A review on the status and development of hyperaccumulator harvests treatment technology

Yongzhen Fu1,a, Shaohong You1, 2, *, and Xiangpin Luo1
1*Environmental Engineering, Guilin University of Technology, Guilin, Guangxi, 541004, China
2Guangxi Key Laboratory of Environmental Pollution Control Theory and Technology for Science and Education Combined with Science and Technology Innovation Base, Guilin, Guangxi, 541004, China
*2120180274@glut.edu.cn
*Corresponding author’s e-mail: 646761963@qq.com

Abstract. Phytoremediation is a low cost and green remediation technology, which is widely used in remediation of soil polluted by heavy metals such as cadmium and manganese. However, with the extension and implementation of phytoremediation technology in soil remediation, the disposal of a large number of hyperaccumulator plant harvests has become a hot topic in the field of phytoremediation. These harvests generally contain high concentrations of heavy metals, which can cause secondary contamination if improperly disposed of. This paper reviews the traditional disposal techniques that can be processed by composting process, compaction landfill, Liquid phase extraction, incineration, Ashing and Pyrolysis as well as emerging resource disposal technologies such as phytomining and supercritical water technology and identifies current issues with phytoremediation plants disposal. The possible research directions in the future are also prospected.

1. Introduction
Soil is the basic resource for human survival, the central link between the organic and inorganic, biological and non-biological worlds in the natural environment, and an important part of the human ecological environment. [1]With the unreasonable development and utilization of soil mineral resources, sewage irrigation, and the extensive application of chemical fertilizers and pesticides, the rapid industrialization and urbanization have discharged a large number of heavy metals into the ecosystem. After heavy metals enter the soil ecosystem, they stress the soil ecosystem through the interaction with soil multi-media components[2], damage the living environment of plants and microorganisms, resulting in the deterioration of soil quality, thus posing a threat to crops. The overall state of the country's soil environment is not optimistic. In some areas, soil pollution is serious, the quality of cultivated land is worrying, and the soil environment in land abandoned by industry and mining is a serious problem. The overall rate of soil exceeding the national standard is 16.1%[3].

In recent years, with the rapid development of phytoremediation technology, hyperaccumulator has gradually become the focus of environmental engineering research. However, the transfer and accumulation of heavy metals in remediation plants also brings a "hidden" hazard of different properties. How to dispose of hyperaccumulator plant harvest has not been paid attention to, and the harvest has been in the primary stage of research. Once improperly disposed, it will cause a large
number of "secondary pollution", which also makes the safe disposal of remediation plants an urgent problem to be solved.

2. Traditional disposal techniques for hyperaccumulator harvests

Domestic and foreign scholars have conducted some studies on the disposal of restored plants as hazardous wastes based on the principles of harmlessness, recycling and reduction. The advantages and disadvantages of various technologies and the feasibility of their application are mainly introduced below.

2.1. Composting process

Composting is an efficient organic solid waste treatment method. Through the degradation and stabilization of plants by microorganisms, the biomass of plants can be reduced for subsequent transportation and centralized treatment. Hetland et al. [4] used the sunflower (Helianthus Annuus) biomass after repairing Pb soil pollution as raw material, crushed it into particle size ≤ 0.16cm, and then placed in a 125ml borosilicate container for compost. After two months of continuous aeration, it was found that the Helianthus Annuus biomass decreased by about a quarter. However, it was found that some Pb in Helianthus Annuus could be dissolved by organic solvent in the leaching experiment of composting products. Therefore, the products after composting need to be further treated before they can be put into the environment. Singh and Kalamdhad [5] found in composting Eichhornia crassipes for 30 days that the heavy metals were mostly present in the composting products in the form of residues, with Cd and Cu concentrations increasing less than other elements. Cao et al. [6] conducted a composting experiment on Pteris vittata L which is rich in As under the condition of continuous aeration. After 120 days of composting, the biomass of Pteris vittata L was reduced by about 35%, and most of the As would be dissolved in leachate during composting.

2.2. Compaction landfill

Municipal solid waste (MSW) is often treated by compressed landfill, and some foreign scholars have proposed the method of compressed landfill to treat the hyperaccumulator after heavy metal enrichment[7]. The compressed landfill system consists of a compression system and a leachate collection device. The biomass is compressed by means of physical pressure to reduce volume. The compaction method is similar to the composting method. During the treatment process, the leachate containing high heavy metals will be produced, and the leachate will need secondary treatment. Compacting landfills take less time to process than composting for the same biomass of plants. However, the leachate collected during compaction must be retreated, otherwise heavy metals may re-enter the environment, which will greatly increase the treatment cost. Therefore, compaction landfill can only be used as a pretreatment method for hyperaccumulator. At present, the technology of extracting heavy metals from plants by chelating agents is still in the laboratory research stage, but has not been popularized in industry, and more leaching agents need to be further studied and improved.

2.3. Liquid phase extraction

In 1995, Salt et al. [8] proposed the method of liquid phase extraction to extract heavy metals from Hyperaccumulator. The extraction agent and extraction conditions are the key to liquid phase extraction. Hetland et al. [4] used EDTA as a chelator to extract Pb from sunflowers (Helianthus Annuus). When the ratio of Pb content to EDTA in plants is 1:4.8 and under the condition of pH 4.5 at the same time, 98.5% of Pb in plants can be extracted by continuous extraction. Moreover, the extracted heavy metals and chelating agents can be reused, and the residue generated during the experiment can be directly discharged. It can be seen that the liquid phase extraction is an effective method for hyperaccumulator products[9].
2.4. Incineration
The method of incineration is a process in which the super-enriched plant products after remediation of heavy metal pollution in soil are put into an incinerator and pumped into the air, and the plants are oxidized and decomposed under the conditions of oxygen and high temperature[10, 11]. During the incineration process, organic substances in plants are decomposed. Heavy metals are oxidized with oxygen at high temperatures, and are enriched in ash and fly ash, or some heavy metals with low boiling points are volatilized into the air. Some physical properties of heavy metals can be used to recover heavy metals in the process of super-enrichment by incineration. Heavy metals will not be destroyed in the process of incineration. Volatile heavy metals such as Cd, Hg and As will be completely gasified under high temperature conditions. It can be considered to use the principle of condensation to recover heavy metals in the incinerator tail gas treatment according to different condensation points of heavy metals. The non-volatile heavy metals will remain in the bottom ash or be brought into the fly ash. After collecting the bottom ash and fly ash, the centralized treatment can prevent the heavy metals from polluting the environment again. Lu et al.[12] used the horizontal tube furnace under a temperature of 550, 750, 950℃, respectively to burn Cd/hyperaccumulation plants with recent experiments, the results showed that Cd in plants with the increase of the burning temperature more Cd to evaporate into the flue gas, when burning temperature is 850 ℃, Cd in Sedum alfredii Hance ash content is 590 mg/kg, and only 57.8 mg/kg in bottom ash, shows that under the temperature on the extraction of the day about 90% of the Cd have evaporated into the fly ash. Zhong D X et al.[13] also conducted an incineration experiment on Sedum plumbizincicola to study the characteristics of heavy metals (Cd, Zn, Pb) in ore companion Sedum plumbizincicola at high temperature. The results show that when the incineration temperature is less than 380℃, Cd can be enriched in the bottom ash. When the temperature is 350-650℃, 95% and 90% Pb and Zn are respectively in the bottom ash; when the temperature is > 650℃, a large amount of Zn and Zn in Sedum plumbizincicola volatile into the fly ash.

Incineration is currently an effective method for the disposal of super-enriched plants, but attention must be paid to the temperature conditions during the treatment to avoid atmospheric pollution caused by volatile heavy metals entering the atmosphere. At present, incineration is one of the commonly used methods for the treatment of super-enriched plant remediation products.

2.5. Ashing
Ashing can significantly reduce the weight and volume of harvested plants. Hetland et al.[4] explored the feasibility of lab-stage incinerators, in which plants containing lead, which is mostly found in ash, were burned with coal and lost 90% of their weight. These results show that the method is feasible in plant reduction, but it still needs experimental data and how to deal with ash is still a problem to be solved. Heavy metals from ash can be recovered, but the feasibility and cost of the recovery process require further study.

2.6. Pyrolysis
Pyrolysis refers to the process of decomposition of substances at high temperature under the condition of hypoxia or anaerobic conditions. Three phase products, namely pyrolytic carbon (solid phase), pyrolytic oil (liquid phase) and pyrolytic gas (gas phase), are produced after the pyrolysis of plants[14]. No harmful gases will be produced during the pyrolysis process, and the pyrolysis gas can be used as fuel. Before the pyrolysis of hyperaccumulator, they also need to be air-dried and dehydrated in order to reduce the moisture in the bio-oil. Before the pyrolysis, they need to be ground as much as possible, because the smaller particles can react quickly and completely. Process parameters in the process of decomposition at high temperature: raw material properties, pyrolysis temperature, retention time, heating rate, reaction atmosphere and additives, etc., will affect the types of products. The distribution of heavy metals is also different in tar, coke and pyrolysis gas under different pyrolysis conditions. Lievens et al.[15, 16] studied the distribution of heavy metals in the pyrolytic products of Betula and sunflower at different temperatures (350, 400, 500, 600℃) and
different carriers (sand and fumigated silica). The results show that heavy metals are easy to be enriched in coke during low-temperature pyrolysis, and heavy metals Cd is more volatile than Cu, Pb and Zn at 400 °C pyrolysis temperature, among which Pb and Cu are mainly retained by silica fume. Wu Xianhao et al.[17] carried out pyrolysis experiments on hyperaccumulator *Pteris vittata* L after soil restoration, and studied the migration characteristics of various metals. The results showed that the high temperature promoted the volatilization of heavy metals, and the intensity was Pb=Cd>, Zn >, Cr >Cu≈Ni in turn. When the pyrolysis temperature was between 500-900 °C, heavy metals were highly enriched in the bottom ash, which was convenient for recycling and reuse. The leaching characteristics of heavy metals in the bottom ash decreased as the pyrolysis temperature increased. This indicates that high-temperature pyrolysis may promote more stable morphological changes of heavy metals in plants, which can reduce secondary pollution.

3. Emerging resource disposal technologies

3.1. Phytomining technology

The process by which heavy metals are absorbed by hyperaccumulators and obtained from plants is called Phytomining[18]. With the help of a solution of ammonium, the flax can absorb gold from the soil into the plant. The flax can be burned into ashes to obtain gold, which is of high economic value because of the high price of gold[19]. This technology has also been used to obtain nickel, another metal of high economic value. According to the calculation, each hectare of nickel hyperaccumulator can recover 71 kilograms of nickel at one time[20]. *Salix Viminalis* is used not only as an energy plant, but also to hyperaccumulate cadmium[21, 22]. It can be used to repair cadmium contaminated areas. In addition, *Thlaspi caerulescens* and *Sedum plumbizincicola* can be used to remediation of zinc-contaminated soil, which can be used as a plant zinc ore after harvest and incineration[23].

Rosenkranz et al.[24] believed that remediation plants need strong enrichment ability and large biomass for target metals, so as to achieve considerable metal output and lay economic foundation for large-scale industrialization. With the in-depth study of Phytomining technology, in order to achieve the maximum metallurgical efficiency, we should make the hyperaccumulator extraction technology of different target metals targeted, and at the same time look for the repair plants with higher metallurgical efficiency[25]. In addition, the technological parameters of Phytomining are optimized constantly, so that Phytomining can be applied commercially on a large scale and produce more environmental and resource benefits and economic benefits.

3.2. Supercritical water technology

When the temperature and pressure of water exceed the critical point (374°C, 22.1 Mpa), it is called Supercritical water (SCW). Supercritical water technology, which transforms plants into gases (CO, H₂, CO₂, CH₄ and N₂) and liquids (liquid fuel and valuable chemicals) through supercritical water biomass gasification and liquefaction processes, respectively[26]. It is an emerging energy conversion technology. Carrier M et al.[27] used subcritical water (300°C, 25MPa) and supercritical water (400°C, 25MPa) to treat the fern (*Pteris vittata* L.) leaves contaminated with As and uncontaminated, and found that the biomass of the leaves decreased by 70%~77%. Supercritical water treatment reduced the content of carbon and inorganic substances in the leaves of *Pteris vittata* L. The high content of As, Fe and Zn in the As contaminated *Pteris vittata* L. leaves decreased the content of carbon in the liquid phase and inhibited the formation of cyclopentenone and benzenediol. Al, Fe, P, Zn and Ca are mainly in the solid phase, while As and S are transferred to the liquid phase. As in the liquid phase can be removed by adsorption by hydrated iron oxide. However, under supercritical conditions, some inorganic salts such as NaCl and Na₂SO₄, insoluble in supercritical water, tend to form precipitation, which may clog equipment or reduce catalyst efficiency through interaction[28]. In addition, because some heterocyclic atoms (such as Cl and S) can be converted into corresponding acids (such as HCl and H₂SO₄), the liquid is highly corrosive to the equipment[29].
3.3. Synthesis of nanoparticles

Compared with the traditional technology of synthesizing metal nanoparticles, which is expensive and harmful to the environment, the biosynthesis of metal nanoparticles by repairing plants has gradually become a new green resource recovery method[30]. Qu J et al.[31] synthesized Cu/ZnO nanoparticles by extraction of chlorophyll and metal from Brassica juncea L., a Cu hyperaccumulator, and obtained carbon nanotubes (CNTs) from the vascular bundles of Brassica juncea L. as raw materials. Using Zn zinc hyper-accumulator (Sedum alfredii Hance) plants as raw material, Wang D et al.[32] synthesized the zinc oxide nanoparticles (ZnO NPs) with photocatalytic activity against organic pollutants. These studies have broken through the traditional idea of remediation plant disposal and constitute a new insight into recycling of hyperaccumulator plants and phytoremediation resource disposal.

3.4. Hydrothermal upgrading

Hydrothermal upgrading (HTU) is a technology to transform biomass to high heat value biofuels. In general, biomass can be treated with water for 5~20 min under subcritical conditions (300~350 °C, 10~18 MPa) to produce organic liquid with heat value of 30~35 MJ·kg⁻¹, i.e. bio-crude oil[33]. In recent years, some researchers have found that hydrothermal upgrading can be used as a resource disposal technology for heavy metal enrichment plant biomass. Le Clercq et al.[34] confirmed that hydrothermal upgrading technology could effectively recover Ni from Ni hyperaccumulator and obtain biofuels. Yang et al.[35] used hydrothermal upgrading to treat Sedum alfredii Hance harvest. After treatment for 60s under the condition of 22.1Mpa, 37CTC and 10mg/K₂CO₃, over 99.5% of heavy metals (Cu, Pb and Zn) were removed from sedum alfredii Hance harvest.

4. Prospect

The disposal of hyperaccumulator plant harvest is a hot topic in the field of phytoremediation. At present, there are few studies on the disposal of hyperaccumulator plant harvest. The treatment of hyperaccumulator plants is mainly based on the disposal technology of waste. The process is relatively simple, and there are few advanced technologies aiming at the characteristics of remediation plants. It is necessary to conduct more systematic and in-depth research on the technical principle of hyperaccumulator plants recovery, so as to improve its recovery efficiency and utilization value. The disposal of hyperaccumulator plant harvest needs special technical support and special technological principle and technology, so that its comprehensive utilization can have certain economic benefits and pollutants can be properly treated to avoid secondary pollution. In addition, there are few studies on the economic feasibility assessment and environmental impact assessment of the disposal technology of hyperaccumulator plant harvests, and such studies should be strengthened in the future.

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References

[1] Xing Y, Qiao D, Zhu G, et al. Research Progress of Heavy Pollution in Soil and Phytoremediation Technology[J]. Chinese Agricultural Science Bulletin, 2014, 30(17) :208-214.

[2] Newman, M. C. , McIntosh, A. W. , (1991) Metal ecotoxicology:Concepts and applications[M]. Boca Raton:Lewis Publishers& CRC Press.

[3] Ministry of Environmental Protection, Ministry of Land and Resources. Bulletin of the National Survey of Soil Pollution[R]. 2014, 04, 17.

[4] Hetland M D, Gallagher J R, Daly D, et al. Processing of plants used to phytoremediate lead contaminated sites [M]. Leeson A, Foote E A, Bankes M K, et a (1Eds.) . The sixth international in situ and on-site bioremediation symposium, San Diego, California, 4 -7, June.
Battelle Press. Columbus, Richland, 2001:129-136.

[5] Singh J, Kalamdhad A S. Concentration and speciation of heavy metals during water hyacinth composting [J]. Bioresource Technology, 2012(3) , 124:169-17.

[6] Cao X, Ma L, Shiralipour A, et al.Biomass reduction and arsenic transformation during composting of arsenic-rich hyperaccumulator *Pteris vittata* L[J]. Environmental Science & Pollution Research International, 2010, 17(3) :586.

[7] Ghosh, M, Singh, S. P. A review on phytoremediation of heavy metals and utilization of its byproducts[J]. Applied Ecology & Environmental Research, 2005, 3(1) :1-18.

[8] Salt D E, Blaylock M, Kumar N P, et al.Phytoremediation: A novel strategy for the removal of toxic metals from the environment using plants[J]. Biotechnology, 1995, 13(5) :468-474.

[9] Sas-NowosielskaA , Kucharski R , Ma?Kowski E , et al.Phytoextraction crop disposal--an unsolved problem. [J]. Environmental Pollution, 2004, 128(3) :373-379.

[10] Yan X L , Chen T B , Liao X Y , et al.Arsenic transformation and volatilization during incineration of the hyperaccumulator *Pteris vittata* L. [J]. Environmental ence& Technology, 2008, 42(5) :1479.

[11] Lu S , Du Y , Zhong D , et al.Comparison of Trace Element Emissions from Thermal Treatments of Heavy Metal Hyperaccumulators[J]. Environmental ence& Technology, 2012, 46(9) :5025.

[12] Lu S, Du Y, Zhong D, et al.Comparison of trace element emissions from thermal treatments of heavy metal hyperaccumulators[J]. Environmental Science and Technology, 2012, 46(9) :5025-5031.

[13] Zhong D X, Zhong Z P, Wu L H, et al.Thermal characteristics and fate of heavy metals during thermal treatment of Sedum plumbizincicola, a zinc and cadmium hyperaccumulator[J]. Fuel Processing Technology, 2015, 131(8) :125-132.

[14] Shang P, Sheng K, Liu J, et al. Research progress of heavy metal transformation and migration behavior during pyrolysis of phytoremediating plants[J]. Renewable Energy Resources, 2020, 38(03) :285-291.

[15] Lievens C, Yperman J, Vangronsveld J, et al.Study of the potential valorisation of heavy metal contaminated biomass via phytoremediation by fast pyrolysis: Part I. Influence of temperature, biomass species and solid heat carrier on the behaviour of heavy metals[J]. Fuel, 2008, 87(10-11) :1894-1905.

[16] Lievens C, Yperman J, Cornelissen T, et al.Study of the potential valorisation of heavy metal contaminated biomass via phytoremediation by fast pyrolysis: Part II: Characterisation of the liquid and gaseous fraction as a function of the temperature[J]. Fuel, 2008, 87(10–11) :1906-1916.

[17] Wu X , LI J , Wang Y, et al.Fate and leaching characteristic of heavy metals during pyrolysis of hyperaccumulator[J]. Acta Scientiae Circumstantiae, 2017, 37(7) :2707-2712.

[18] A. van der Ent, A. J. M. Baker, M. M. J. van Balgooy, A. Tjoa. Ultramafic nickel laterites in Indonesia (Sulawesi, Halmahera) : Mining, nickel hyperaccumulators and opportunities for phytomining[J]. Journal of Geochemical Exploration, 2013, 128.

[19] Anderson CWN, Brook RR, Chiarucei A. Phytomining for nickel , thallium and gold[J]. Journal of GeochemicalExPloration, 1999, 67:407~415.

[20] Robinson B H, Brooks R R, Howes A W, Kirkman J H, Gregg P E H. The potential of the high-biomass nickel hyperaccumulator*Berkheyacoddii* for phytoremediation and phytomining[J]. Journal of Geochemical Exploration, 1997, 60: 115-126.

[21] Bungar R, Hüttle R F. Production of biomass for energy in post-mining landscapes and nutrient dynamics[J]. Biomass and Bioenergy, 2001, 20: 181-187.

[22] Hammer D A ,Kayser A , Keller C . Phytoextraction of Cd and Zn with Salix viminalis in field trials[J]. Soil Use and Management, 2010, 19(3) :187-192.

[23] Brown S L, Chaney R L, Angle J S. Zinc and cadmium uptake by hyperaccumulator *Thlaspi caerulescens* and bladder campion for zinc and cadmium contaminated soil[J].
[24] Rosenkranz, Kidd, Puschenreiter. Effect of bacterial inoculants on phytomining of metals from waste incineration bottom ash[J]. WASTE MANAGE, 2018.

[25] Zhang X, Laubie B, Houzelot V, et al. Increasing purity of ammonium nickel sulfate hexahydrate and production sustainability in a nickel phytomining process[J]. Chemical Engineering Research and Design, 2016, 106.

[26] Loppinet-Serani A, Aymonier C, Cansell F. Current and foreseeable applications of supercritical water for energy and the environment[J]. Chemsuschem, 2010, 1(6):486-503.

[27] Carrier M, Loppinet-Serani A, Absalon C, et al. Conversion of fern (Pteris vittata L.) biomass from a phytoremediation trial in sub- and supercritical water conditions[J]. Biomass & Bioenergy, 2011, 35(2):872-883.

[28] Loppinet-Serani D A, Aymonier C, François Cansell. Supercritical water for environmental technologies[J]. Journal of Chemical Technology & Biotechnology, 2010, 85(5):583-589.

[29] Kritzer P. Corrosion in high-temperature and supercritical water and aqueous solutions: a review[J]. J. supercriti. fluids, 2004, 29(1):1-29.

[30] Ahmed S, Annu, Ikram S, et al. Biosynthesis of gold nanoparticles: A green approach[J]. J PhotochemPhotobiol B, 2016:141-153.

[31] Qu J, Luo C, Cong Q, et al. Recycling of the hyperaccumulator Brassica juncea L.: Synthesis of carbon nanotube-Cu/ZnO nanocomposites[J]. Journal of Material Cycles & Waste Management, 2014, 16(1):162-166.

[32] Wang D, Liu H, Ma Y, et al. Recycling of hyper-accumulator: Synthesis of ZnO nanoparticles and photocatalytic degradation for dichlorophenol[J]. Journal of Alloys and Compounds, 2016, 680:500-505.

[33] Srokol Z, Bouche A G, Estrik A V, et al. Hydrothermal upgrading of biomass to biofuel; studies on some monosaccharide model compounds[J]. Carbohydrate Research, 2004, 339(10):1717-1726.

[34] Clercq M L, Adschiri T, Arai K. Hydrothermal processing of nickel containing biomining or bioremediation biomass[J]. Biomass & Bioenergy, 2001, 21(1):73-80.

[35] Yang J G, Tang C B, He J, et al. Heavy metal removal and crude bio-oil upgrade from Sedum alfredii Hance harvest using hydrothermal upgrading. [J]. Journal of Hazardous Materials, 2010, 179(1-3):1037-1041.