Fitorudarenje; Hiperakumulatori; Izdvajanje metala; Hidrometalurgija; Pirometalurgija.
