Letter to Editor

Enrichment of *Salix viminalis* Wood in Metal Ions by Phytoextraction

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Abstract

Salix viminalis is a plant widely applied as a source of renewable energy. It is also known as a possible biofilter for extraction of soil and water contaminants. The current study presents preliminary results on heavy metal ion uptake (Cu^{2+}, Cr^{3+}, Zn^{2+}) by living plants of *Salix viminalis*. In relation, a new concept of further utilization of ion-enriched wood is proposed as raw material for carbon-based catalyst fabrication by heat treatment of metal-impregnated partly dried biomass. Particular attention is paid to the distribution of heavy metal ions along the plant stem, since one intends to exploit natural transport and distribution of metal ions in living plants. The uptake from water solution and subsequent accumulation of ions in plant tissues was investigated regarding the form in which ions were present in water solution. Accumulation rates were higher for ion complexes with EDTA in comparison to aqua complexes.

Keywords: *Salix viminalis*, phytoextraction, metal uptake, activated carbon

Introduction

The global energy crisis in recent years has focused attention on so-called renewable energy sources. Decreasing amounts of gas/oil resources and coal deposits (i.e. fossil fuels), as well as the insufficient potential of solar/wind energy installations, have turned attention toward renewal fuels. One of them is short-rotation cropping of *Salix viminalis* for biomass production. Plantations of this kind, also called short rotation forests, are mostly cultivated in the northern middle climate zone [1-4]. The efficiency of dry-weighted biomass production is usually impressive [4], but depends on soil, climate and planting method conditions.

Thus, *Salix viminalis* planting is permanently considered from various points of view, including improvement of efficiency in biomass production [5], caloric properties upgrade [6], decreased mortality level [7], economics of Salix crops planting [8] or predictions on further development in this field [9].

Salix viminalis has been found to be useful in the context of phytoremediation. The use of industrial wastewaters is possible due to the extraordinary tolerance of *Salix viminalis* to heavy metal ions often present in wastewaters. The tolerance includes long-term accumulation of some compounds [10]. The application of plants to phytoremediation of metal-contaminated lands has been carefully reviewed by [11] Pulford and Watson. One can find a number of reports on heavy metals uptake by *Salix viminalis*, eg. Cd [12]; Cd, Cu, Zn [13]; Cd, Cr, Cu, Ni, Pb, Zn [14]; Cu, Zn [15] as well as radioactive Cs and Sr [16].

The main aim of this paper is to convince the environmental research community that the above-mentioned application list of *Salix viminalis* may be extended to research attempts typical for nanomaterials fabrications. In this sense, *Salix viminalis* can be regarded as an inexpensive and easily accessible raw material for further fabrication process. In particular, the current report intends to show that living *Salix viminalis* accumulates high amounts of heavy metal ions from water solutions, durably enriching the wood from *Salix viminalis*. The term "wood" means cut and dried stems of the crops, enriched with

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heavy metal ions prior to further elaboration. Up to now, the idea to use such wood for fabricating active carbons containing nano-crystallites of selected metal derivatives has not been presented in literature. In our opinion it is worth being published first as a short communication addressed to readers, of a journal devoted to environment research since traditional applications of *Salix viminalis* are in strong relation to this area of science. The new view of *Salix viminalis* is in contrast to well-know a traditional energetic exploitation of the plant. It is the authors' intention to convince scientific audience to treat *Salix viminalis* as a precious precursor for fabrication of a variety of carbon-based adsorbents and catalysts.

Experimental

Young shoots of *Salix viminalis* from a plantation located near Toruń (Poland) were cut and transported to the laboratory, then defoliated. After that some of them were put into vessels with water and left until fresh leaves and roots sprouted. We selected most vital plants similar in shape and size and moved them to glass vessels filled with 1.5 dm^3 of Cu, Cr and Zn salts solutions, and left in a laboratory exposed to daylight.

The solutions were prepared from accurately weighed portions of sulfate salts ($CuSO_4 \cdot 5H_2O$, $Cr_2(SO_4)_3 \cdot 18H_2O$ and $ZnSO_4 \cdot 7H_2O$) and dissolved in demineralized water. The primary concentration of each metal ion was 0.01 M. Additionally, complexing agent i. e. EDTA in water solution was added in the amount calculated based on the assumption that EDTA was capable of forming bichelates.

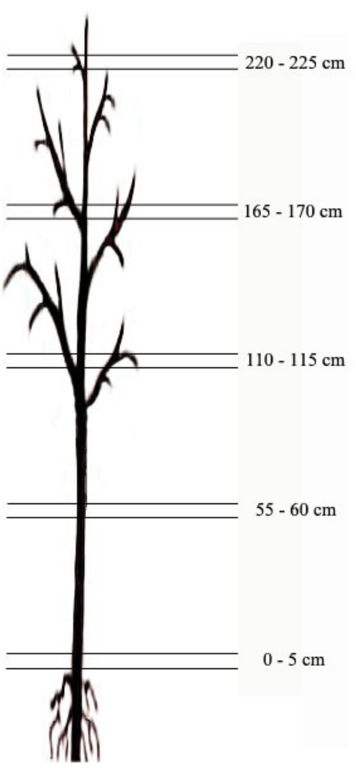

Fig. 1. Sampling wood material from *Salix viminalis* species planted in metal ion solutions.

The additional means of EDTA aimed at higher metal ion uptake by *Salix viminalis*. This experimental method is based on the assumption that plants should be more tolerant to chelated metal ions, since after complexation their chemical properties (including toxicity towards plants) are different than properties of aquacomplex heavy metal ions. However, there is no common agreement among the authors about the positive influence of chelation on the metal ion uptake by *Salix viminalis* and other short rotation woody crops, but some reports suggest that the presence of complexing agent in solution (e.g. in soil) may have positive influence on ion uptake by plants [17]. According to studies some plants, including *Salix viminalis,* tolerate much higher heavy metal ion concentrations provided the ions are in the form of a complex. EDTA was selected due to its outstanding complexing abilities commonly utilized in analytical chemistry.

Stoichiometric proportions must ensure complete complexation of metal ions. Therefore, molar ratios EDTA / metal ion for Cu^{2+}, Zn^{2+} and Cr^{3+} were 1:1, 1:1, and 3:2, respectively. After six weeks the still living stems of *Salix viminalis* were removed from the vessels and divided into fragments, as depicted in Fig. 1. The selected short (5 cm) fragments taken from the stem were put into a porcelain crucible and mineralized in furnace for 4-6 hours. The time was dependent on sample mass. The remaining ash was treated with 10 cm^3 of HNO_3 (p.a.) and filled up to 100 cm^2 with demineralized water.

Metal concentration was measured using flame-excitation atomic absorption spectrometry (FAAS), which as a commonly applied analytical method also is applicable to the determination of metals in plant samples [18]. A 1N Carl Zeiss-Jena ASS spectrometer with acetylene-air atomizer burner was applied. The following settings were applied: λ=324.8 nm and d=0.20 mm for Cu^{2+} analysis;

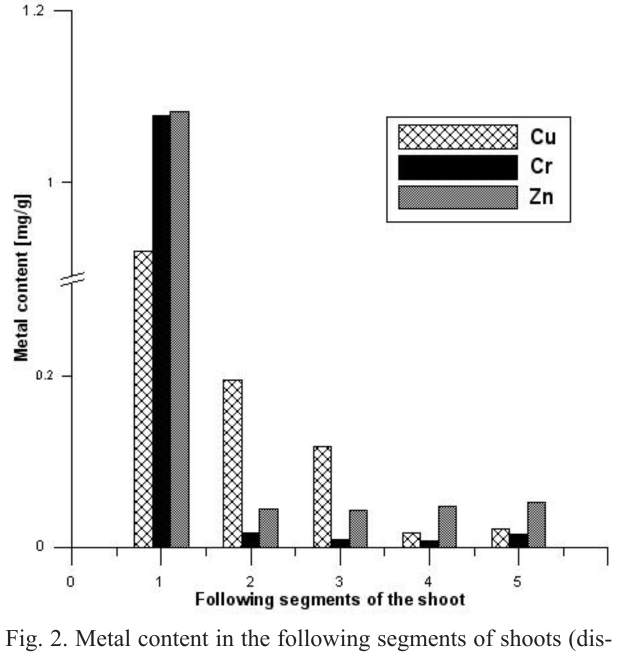

Fig. 2. Metal content in the following segments of shoots (distance from rhizosphere: 1.1-5 cm; 2.55-60 cm; 3.110-115 cm; 4.165-170 cm; 5.220-225 cm).

λ=357.9 nm and d=0.06 mm for Cr^{3+} analysis; λ=213.9 nm and d=0.36 mm for Zn^{2+} analysis (where λ is wavelength and d is diameter of gap).

In parallel, some additional experiments were performed with impregnation of cut stems of *Salix viminalis* with metal ions. This attempt included two kinds of wood samples:

I. "fresh" stems in which natural capillary suction was still active and
II. dried stems that did not preserve the ability to transport metal ions. The latter wood samples were subjected to "forced" impregnation.

Discussion of Results

Data dealing with the metal content in each segment of wood are depicted in Fig. 2. The results are mean values of 3 independent measurements for each metal and each segment of the plant. As expected, it is readily seen that concentrations of all metals is much higher in the first 5 cm long segment, which is closer to the rhizosphere than in other ones. The exact values are 0.92 $mg\cdot g^{-1}$, 1.07 $mg\cdot g^{-1}$, 1.08 $mg\cdot g^{-1}$ for Cu, Cr and Zn, respectively. These amounts are also higher than those reported by other authors [13], [15]. In further segments the amounts of metals are much lower. In the case of Zn and Cr the decrease is very dramatic, but for Cu the decrease is less spectacular. Thus, in segments 2 and 3 the content of Cu is the highest. Other authors have reported about less differentiated metal content distribution along the stem [19]. Such differentiated results are quite often reported in literature and therefore are not a surprise. There are several possible reasons for such an inconsistency which may be attributed to:

i different vegetation times in contact with metals ranging from weeks to years,
ii exposure to solutions of different metal ion concentrations (relatively high in the current study),
iii metal ion uptake from different environments (solution in the current study or soil in other reports),
iv the presence and kind of complexing agent (EDTA in the current study).

In summary, the absence of natural conditions, as well as abnormal vegetation conditions, might seriously influence

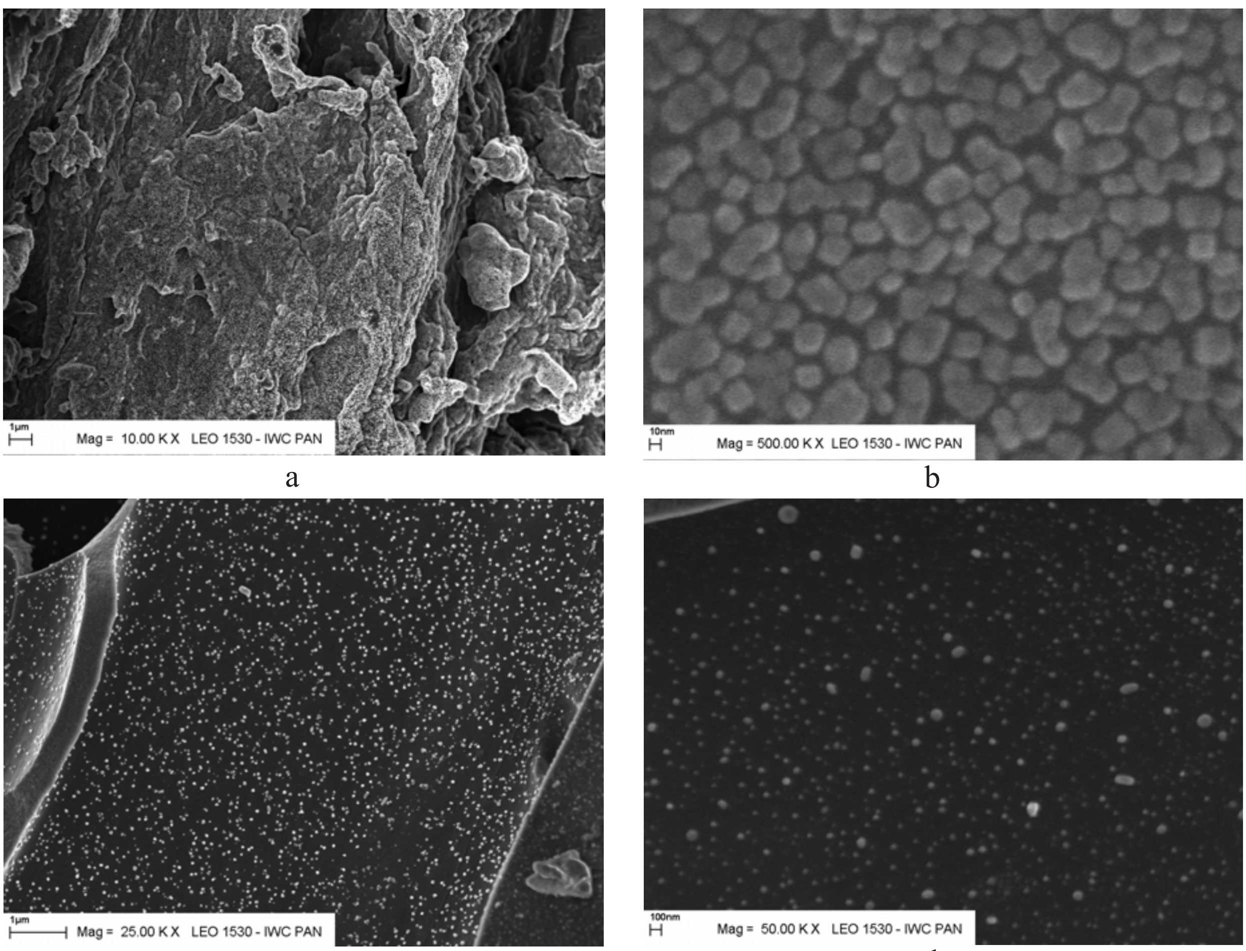

Fig. 3. Distribution of zinc oxide crystallites in carbon matrix: (a) and (b). Sample obtained via carbonization of *Salix viminalis* wood heavily enriched with Zn^{2+} ions [22]. The images correspond to the sample investigated by XRD. XRD spectrum depicted in Fig. 4. Distribution of metal-containing nanocrystlites in carbon matrix: (c) lanthanum and (d) manganese. Sample obtained via carbonization of *Salix viminalis* wood enriched with La^{3+} and Mn^{2+} ions (non-chelated with EDTA) by natural ion transport in living parts of *Salix viminalis* exemplar.

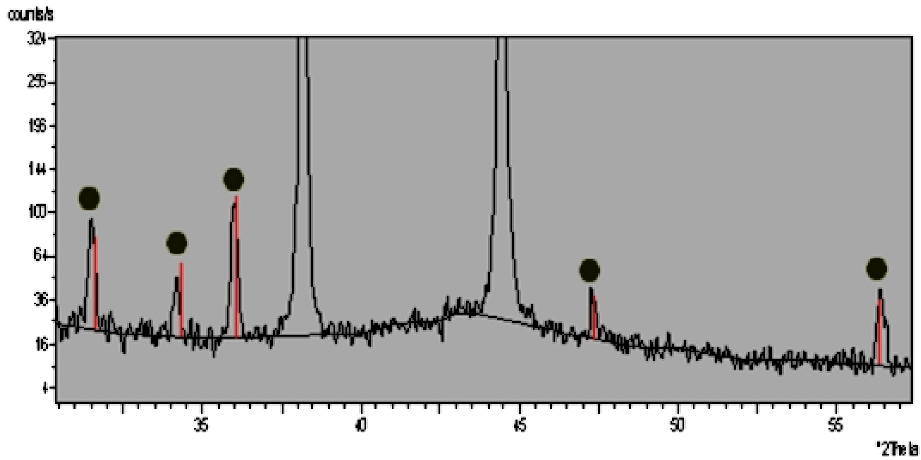

Fig. 4. XRD spectrum of a carbon sample obtained from *Salix viminalis* wood heavily enriched with Zn^{2+} ions. Peaks marked with bullets correspond to the patter spectrum of ZnO. SEM images of the sample are depicted in Figs 3a and 3b. Two remaining peaks are resulting from a metal sample holder.

the mechanism of ion uptake, transport and distribution. However, the target of the study is not phytoremediation but efficient enrichment of the wood samples in metal ions which later may convert to inorganic clusters.

The novelty of the current report consists in the exploitation of *Salix* tolerance to extraordinary high concentration of heavy metals enabling long-term distribution of metal in plant tissues. Additionally, very high metal content has been discovered in a still living plant in which live processes were still proceeding. At the current stage of research, further increases of heavy metal concentration in the upper part of the plants is not excluded since the high metal concentration in root-close zone was not a lethal dose.

On the other hand, a high metal content in the organic matrix (plant cells) can be exploited in an unusual way. Plant tissues, particularly woody plants, after cutting and drying are standard raw material for fabrication of active carbons. Upon increased temperature in oxygen-free conditions, organic matter transforms into a carbon matrix. So it proceeds in the case of wood from *Salix viminalis*. In general, it is a so-called hard wood, particularly useful for active carbon fabrication as proven in other study [20]. Carbonization of the wood leads to the formation of carbon adsorbents, whose pore structure resembles a perfect carbon molecular sieve. Such carbons are characteristic because of an exclusive presence of nanopores of uniform size. Pore size distribution function (PSD) is monomodal (PSD maximum is placed at ca. 0.8 nm) and extremely narrow. It makes such carbon an excellent candidate for typical molecular sieve applications like air separation and/or gas storage. The discovery has an evident environmental aspect. Active carbons, including carbon molecular sieves, can be produced from an inexpensive and renewable raw material, i. e. wood of *Salix viminalis*. In this way one may save forests and woods that typically serve as resources for active carbon production. The situation is even more dramatic since usually precious trees are exploited (oak and other [21]), whose time of growth is long.

The transformation of organic tissues of *Salix viminalis* into the carbon matrix is an evident (and requested) phenomenon that will certainly take place upon oxygen-free heat treatment. A question should be answered concerning inorganic components that have been consciously introduced in the tissues of living *Salix viminalis* prior to carbonization. The extraordinary tolerance of *Salix viminalis* to high heavy metal ion concentration allows it to distribute the ions all over the plant to the cells where they are usually accumulated. Therefore, one may expect that the ions will be scattered over the whole plan with different zone identity as described above. At the beginning of the research, we assumed that the introduced metal ions will transform into appropriate metal derivatives like metal oxides.

In a supplementary study [22], after carbonization of metal ion (Zn^{2+})-saturated wood of *Salix viminalis*, the performed SEM studies proved the existence of nano-sized inorganic clusters [22] (Fig. 3). The clusters were of relatively uniform size and were quite homogenously scattered. XRD studies proved the formation and existence of appropriate metal derivatives like zinc oxide in carbon matrix (Figs 3a, 3b and 4) obtained by carbonization of *Salix viminalis* wood saturated with Zn^{2+} ions. The phenomenon is observable for all investigated wood samples (Figs. 3c and 3d), including La^{3+} and Mn^{2+} metal ion enrichment as depicted in Fig. 1. For better observation of the mentioned transformation of Zn^{2+} ions into ZnO clusters, Figs 3a, 3b and 4 correspond to wood samples heavily doped with Zn^{2+} ions prior to carbonization [22].

We assume that the uniform distribution and nanometric dimensions of metal oxide crystallites (and/or other metal derivatives) results from good distribution of metal ions due the biological transport of ions in living plants [23], and in the case of *Salix viminalis* plants whose roots were in contact with heavy metal ion solutions.

We have proposed to exploit the observed phenomenon of the formation of metal-containing inorganic clusters in the carbon matrix for the fabrication of complex, carbon-based catalysts [23]. Such materials exhibit catalytic activity in several processes. Metal oxides as well as other transition metal species, particularly when dispersed and supported on a conductive background (carbon matrix) are effective catalysts in some processes like oxygen reduction [24]. Because of that they have found an application to the construction of cathodes in fuel cells [25] and metal-air batteries [26].

Conclusions

The performed research proved that *Salix viminalis* can be efficiently enriched with metal ions due to natural transport and distribution mechanisms existing in living plants. Enrichment is possible due to the extraordinary tolerance of *Salix viminalis* to even relatively high concentrations of heavy metal ions (Cu, Zn, Cr) in water solution in contact with the plant roots for 6 weeks. The high metal uptake and accumulation was additionally achieved by chelation of the ions with EDTA prior to the saturation process. Carbonization of metal ion enriched wood allowed us to obtain a hybrid material in which inorganic nanoclusters are uniformly suspended in the carbon matrix. The carbon matrix is formed during pyrolysis of organic matter (plant tissues), while inorganic nanolcusters grow from metal ions present in the enriched wood. The research proves that beside typical "environmental" applications, *Salix viminalis* can serve as a valuable raw material for active carbon fabrication.

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