Energy plants as biofuel source and as accumulators of heavy metals

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Abstract

Fossil fuel depletion and soil and water pollution gave impetus to the development of a novel perspective of sustainable development. In addition to the use of plant biomass for ethanol production, plants can be used to reduce the concentration of heavy metals in soil and water. Due to tolerance to high levels of metals, many plant species, crops, non–crops, medicinal, and pharmaceutical energy plants are well-known metal hyperaccumulators. This paper focuses on studies investigating the potential of *Miscanthus* sp., *Beta vulgaris* L., *Saccharum* sp., *Ricinus communis* L. *Prosopis* sp. and *Arundo donax* L. in heavy metal removal and biofuel production. Phytoremediation employing these plants showed great potential for bioaccumulation of Co, Cr, Cu, Al, Pb, Ni, Fe, Cd, Zn, Hg, Se, *etc*. This review presents the potential of lignocellulose plants to remove pollutants being a valuable substrate for biofuel production. Also, pretreatments, dealing with toxic biomass, and biofuel production are discussed.

Keywords: pollutants; bioaccumulation; bioenergy.

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1. INTRODUCTION

Heavy metals and metalloids present a great problem because they cannot be degraded in nature, therefore upon release they enter the natural biogeochemical cycles. The sources of these pollutants are the metallurgical and petrochemical industries, municipal landfills, wastewaters, fertilizers, pesticides, burning fossil fuels emissions, *etc*. The threat that heavy metals present causes decreased quantity and quality of crop yields and agricultural products, and loss of fertile soil, freshwater, and ecosystems [1]. Furthermore, problems related to energy and environmental protection are one of the burning issues in the 21st century [2]. Biogas/biomethane represent the future of green energy. The world's energy consumption should be taken into account the pollution caused by the use of fossil fuels accompanying the growth of total energy consumption [3]. Uncontrolled human activity, as well as energy consumption, has led to an increase in environmental pollution. Therefore, the use of energy plants in phyto and bioremediation could be a sound solution for a cleaner future [4]. Some plants have natural resistance and the ability to accumulate heavy metals in their tissues without symptoms of poisoning [5]. Phytoremediation is a green technology that is widely accepted due to its natural removal of pollutants [6]. The presence of heavy metals in the soil harms the growth and development of plants, as well as the loss of mineral balance, and thus the loss of yield and crop quality [7]. Increased interest in energy crops stems from their potential use as a carbon-neutral and environmentally friendly renewable and sustainable power resource [8]. Energy crops can be divided into two groups. The first group of annuals includes sweet and fiber sorghum, kenaf, and oilseed rape. While the second group of perennials is further classified into agricultural, such as wheat, sugar beet, cardun, reed, miscanthus, *etc.* and forest species: willows, poplars, eucalyptus, and black grasshopper [9]. Increased bioenergy demands, as well as a noticeable tendency towards renewable energy sources, have conditioned the increasing use of biomass. In line with this, sound solutions should be within the energy crops for biofuels and biomethane production [8], thus used in sustainable phytoremediation of metal-contaminated soils [10,11]. Short rotation coppice (SRC) are energy plants with a high ability to remediate heavy metals and organicpollutants. The advantage of using these plants is in their viability is up to 30 years before replanting [12].

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1. 1. Phytoremediation capacities of energy plants

The synergy of potential energy crops in phytoremediation programs is a new direction in obtaining energy sustainability. It includes the creation of new bioenergy resources and the phytoremediation of contaminated land. The reason for the use of some energy crops is reflected in their high phytoremediation potential. These are primarily *Miscanthus* sp., *Ricinus* sp., *Jatropha* sp. and *Populus* sp. Furthermore, the popularization of phytoremediation has contributed to a better insight into the process of removing pollutants from the environment. A wide range of physical, chemical, and biological remediating processes such as soil washing, chemical, and physical solidification/stabilization, chemical oxidation or reduction, *etc*. are used but marked as invasive. Due to resource and financial conservation strategies, environmental protection strategies such as green remediation/ phytoremediation have been recognized as promising [13]. Therefore, it is believed that energy crops would contribute not only to energy but also to environmental stability [14]. Recently, heavy metal removal by energy plants has been linked to thermochemical treatments. The method of valorizing contaminated biomass from phytoremediation and increasing metal and energy recovery are gaining attention. Biochemical conversion coupled with thermal treatment enables the extraction of Hg and Cd from biomass before further processing. Therefore, bioenergy plants are used to remove pollution and produce biofuels [15].

1. 2. Prerequisites for biofuel production

Lignocellulosic biomass (LCB) is composed of cellulose, hemicellulose, and lignin polymers, in which the ratio of the polymer depends on their origin [16]. Biochemical conversion of plant biomass into biofuels and biomaterials includes a pretreatment, via a combination of ozonolysis, alkaline, or acids, before enzymatic hydrolysis of polysaccharides into sugars [17,18]. After that step, sugars are converted to fuel molecules or other biomaterial molecules yeast or bacteria [19].

2. PHYTOREMEDIATION AND BIOFUEL PRODUCTION OF ENERGY PLANTS

2. 1. *Miscanthus.* sp

2. 1. 1. Phytoremediation

Miscanthus sp. is related to warmer regions, although one perennial species *Miscanthus gigantheus* can withstand harsh weather conditions in Central Europe [22]. *Miscanthus spp* is shown to be a promising genus for biofuel production regarding its lignocellulose content. *M × giganteus*, *M. sacchariflorus*, and *M. sinensis* clones were investigated by Arnoult *et a*l. [23]. *Miscanthus* is recognized as a poor heavy metal bioaccumulation plant. However, it has bioaccumulation potential for Cd, Cr, Cu, Ni, Pb, and Zn. It was reported that *M. sacchariflorus* heavy metal oncentration was 10, 2, and 20 ppm for Zn, Cd, and Pb, respectively. Furthermore, *M. sacchariflorus* biomass production was not disrupted in sewage sludge with the presence of Fe, Mn, Mo, B, Ba, Sr, As, Sn, Li, and Ti [24]. This plant, in particular, *M. × giganteus* J. M. Greef & Deuter ex Hodk. & Renvoize and *M. Sinensis* are also known as excellent phytoremediation species [12, 25-27]. The phytoremediation potential of *Miscanthus giganteus* grown on soil contaminated with Hg and Cd was reflected in resistance to cadmium (45–6758 μg kg $^{-1}$), and mercury (8.7–108.9 μg kg $^{-1}$). It was also found that in three years *Miscanthus giganteus* accumulated up to 293.8 μg Cd and 4.7 μg Hg per year in aboveground biomass, without a significant impact on biomass growth and productivity [27]. *M. giganteus* sequestrates inorganic pollutants in roots. According to Zhao *et al*. [26], *Miscanthus sinensis* is also a very suitable candidate for phytoremediation of soil contaminated with a high concentration of Hg (up to 706 mg kg^{-1}). Positive effects of *M. sinensis* on the diversity and abundance of soil microbial community are shown, also essential for phytostabilisation and phytoextraction [26]. Germaine *et al*. [28] showed the link between microbial communities (*Proteobacteria, Pseudomonas, and Acineto-bacter)* and 11 *Miscanthus*. sp rhizomes in organic pollutant removal. Moreover, the aboveground biomass (AGB) increase of *Miscanthus* species was related to the presence of endophyte bacterium. The presence of *Pseudomonas koreensis* AGB1 increased *Miscanthus sinensis* AGB by 54 %, [29]. *Miscanthus sinensis* compared with *M. × giganteus* showed a better ability to grow on soil contaminated with inorganic pollutants, and a high capacity for removal of organic pollutants. *M. × giganteus* showed a high ability to grow on soil contaminated with Cd, Zn, and Pb. Opposite

M. × giganteus, M. sinensis showed a high ability to remove organic pollutants [25]. *Miscanthus genotypes: M. x giganteus, M. sinensis,* and *M. floridulus* are good candidates for Zn, Cr, and Cd removal [30].

2. 1. 2. Biofuel production

Miscanthus cell wall contains 32.7 to 49.5 % cellulose, 21 to 34.8 % hemicellulose, and 17.8 to 27.7 % lignin [31]. According to Kricka *et a*l. [32], *Miscanthus × giganteus* with 41 % cellulose content can be used in both liquid and solid biofuel production. In a line with this Lee and Kuan, [31], determined that *Miscanthus floridulus*, *Miscanthus sinensis*, *Miscanthus sacchariflorus,* and *Miscanthus × giganteus* cellulose content of 37.2, 37.6, 38.95, 41 wt.% respectively, 0.233, 0.221, 0.213, 0.211, and 0.233 g of bioethanol, respectively. Application of 1 % NaOH at 121 °C for 60 min on *Miscanthus ×giganteus* and *M. sinensis 'Gracillimus'*, resulted in 34.1 and 30.0 % glucan and 11.3 and 13.6 % xylan contents, respectively. Interestingly, *Miscanthus* x g biomass can be used for high-quality briquettes. The method applied was the pressure agglomeration process a hydraulic briquette machine with an open hydraulic working chamber. Energy potential estimation was more than 17.5 MJ kg^{-1} [33]. Furthermore, instead of ethanol, products of fermentation can be isobutanol if fermentation is performed with *Clostridium sp*. Compared to ethanol, isobutanol has a higher energy density, and low absorption of moisture from the air, therefore it is less corrosive [34-36]. As the pre-treatment thermochemical saccharification by H_2SO_4 or NaOH was used. Biological saccharification and fermentation included two anaerobic bacteria *Fibrobacter succinogenes* and *C. acetobutylicum.* Application of 100 mol m^{-3} H_2SO_4 resulted in 44.4 ± 8.5 g m^{-3} ethanol and 19.7 ± 3.5 g m^{-3} buthanol, while with 200 mol m^{-3} NaOH 39.7 ± 8.6 g m^{-3} ethanol and 4.3 ±0.33 g m^{-3} buthanol were produced [36].

2. 2. *Beta vulgaris* L.

2. 2. 1. Phytoremediation

Sugar beet (*Beta vulgaris* L.) is a plant whose wide genetic variation reflects adaptive morpho-physiological features under moderate and severe drought conditions [37] and high heavy metal presence [38,39]. Specifically, an efficient antioxidant system and redox signaling within some genotypes enable *B. vulgaris* tolerance to drought stress [37]. *Beta vulgaris* L. var. *cicla*. is a plant of large biomass with a short growth period and high Cd uptake and accumulation potential [39] Papazoglou and Fernando [38] suggest that sugar beet plants are proven to grow in soil containing diethylenetriamine pentaacetic acid, DTPA-extractable Cd and Ni concentrations up to 236 and 75.4 mg kg^{-1} respectively, given the same biomass quality as those grown in soil without high metal concentrations. Enhanced extraction of Cd can be achieved by adding organic amendments such as cornstalk biochar. Biochar at the concentration of 5 %, decrease the DTPA-extractable Cd concentration compared to *B. vulgaris* grown on soil without the presence of biochar. Results indicate growth of about 267 % of root dry mass and an increase in Cd plant accumulation of 206 %. Notably, there was an increase in matter-bound Cd and residual Cd, and a decrease of Fe–Mn oxides-bound Cd of about 40 % [39]. Furthermore, biochar increases the C / N ratio, up to 400, while a ratio of approximately 20 represents the threshold for N Immobilization in organic materials [40]. This species exposed to high concentrations of zinc sulfate in the nutrient solution (50, 100, and 300 µM) showed signs of reduction in total biomass (root and shoot) [41].

2. 2. 2. Biofuel production

Climate change has contributed to the setting of specific targets related to alternative renewable energy sources. The European Union has extended the use of energy crops such as sugar beet as raw materials to produce ethanol and methane. The high concentration of easily fermentable compounds has given the use of sugar beet a special place. Glucose fermentation is essential for ethanol production. Being placed as a part of a sugar factory, a factory for ethanol production, apart from glucose, uses raw or thick juice. To gain quality fuel, beetroot quality is crucial, the same as used in sugar production. The plant potential in biogas production is linked to the crude nutrient amount, low lignin, and the same amount of hemicellulose and pectin [42,43]. Sugar beetroots contain 23–24 %, dry matter from which the largest part is organic (easily-decomposable carbohydrates, the N-free solutes). A small part of crude fiber such as lignin does not exhibit potential for the ethanol production fermentation process, in contrast to sugar beet leaves that can be used as a biofuel feedstock. The enzymatic liquefaction (pectinase and cellulase enzymes) was used for increased fermentable sugar recovery [44-46]. Surprisingly, investigation of sugar concentration in different species varieties to methane production to only dry matter importance, not sugar concentration. One report regarding this plant goes into reducing greenhouse effects with biofuel production. Carbon Intensity (CI) is used to measure all greenhouse gas emissions associated with the life cycle assessment (LCA) of a fuel. Additionally, CI sugar beet ethanol was 28.5 g CO_2e/ MJ_{EtOH} (Carbon Dioxide Equivalent/Conversion rates (Efficiencies)). This study presents an energy analysis of sugar beet-based ethanol production and CO_2 emissions [47]. The current production of table sugar or sucrose amounts to 160 million tons of sugar per year [48]. Sugar beet sucrose content was conditioned, therefore enabling the production of 100 to 120 L ethanol per t of sugar beet or approximately 5000 L/ha in mild climates [47-48].

2. 3. *Saccharum* sp.

2. 3. 1. Phytoremediation

According to the US Department of Agriculture *Saccharum sp.* contains thirteen species [49]. Sugarcane (*Saccharum officinarum* L.) is a recognized phytoremediation plant due to its biomass abundance, fast growth, and moderate uptake and accumulation of heavy metals such as Cu, Cd, Se, Pb, and Mn [50-52]. The *Saccharum officinarum* L. plant was found to be a good phytoremediator of lindane-rich garden soil, with degraded 600 mg L^{-1} of lindane. The efficiency of sugarcane was enhanced by root-inoculation with yeast Candida VITJzN04 because yeast produces growth hormone and solubilizes insoluble phosphates [53]. Therefore, the lindane-removal rates by sugarcane baggase bio-stimulated with yeast has the shortest $t_{1/2}$ (half-life period) for lindane degradation 7.1 days, compared with 13.3 days (yeast), 43.3 days (Saccharum) [53]. Furthermore, *Saccharum officinarum* L. is also used in fluoride (F^-), and bioaccumulation. The Sugarcane potential was estimated at 1000–1200 mg F^- kg^{-1} dry weight [55]. Furthermore, *Saccharum officinarum* L. was also able to remove fluoride from an aqueous environment [56].

The root zones of *S. officinarum* were amended with *Aspergilus flavus, Paecilomyces sp., Mucor sp., Penicillium sp.,* and *Trihoderma viride* efficiently degraded petroleum hydrocarbon from crude oil contamination [57]. Also, *S. officinarum* growth and development are influenced by the Fe soil content. Therefore, a study regarding the Fe accumulation potential of a plant showed that the addition of Fe-EDDHA (the chelate ferric-ethylenediamine-N, N′-bis(2-hydroxyphenyl acetic acid) increased accumulation of Fe [58]. Sugarcane exposure to copper-based compounds/nano-materials showed good bioaccumulation potential. The performed studies indicate an increased rate of Cu bioaccumulation. Translocation of Cu from the roots to the aerial parts enhanced to some extent with copper level. Therefore, an increase in the bioavailability of Cu in the soil treated with higher Cu levels could be a probable reason for that phenomenon [59]. Increased uptake of polychlorinated biphenyls (PCBs) and cadmium by *Saccharum officinarum* L. was achieved by adding tea saponin. Application of 0.01 % saponin significantly increased the uptake of PCB, while 0.3 % tea saponin assisted in increasing the uptake of Cd in roots, stems, and leaves by 96.9, 156.8, and 30.1 %, respectively [60]. In partially consolidated bioprocessing, which involved enzymes laccase (*Pleurotus djamor*) and holocellulase (*Trichoderma reseei* RUT C30), *Saccharum spontaneum* L. and *Saccharum spontaneum* biomass has been transformed into 62 g dm^{-3} ethanol.

Saccharum spontaneum L. known as wild sugarcane or kans grass showed apart from the ability to grow on heavy metal polluted sites, great efficiency to clean fly ash dumps, acid mine dumps, and sewage sludge [61,62]. *S. spontaneum* the rhizosphere amended with phosphate-solubilizing bacteria *Bacillus anthracis* strain MHR2, *Staphylococcus sp.* strain MHR3, and *Bacillus sp.* strain MHR4 showed potential in heavy metal removal from dumpsites [63]. The accumulation of Cu, Sn, and Pb/Zn are due to the adaptability of the plant to tailing environments. Exposure to different concentrations of Pb in soil (0, 100, 250, 500, and 1000 mg kg^{-1}) did not induce macro-toxicity in plants except for the highest Pb concentration used. Also, a greater amount of Pb was found in roots compared to shoots [64]. *Saccharum munja* L., a plant of the same genus, can grow on metal-contaminated coal fly ash dumps and exhibits a high capacity for heavy metal removal. Biological accumulation coefficient/factor (BAC) was defined as the concentration of heavy metals in plant shoots divided by the heavy metal concentration in soil [BAC = $c_{\text{Metal in plant shoot}} / c_{\text{Metal in soil}}$] and indicates the ability of plants to tolerate and accumulate heavy metals. In Zn, Pb, Cu, Ni, Cd, and As removal by *S. spontaneum*, bioaccumulation factors were 8.01, 1.40, 3.02, 0.92, 1.66, and 1.47 mg dm^{-3}, respectively. *S. munja* bioaccumulation factors were higher indicating better perspectives in using this plant, amounting to 8.54, 1.66, 3.24, 0.76, 1.63, and 1.41 mg dm^{-3}, respectively [65]. Furthermore, *Saccharum arundinaceum* (Retz.) is used for cleaning the soil from heavy metal contamination around mining areas, farmland, *etc*. A mitigating circumstance in this process is the presence of sulfuric acid as a result of acid mine drainage when the mining activities expose sulfur-bearing minerals to atmospheric oxygen, moisture, *etc*. Thus, *S. arundinaceum* had the advantages of accumulating metals Cu, Zn, Pb, and Cd, with the emphasis on Cu because of the presence of strong acid in the mining soil environment [66].

2. 3. 2 Biofuel production

In a study by Kataria and Ghosh [71], *S. spontaneous* was pretreated with cellulolytic enzyme from *Trichoderma reesei*, followed by bioconversion to bioethanol performed with *Saccharomyces cerevisiae*. The total estimated bioethanol production was 0.46 g g^{-1}. Also, *Saccharum spontaneum* saccharification with *A. oryzae* enzymes with subsequent fermentation with *Pichia stipitis* NCIM3498 resulted in 0.38 g g^{-1} bioethanol production [72]. *Saccharum arundinaceum* subjected to simultaneous treatment with 3 enzymes (laccase, cellulase, and β-glucosidase) showed a great saccharification outcome of 205 ± 3.73 mg g^{-1} total reducing sugar, with the final ethanol concentration of 4.18 ± 1.14 g dm^{-3} [73].

2. 4. *Ricinus communis* L.

2. 4. 1. Phytoremediation

Ricinus communis L., commonly termed Castor, is well known for its ability to grow under harsh conditions. These include floods, extreme pH, high temperature, high salt content, harmful microorganisms, fungi, nematodes, and insects as well as smog, and SO_2 [75,76]. This plant with high oil content is not only considered an energy crop but also good wastelands remediator because of its high biomass productivity, comparable to *Brassica juncea* [77,78], as well as high antioxidant content and heavy metal bioaccumulation capacity [79]. Both stem and leaf flavonoid content enables good antioxidant activity [80]. *Ricinus communis* L. was shown in different studies to exhibit the potential to remove Cd [77], Ni, Zn, Fe [78], and Pb [81], and to tolerate Cu, Fe, Mn, and Zn [82,83]. Furthermore, *R.communis* removes organic contaminants like pesticides [84]. At places like different types of Cu-mine soils and slags rich in Cu, As, Fe, and Zn, Castor showed good bioaccumulation capacity [85]. Also, mine tailings are sources of a wide range of heavy metals (Cu, Zn, Mn, Pb, and Cd) [86]. Furthermore, Castor successfully removed Pb, Cd, and Zn at more than 70 %, and reduced BOD, and COD values in wastewater [87]

2. 4. 2 Biofuel production

Ricinus communis L. is a highly valuable plant for biofuel production [87]. The biomass carbon content is between 40 and 43 %, which nominates this plant for biogas production [88]. According to Sharma *et al.* [89], pretreatment of lignocellulosic substrates by the Dattas method enhances biogas (methane) production. For untreated and treated *R. communis* the maximum yield biogas production was 86.6 and 120.9 l kg^{-1} respectively, and methane content was 44.2 and 50.9 % respectively. Greenhouse gas (GHG) emission using compressed natural gas (CNG) as a primary fuel and castor (*Ricinus communis*) oil methyl ester (COME) was evaluated in a study by Mahla and Dhir, [90]. The study aimed to show GHG release using various blends (B10 and B20), where B20 fuel is a blend of 20 % biodiesel and 80 % conventional diesel, and B10 fuel is a blend of 10 % biodiesel and 90 % conventional diesel. Research showed increased NO_x and HC emissions, whereas CO emissions decreased by 31.6 and 37.4 % for B20-CNG and D-CNG. Also, this is a plant rich in cellulose (50 %) and hemicellulose (17 %) [89], thus promising for the use in production of biodiesel by transesterification of castor oil, shown to be up to 91 % [91]. *R. communis* biodiesel properties resemble that of diesel. Umale *et a*l. [92] compared GHG emissions using B20 and B10 castor biodiesel blends used in the engine at compression ratios (CR) of 16.5 and 17.5, respectively. The aim of the study was also to determine how efficiently the engine converts fuel supplied into useful work *via* brake-specific fuel consumption (BSFC). Results showed that the B20 castor biodiesel blend used in the engine at CR 16.5 showed lower BSFC than the B10 castor biodiesel blend and *vice versa* at CR 17.5. One more indicator is the brake thermal efficiency, which measures the efficiency of internal combustion engines. The higher the brake thermal efficiency, the lower the fuel consumption, and greenhouse gas emissions. And in this study, both B10 and B20 had higher break thermal effects. Both blends were used in the engine at CR 17.5. Also, used B10 showed lower CO and HC emissions, and comparatively higher NOX emissions, while B 20 showed lower NOX, and comparatively higher CO and HC emissions [92].

2. 5. *Prosopis* sp

2. 5. 1. Phytoremediation

Prosopis juliflora (Sw.) DC, also known as Velvet Mesquite or simply *Prosopis. Prosopis* spp similar to *Ricinus communis* L. can tolerate and grow in arid, alkaline pH, and, saline soil, and extreme temperatures [92]. This plant is recognized to have a high ability to grow on different soil exhibiting high phytoremediation potential. Having the ability to tolerate high amounts of heavy metals, *P. juliflora* grows on the soil containing Cd, Co, Cr, Fe, Mn, Ni, Pb, and Zn up to 26, 22, 2243, 137, 9.4, 34, 18 and 14 mg kg^{-1}, respectively [93]. One of the biggest concerns in environmental protection is fluorosis, related to air pollution, caused by coal burning, and fluoride (F) related to soil contamination. However, it is found that *P. juliflora* has also the potential for tolerance and accumulation of F, yielding 4.41 mg kg^{-1} dw in the stem, 12.97 mg kg^{-1} dw in leaves, and 16.75 mg kg^{-1} dw in roots [94]. Also, it was shown that the presence of iron oxide nanoparticles (Fe_3O_4 NPs) enhanced the phytoremediation potential of this plant of F [95]. Ramírez *et a*l. [93], investigated the potential of *Prosopis laevigata* for heavy metal phytoremediation in soils polluted with a high concentration of aluminum, titanium, chromium, and zirconium up to 4.1, 14, 1.6 and 2.5 g kg^{-1}, respectively. However, at a high concentration of Cr of 435 mg kg^{-1} in the soil a lack of phytoremediation potential was observed. This study revealed that *P. laevigata* inoculated with *Bacillus* sp. showed the ability to bioaccumulate chromium Cr [93].

2. 5. 2. Biofuel production

Prosopis juliflora (Sw.) DC is rich in holocellulose (60 – 65 %), therefore, it is considered for bioethanol production [80,97-99]. In such a study, Sivarathnakumar *et al* [99] used *Kluyveromyces marxianus* leading to the increased sugar content by applying auto-hydrolysis with acid hydrolysis as a pre-treatment. Saccharification and fermentation processes resulted in 21.45 g dm^{-3} of bioethanol, produced from product and biomass yields of 0.67 and 0.28 wt.%, respectively [99].

Pasha *et a*l. [100], investigated the same process using a thermotolerant *Saccharomyces cerevisiae* VS_3 strain. As a pre-treatment strong acid and enzyme hydrolysis was applied. In this process, 80.76 % of biomass yield was converted into 84 g dm^{-3} total carbohydrates. To improve the fermentative efficiency of sugar to bioethanol production ethyl acetate extraction was employed. With 88% efficiency, *S. cerevisiae* enabled 30.0 g dm^{-3} ethanol production of 0.431±0.021 g ethanol per g sugar of utilized sugars. Thus, efficient pre-treatment induces greater production of bio-ethanol. There are some suggestions that a combination of ionic liquid (IL)-based pretreatment with pretreatment agents surfactants/salts/deep eutectic solvent [101], can be successful [102]. Ionic liquids can remove hemicellulose and lignin to some extent, also has a role in decreasing the surface tension between the two liquid phases during pretreatment and have an additive effect. Surfactant pretreatment with dodecyl benzene sulfonic acid, or dilute acid pretreatment improves lignin solubility, reduce unproductive binding to the enzyme, modifying the biomass surface. Then, pretreated biomass should be further enzymatically saccharified with cellulose or xylanase [103].

Investigating sources of important robust enzymes Vaid *et al* [102], reported that Bacillus spp, in particular, *B. amyloliquefaciens SV29* has the potential of secreting IL-stable enzymes. Furthermore, saccharification of *Prosopis juliflora* with xylanase released from *B. pumilus* strain MK001 resulted in 15.5 wt. %of sugars and reached 20.0 % saccharification efficiency. Further fermentation process with *Pichia stiptis had a* release of saccharified hydrolysates and an outcome of 0.36 wt.% ethanol yield [104]. Besides *P. juliflora, P. pallid* is also considered for bioethanol production, whereas sugar (40 %) can be converted into 18.9 % ethanol [105]. The production of bioethanol depends on the type of microorganisms. Therefore, da Silva *et al.* [97] investigated the efficiency of two microorganisms *Zymomonas mobilis* and *Saccharomyces cerevisiae* in ethanol synthesis. By cultivating Z. *mobilis* in *P. juliflora* pods after

36 h in static conditions the highest concentration of ethanol was reached (141.1 g dm^{-3}), While under the same conditions, after applying *S. cerevisiae* the highest ethanol production (44.32 g dm^{-3}) was achieved after 18 h [97].

2. 6. *Arundo donax* L.

2. 6. 1. Phytoremediation

Arundo donax L., commonly termed "giant cane" or "giant reed", is a non-food crop adapted to different kinds of environments. The phytoremediation potential of this plant in As removal has been estimated in a study conducted by Mirza *et al*. [106]. Cultivated in different hydroponics conditions with increasing doses of As (0, 50, 100, 300, 600, and 1000 µg dm^{-3}), *A. donax* showed the ability to accumulate up to 600 µg dm^{-3} [106], and good bioaccumulation potential in Zn, Cr, and Pb removal from the growing medium. In the range of 450 and 900 mg Zn kg^{-1}, 300 and 600 mg Cr kg^{-1}, and 450 and 900 mg Pb kg^{-1}, *A. donax* biomass slightly decreased, but a severe reduction was noticed at 600 mg Cr kg^{-1} [1]. Soil rich in Ni did not cause any decrease in the growth and development of A. donax. High content of Ni was found in shoots, indicating a good hyperaccumulation ability [107]. *A. donax* amended with *Trichoderma harzianum*, *Saccharomyces cerevisiae*, and *Wickerhamomyces anomalous was* individually exposed to two different concentrations of Ni, Cd, Cu, As, Zn, Pb, V, and Hg. *A. donax* and mycorrhized *A. donax* with *T. harzianum* stand out as Cd, Pb, and Hg bioaccumulators. The mean bioaccumulation percentage values were for Hg 0.60 %, for Pb 0.54 % and for Cd 0.42 % [108]. Furthermore, *A. donax* was exposed to different Cd concentrations of (0, 50, 100, 250, 500, 750, and 1000 µg dm^{-3}), in a hydroponic and soil environment. Although better performance was observed in hydroponic conditions *A. donax* is considered a Cd hyperaccumulator [109]. Additionally, grown in non-ferrous soil giant reed showed high phytoremediation potential for Cd and Pb removal [110]. Also, broad tolerance of *A. donax* to Cd, Cr, Cu, Ni, and Pb was shown in literature reporting the tolerance values of 0.5 mM, 0.2 mM, 2 mM, 0.5 mM, and 1 mM, respectively [111]. Also, a comparison between accumulating capabilities regarding some heavy metals showed that *A. donax* accumulates Zn > Ni > Cu > Cd [112]. According to Alshaal *et al.* [113], *A. donax* is strongly recommended for phytoremediation of bauxite residue or red mud being capable to accumulate and translocate heavy metals, especially Ni, but also Co, Pb, Cd, and Fe [113], As and Hg [114], Se [115], nitrate [116], Cu [117,118].

2. 6. 2. Biofuel production

Multi-applicable *A. donax* has found a place among high biomass yield energy plants, suitable for biofuel production [119-121]. Giant cane rich in cellulose is considered a good bioethanol source with pre-treatment to degrade cellulose into fermentable sugars [122]. De Bari *et al.* [119] used the steam explosion as pre-treatment and then pretreated biomass was exposed to saccharification and fermentation. After these steps, high gravity hydrolysis was applied with subsequent fermentation using *S. cerevisiae* to reach the production of ethanol concentration of 51 g dm^{-3}. *A. donax* pretreated with commercial cellulase (Multifect®) from Trichoderma reesei, produced 75 dm^3 of ethanol per ton of *Arundo* biomass [125]. Another study suggested that plants were able to produce 20 g dm^{-3} oxalic acid [126] and 8.2 g dm^{-3} ethanol [127]. Giant reed biomass pre-treated with diluted acid or liquid hot water can be converted with bacteria as a fermentative organism. Locaes *et al.* showed that the usage of commercial enzymes boosts ethanol production from 0.44 to 0.47 g dm^{-3}. Also, this study showed a great difference when ethanol production was carried out without saccharification, resulting in 7.5 g dm^{-3} of ethanol [129].

3. DISCUSSION

Recently, fossil fuel depletion brought alternative energy sources to become the "new normal" energy sources. Furthermore, energy stability is on the same level of importance as the elimination of environmental pollution. Recent studies indicate multitasking approach as phytoremediation and biofuel production from the same source - energy plants. There are a plethora of energy crops and non-crops used for this purpose. Structural properties and physiology enable these plants to clean up soil from heavy metals and then use it for biofuel production. The candidates and multiple potential plant species are presented in Table1. and Table 2.

Table 1. The bioaccumulating potential of energy plant species

Plant species	Bioaccumulation potential	References
Miscanthus × giganteus J.M. Greef & Deuterex Hodk. & Renvoize	Hg, Cd, Zn, Pb, Cu, Mn, Ti, As, Fe and Zr	[24-30]
Miscanthus sinensis	Hg, Cd, Zn, Cr	[26,30]
Miscanthus sacchariflorus	Zn, Cd, Pb, Fe, Mn, Mo, B, Ba, Sr, As, Sn, Li, and Ti	[24,30]
Miscanthus floridulus	Zn, Cr and Cd	[30]
Beta vulgaris L.	Cd	[39]
Beta vulgaris L.	DTPA-extractable Cd and Ni	[38]
Saccharum officinarum L.	Cu, Cd, Se, Pb, and Mn	[50-52]
Saccharum officinarum L.	gamma-HCH or lindane	[53,54]
Saccharum officinarum L.	F^-	[56]
Saccharum officinarum L.	Fe	[59]
Saccharum officinarum L.	PCBs and Cd	[60]
Saccharum spontaneum L.	Cu, Sn, and Pb/Zn	[11,64]
Saccharum munja	Zn, Pb, Cu, Ni, Cd, and As	[65]
Saccharum.arundinaceum	Cu, Zn, Pb, and Cd	[66]
Ricinus communis L.	Cd	[77,84]
Ricinus communis L.	Ni, Zn, and Fe	[78]
Ricinus communis L.	Pb	[81]
Ricinus communis L.	B, and tolerate Cu, Fe, Mn, and Zn	[82,83]
Ricinus communis L.	Cd, Pb, Ni, As, Cu	[84]
Ricinus communis L.	Pesticides	[84]
Prosopis juliflora (Sw.) DC	Cd, Co, Cr, Fe, Mn, Ni, Pb, and Zn	[94]
Prosopis juliflora (Sw.) DC	fluoride (F)	[95]
P. laevigata	Al, Fe, Ti, and Zn	[93]
P. laevigata inoculated with *Bacillus* sp.	Cr	[93]
Arundo donax L.	As	[106]
Arundo donax L.	Zn, Cr, and Pb	[1]
Arundo donax L.	Ni, Cd, Cu, As, Zn, Pb, V, Hg.	[108]
Arundo donax L.	Cd	[110]
Arundo donax L.	Cd, Cr, Cu, Ni, and Pb	[111,117,118]
Arundo donax L.	Ni, Co, Pb, Cd, and Fe	[113]
Arundo donax L.	As and Hg	[114]
Arundo donax L.	Se	[115]
Arundo donax L.	Nnitrates	[116]

As presented, there is a strong bioaccumulation potential in all selected plants. Silvergrass plants are recognized as heavy metal bio accumulators. *Miscanthus × giganteus* J.M. Greef & Deuter ex Hodk. & Renvoize, chiefly removes Hg, Cd, Zn, and Pb, Cu, Mn, Ti, As, Fe, and Zr, and *Miscanthus sacchariflorus* besides Zn, Cd, Pb, Fe, removes Mn, Mo, B, Ba, Sr, As, Sn, Li, and Ti. Moreover, this plant gave good results in bioethanol production. *Miscanthus × giganteus J.M. Greef & Deuter*, *ex Hodk. & Renvoize* under biological saccharification and fermentation with anaerobic bacteria *F. succinogenes* and *C. acetobutylicum* yielded 44.4 ± 8.5 g m^{-3} ethanol and 19.7 ± 3.5 g m^{-3}buthanol. Sugar beet, *Beta vulgaris* L. is suitable for Cd, DTPA-extractable cadmium, and Ni removal. An excellent result was achieved with enzymatic liquefaction (pectinase and cellulase enzymes) to produce 100-120 dm^{-3} ethanol/sugar beet.

Table 2. Biofuel production from energy plants

Plant species	Pretreatment/ Treatment applied	Biofuel produced	Ref.
Miscanthus × giganteus J.M. Greef & Deuter ex Hodk. & Renvoize	100 mol m^{-3} H_2SO_4	9572 g m^{-3} saccharides from acid treatment yielded 44.4 ± 8.5 g m^{-3} of ethanol 19.7 ± 3.5 g m^{-3} of buthanol	[36,37]
Miscanthus × giganteus J.M. Greef & Deuter ex Hodk. & Renvoize	200 mol m^{-3} NaOH	4054 g m^{-3} saccharides from alkali treatment yielded 39.7 ± 8.6 g m^{-3} of ethanol 4.3 ± 0.33 g m^{-3} of buthanol	[36,37]
Miscanthus × giganteus J.M. Greef & Deuter ex Hodk. & Renvoize	Biological saccharification and fermentation with anaerobic bacteria *F. succinogenes and C. acetobutylicum*	2504 g m^{-3} saccharides yielded 0.091 g m^{-3} of ethanol	[36,37]
Miscanthus sinensis	1 % NaOH at 121 °C for 60 min/ozonolysis	From 37.6 wt.% of cellulose, 0.221 g of ethanol was produced	[31]
Miscanthus sacchariflorus	1 % NaOH at 121 °C for 60 min/ozonolysis	From 38.95 wt.% of cellulose, 0.213 g ethanol was produced	[31]
Miscanthus floridulus	1 % NaOH at 121 °C for 60 min/ozonolysis	From 41 wt.% of cellulose, 0.233 g ethanol was produced	[31]
Beta vulgaris L.	Enzymatic liquefaction (pectinase and cellulase enzymes)	103.5 dm^3 per tonne (wet weight)	[47-48]
Beta vulgaris L.	Enzymatic liquefaction (pectinase and cellulase enzymes)	Enhanced bioethanol production-from 10 wt.% fermented sugars	[47-48]
Saccharum officinarum L.	Steam pretreatment with SO_2 and H_2O_2	Bioethanol 0.95 g dm^{-3} (ethyl alcohol)	[67,68]
Saccharum officinarum L.	Saccharification, fermentation, and rectification	10.9 g dm^{-3} ethanol	[69]
Saccharum officinarum L.	*S. cerevisiae*, *P. stipitis* and oxalic acid (2-8 wt.%).	7.9 g dm^{-3} butanol	[67,70]
Saccharum officinarum L.	Dilute acid, then fermented with *Clostridium beijerinckii* DSM 6423	62 g dm^{-3} ethanol	[74]
Saccharum officinarum L.	Partially consolidated bioprocessing (PCBP) / laccase (*Pleurotus djamor*) and holocellulase (*Trichoderma reseei* RUT C30),	0.46 g g^{-1} bioethanol / biomass	[131]
Saccharum spontaneum L.	The cellulolytic enzyme (CMCase) from *Trichoderma reesei* / bioconversion in bioethanol with *Saccharomyces cerevisiae*	21.82 ± 0.15 g L^{-1} hydrolysate / 0.40 ± 0.01 g g^{-1} ethanol	[71]
Saccharum spontaneum L.	*A. oryzae* enzymes and then fermented with *Pichia stipitis* NCIM3498	62 g dm^{-3} ethanol	[72]
Saccharum spontaneum L.	Partially consolidated bioprocessing (PCBP) / laccase (*Pleurotus djamor*) and holocellulase (*Trichoderma reseei* RUT C30)	30.78 g dm^{-3} and 31.56 g dm^{-3} of bioethanol	[131]

Plant species	Pretreatment/ Treatment applied	Biofuel produced	Ref.
Saccharum munja	Enzymatic hydrolysate fermented by the co-culture *Saccharomyces cerevisiae* and *Pichia stipitis*	4.18 ± 1.14 g dm^{-3} ethanol	[67]
Saccharum.arundinaceum	Co-immobilized tri-enzyme biocatalytic system for one-pot pretreatment (Laccase, cellulas and β-glucosidase)	biodiesel	[73]
Ricinus communis L	Pre-treatment (Heating of oil and esterification); main treatment (Transesterification) + catalyst (acid / alkaline)	99.07 % of biodiesel (methyl ester) yield	[92]
Ricinus communis L	Esterification-neutralization-transesterification (ENT) process	21.45 g dm^{-3} of bioethanol	[130]
Prosopis juliflora (Sw.) DC	Auto-hydrolysis with acid-hydrolysis, *Kluyveromyces marxianus* enzymes	30.0 g dm^{-3} of bioethanol	[99]
Prosopis juliflora (Sw.) DC	Strong acid and enzyme hydrolysis, *Saccharomyces cerevisiae*	36 wt.% ethanol yield	[100]
Prosopis juliflora (Sw.) DC	Ionic liquid based pretreatment, *Pichia stiptis* release of saccharified hydrolysates	141.1 g dm^{-3}	[104]
Prosopis juliflora (Sw.) DC	*Zymomonas mobilis* enzymes	51 g dm^{-3} bioethanol	[97]
Arundo donax L.	Steam explosion as pre-treatment than *S. cerevisiae* amendment saccharification and fermentation	4.8 g dm^{-3} bioethanol	[119]
Arundo donax L.	pretreatment by 2 vol.% of H_2SO_4, followed by enzyme hydrolysis by *Zymomonas mobilis*	8.20 g dm^{-3} of ethanol	[123]
Arundo donax L.	Dilute oxalic acid as a pretreatment, Scheffersomyces (Pichia) stipitis CBS6054 enzyme hydrolysis	75 dm^{-3} ethanol per t of biomass	[124]
Arundo donax L.	Commercial cellulase (Multifect®) from *Trichoderma reesei*	19.8 g dm^{-3} ethanol	[125]
Arundo donax L.	Dilute oxalic acid	7.5 g dm^{-3} ethanol	[126,127]
Arundo donax L.	Enzymatic hydrolysis of cellulose	Ethanol	[128]
Arundo donax L.	Pre-treated with diluted acid or liquid hot water, *Escherichia coli* amendment	9572 g m^{-3} saccharides from acid treatment yielded 44.4 ± 8.5 g m^{-3} of ethanol 19.7 ± 3.5 g m^{-3} of buthanol	[129]
Arundo donax L.	Process of sonication, aqueous solution amended with copper ($CuSO_4.5H_2O$ or $CuH_{10}O_9S$), manganese ($MnSO_4 \cdot H_2O$ or H_2MnO_5S), and zinc ($ZnSO_4 \cdot 7H_2O$ or $H_{14}O_{11}SZn$) ions, *T. koningii* and *A. niger*	4054 g m^{-3} saccharides from alkali treatment yielded 39.7 ± 8.6 g m^{-3} of ethanol 4.3 ± 0.33 g m^{-3} of buthanol	[122]

Furthermore, besides the already mentioned heavy metals, gamma-HCH or lindane, and F^- are bioaccumulated by *Saccharum officinarum* L. which alongside *S. spontaneum* L. produced 62 g dm^{-3} ethanol in partially consolidated bioprocessing (PCBP) / laccase (*Pleurotus djamor*) and holocellulase (*Trichoderma reseei* RUT C30) treatment. *Prosopis juliflora* (Sw.) DC. remediates soil from Cd, Co, Cr, Fe, Mn, Ni, Pb, Zn, and F. Bioethanol production of 141 g dm^{-3} is possible if applied *Zymomonas mobilis* enzymes. *Arundo donax* L. showed good As, Co, Cd, Cr, Cu, Fe, Ni, Se, Pb, Zn, V, and NO_3- bioaccumulation results, and commercial cellulase (Multifect®) from *Trichoderma reesei* gave the best results in biofuel production, 75 dm^3 of ethanol. The future relies on sustainable techniques that will provide a cleaner environment. In summary, there are many research papers indicating the feasibility of the phytoremediation-bioenergy strategy direction, where energy plants can be used to clean the environment from heavy metals and then used for biofuel production.

4. CONCLUSION

A plethora of organic and inorganic pollutants, especially heavy metals (HMs) have caused soil and water pollution. Moreover, these metals have genotoxic, and mutagenic effects on living beings [131]. Many plant species belonging to different plant families, recognized as useful phytoremediation candidates, can accumulate different pollutants without intoxication [132,133]. Scientists and engineers are working together to explore alternative energy sources because advances will allow the removal of harmful pollutants such as heavy metals while replacing fossil fuels with biofuels. Table 1. depicts various energy plants' roles in phytoremediation and biofuel production. All presented plant species have shown exceptional importance in energy stability without endangering the environment. Plant species with multiple potentials need to be further genetically improved and researched, particularly concerning reducing the toxic effect of heavy metals on subsequent biofuel production. Therefore, the compilation of these two processes has been recognized as a future direction for sustainable energy and environmental protection.

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Energetske biljke kao izvor biogoriva i kao akumulatori teških metala

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(Stručni rad)

Izvod

Nedostatak fosilnih goriva i zagađenje zemljišta i vode motivisali su stvaranje nove perspektive održivog razvoja. Ne samo da se biljna biomasa može koristiti u proizvodnji etanola, već se ista biljka može koristiti i za minimiziranje/eliminaciju teških metala prisutnih u zemljištu i vodi. Rezistentne na visoke koncentracije metala, mnoge biljne vrste, usevi, medicinske i farmaceutske energetske biljke su dobro poznati hiperakumulatori teških metala. Ovaj rad se fokusira na studije koje istražuju potencijal *Miscanthus.sp, Beta vulgaris L, Saccharum sp., Ricinus communis* L. *Prosopis sp i Arundo donak* L. u uklanjanju teških metala i proizvodnji biogoriva. Fitoremedijacija korišćenjem ovih biljaka pokazala je veliki potencijal bioakumulacije Co, Cr, Cu, Al, Pb, Ni, Fe, Cd, Zn, Hg, Se, itd. Takodje, za pretvaranje celuloze u fermentabilne šećere, predtretmani kao što su ozonoliza, tretman bazama ili kiselinama, parom ili toplom vodom, primenjeni su pre enzimske saharifikacije mikroorganizmima. Ovaj pregled predstavlja uvid u potencijal lignoceluloznih biljaka da uklone zagađujuće supstance i ujedno su vredan supstrat za proizvodnju biogoriva. Takođe, razmatrani su predtretmani, bavljenje toksičnom biomasom i proizvodnja biogoriva.

Ključne reči: polutanti; bioakumulacija; bioenergija