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SUITABILITY STUDY OF USING BIRCH AND WILLOW TREES IN PHYTOREMEDIATION OF ACIDIC WASTE SETTLERS

Elżbieta JAROSZ-KRZEMIŃSKA & Ewa ADAMIEC

AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection; al. Mickiewicza 30; 30-059 Krakow, Poland; e-mail: elzbietajarosz@geol.agh.edu.pl

Abstract: Research addresses the issue of assessing the possibility of using birch and willow trees in phytoremediation of acidic waste settlers. In order to determine the suitability of these trees to bioaccumulate metals it was crucial to first characterized the physico-chemical parameters of the waste. Both waste and leaves samples were analyzed with respect to heavy metals concentration using microwave digestion (conc. HNO_3) procedure followed by AAS analyzes. Moreover, the mobility of contaminants from waste was studied using aqueous leaching test as well as sequential extraction procedures. Investigated waste is very inhomogeneous and is characterized with diversity of pH values within sampling points (2.9–7.0) as well as with high concentration of SO_4^{2-} anions (1203–1301 mg/dm^3), Fe (11–19%) and Zn (64–172 mg/kg). Ability to accumulate metals in birch and willow leaves is high. In birch leaves Zn was accumulated up to toxic level of 431 mg/kg, Mn up to 790 mg/kg, Cu up to 9 mg/kg, Pb up to 21 mg/kg. In willow leaves Zn concentration were found to be even higher and reached 679 mg/kg. Concentrations of remaining metals in willow leaves were as follows: Mn up to 173 mg/kg, Cu up to 17 mg/kg and Pb up to 10 mg/kg. Research results confirmed that both birch and willow trees growing on settlers have high tolerance to the adverse living conditions caused by metal stress and low pH of the foundation. These trees can be used for the purpose of phytoremediation of investigated waste settlers.

Key words: settler, acidic wastes, bioaccumulation, heavy metals, phytoremediation

INTRODUCTION

Reclamation of contaminated sites requires a combination of both technical and biological reclamation. Technical reclamation involves mainly leveling of the deposited material, isolating it with proper layer and applying topsoil. Biological remediation is based on planting vegetation on prepared foundation. Phytoremediation is a common solution applied to waste management due to relatively low cost, minimal impact on the environment, and effective results. It is one of the alternative methods of remediation of postindustrial and degraded sites, by using higher plants and their associated microorganisms to remove or immobilize both organic and inorganic contaminants. Creation of the vegetal layer besides improving the aesthetics of the destroyed landscape, has other tangible benefits such as stabilization of the waste surface and protection against wind and water erosion.

Phytoremediation techniques involves phytoextraction, phytostabilization, phytodegradation, phytovolatilization and rhizofiltration (Alkorta et al. 2004, Kacprzak 2007). The most commonly methods applied for the purpose of remediation of heavy metals contaminated sites are phytoextraction and phytostabilization.

Industrial waste due to its physico-chemical characteristics is difficult and often extreme environment for plants (Tordoff et al. 2000). Selection of proper vegetation for the purpose of phytoremediation is crucial. Plants must be chosen adequately to the properties of the foundation. The basic criteria for the selection of plants for phytoremediation of degraded sites area are according to Kacprzak (2007): resistance to contamination, the ability to accumulate as many metals as possible and rapid growth of plants. In addition, the knowledge of the vegetation in the close vicinity of the contaminated site is very useful since these plants can be a potential source of diaspora for the future formation of independently functioning ecosystem (Urbańska et al. 1997, Szarek-Łukaszewska et al. 2009).

The central point of interest is an area of 1.62 ha which comprises of two settlers of acidic waste which have originated from steel manufacture as a result of pickling steel with sulfuric acid. Post processed solutions, containing mostly iron sulfide and iron sulfate were neutralized by lime suspension and in form of sludge deposited into lagoons. In 1993 generating and dumping of these acidic waste have stopped. Waste producer is obliged by law to resolve problem of deposited waste by either utilization or by reclaiming the site.

In some areas within the waste settlers birch and willow trees are present, while no such type of flora may be found in the surrounding vicinity. In the study these two types of trees were analysed for their potential use in the process of settlers reclamation. The aim of the study was to (1) characterize physico-chemical parameters of waste and the mobility of contaminants and to (2) check ability of birch and willow leaves to accumulate metals in their leaves.

SAMPLING AND METHODS

Waste samples were taken from six sampling points, from which three were located in close vicinity to birch and willow trees and other three samples were taken from places with no vegetation. Furthermore, birch and willow leaves were collected every month for six month (from June to November) from three sampling points in order to check variability in metals intake during different seasons.

Waste and leaves samples were analyzed for the heavy metal concentrations. In order to assess complete chemical characterization of waste, physical-chemical parameters i.e. pH, Eh, electrolytic conductivity and total concentration of metals were determined. Moreover buffer capacity of waste was established by performing acid titration procedure. Furthermore in order to reveal the mobility of contaminants in waste and its potential bioavailability to plants aqueous leaching test and sequential extraction procedure were applied. Aqueous leaching test was conducted according to Polish regulations PN-EN 12457-2 compliant to EU standard.

Ion chromatography was used to determine the concentrations of main anions in waste samples. Waste samples were dried in 105°C and digest in the microwave with concentrated nitric acid according to modified SW 3051 EPA procedure. Leaves were first lyophilized and afterwards were treated with the same digestion procedure as waste samples. The metal concentrations were determined with AAS method.

RESULTS AND DISCUSSION

Physico-chemical characteristics of waste

Waste deposited in the settlers is fine grained and uniform with strong orange color derived from high iron content. In deeper sections of waste white layers are present which indicates the presence of gypsum. Investigation has shown that pH and Eh values varied significantly within sampling points. pH values of the waste ranged from acidic (pH 2.9) to neutral (pH 7) (Tab. 1). In places where trees occurred (sampling points O1,O2, O3), pH values were showing slightly acidic (4.5) to neutral conditions (6.9), however in sampling points with no vegetation (O4, O5, O6) pH ~3 reflects strong acidic conditions. Moreover, also Eh values changed significantly within sampling points (31–200 mV), showing weak reducing to oxidizing conditions. Places with vegetation were found to have reducing conditions and consequently sampling points with low pH and no vegetation were presenting oxidizing conditions. The electrolytic conductivity has not revealed any changes within sampling points and ranged between 3–4 mS/cm in all measured waste samples both with and without vegetation.

The results of acid titration experiments for the selected, most representative waste suspensions are presented in Figure 1A. Results exhibit a plateau in the pH of 4 and 5 for the waste sample of neutral pH 7, probable due to presence of small calcium carbonate amount which is consumed by the addition of nitric acid. After addition of the first acid portion, pH dropped from 7.0 to 5.3 showing the good buffer capacity. Addition of the next two portions of acid resulted in decrease of pH by 0.9 unit. In waste sample of pH 4.3 the first addition of acid caused decrease of pH below 2, therefore indicating intermidiate buffer capacity. However in the waste sample of pH 6.3 the first addition of acid caused decrease of pH to 2.03 indicating lack of buffering substances in that waste sample.

Table 1

Physico-chemical parameters of waste and aqueous leachates from waste

Parameter	Metal concentration in waste samples					
	O1	O2	O3	O4	O5	O6
Cu [mg/kg]	18	16	23	23	20	18
Zn [mg/kg]	172	144	72	89	114	64
Pb [mg/kg]	37	27	46	33	43	34
Mn [mg/kg]	95	204	66	103	118	185
Fe [%]	15	14	11	16	17	19
pH	6.3	7.0	4.5	2.9	3.2	3.1
PEW [mS/cm]	3.4	3.3	3.3	3.7	4.0	4.0
Eh [mV]	−25	−31	145	199	200	198
Parameter	Metal concentration in aqueous leachates [mg/dm^3]					
	O1	O2	O3	O4	O5	O6
Cu (0.5)*	b.d.l.	0.06	0.07	0.03	0.05	0.03
Zn (2)	0.01	0.00	0.30	2.45	4.89	1.51
Pb (0.5)	0.04	0.08	0.12	0.08	0.00	0.08
Mn (–)	0.00	0.00	0.57	0.46	0.11	0.33
Fe (10)	0.08	0.08	0.00	2.16	0.08	0.08
F^- (25)	1.92	2.11	2.15	3.17	2.01	0.09
Cl^- (1000)	1.34	2.27	1.62	5.37	0.87	0.66
NO_3^- (30)	1.91	2.80	5.47	12.32	1.78	4.76
SO_4^{2-} (500)	1263	1207	1238	1253	1301	1300
pH	7.1	7.0	4.1	3.2	3.2	3.2

b.d.l. – below detection limit
()* – maximum permissible values according to Dz.U. 2006, nr 137, poz. 984
O1–O3 – waste samples taken from places with vegetation
O4–O6 – waste samples taken from places without vegetation

Concentration of metals in waste, presented in Table 1 revealed very high content of Fe (11–19 wt. %) in all investigated samples. Furthermore, with respect to other examined metals the concentrations were found to be (mg/kg): 66–204 for Mn, 27–46 for Pb, 64–172 for Zn and 16–23 for Cu.

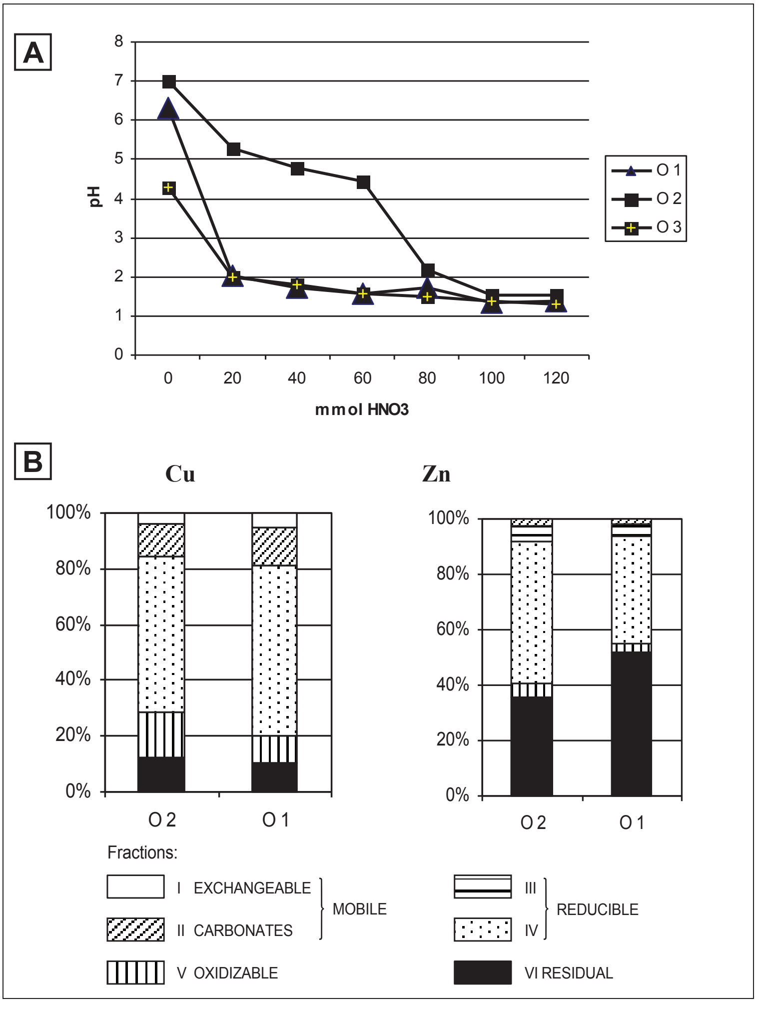

Fig. 1. Buffering capacity of waste (A) and sequential extraction results for selected waste samples (B)

Mobility of contaminants in waste

Mobility of the contaminants in waste were determined by aqueous leaching test and sequential extraction procedure. As indicated by many authors (Tessier et al. 1979, Dold 2003, Bettiol et al. 2008) these methods are commonly used in environmental analysis in the study of bioavailability and mobility of elements present in the soil and sediment systems.

For the aqueous leaching test a suspension of 1:10 solid/liquid ratio was prepared as a procedure in this protocol, and pH of obtained solutions were measured immediately.

Two groups of waste samples were distinguished according to pH values, neutral samples (pH 7.11–7.08) and of acidic ones (pH 3.21–4.14). Table 1 summarizes pH and the metal concentrations in the studied waste leachates. Results revealed that Cu was released up to 0.07 mg/dm^3 , Zn up to 4.89 mg/dm^3, Pb up to 0.12 mg/dm^3, Mn up to 0.57 mg/dm^3 and Fe was leached out up to 2.16 mg/dm^3. In order to detect anions concentrations in aqueous solutions of the waste Ion Chromatography was used. Leachates of all waste samples revealed high concentration of SO_4^{2-} ions (1207–1300 mg/dm^3), whereas other examined anions Cl^-, NO_3^- and F^- were detected at low levels. Results has shown that only Zn and SO_4^{2-} concentration were exceeding maximum permissible values allowed to be introduced to the environment according to Polish Directive Dz.U. 2006, nr 137, poz. 984.

Results of sequential extraction carried out for two selected waste samples, showed that 40–55% of total Zn was associated with the reducible fractions and almost the same portions with residuum (Fig. 1B). In both studied waste samples almost 60% of Cu was combined with reducible fraction and about 30% of this metal was distributed between carbonatic and oxidizable fractions.

The results have shown that about 90% of total Zn is bounded with relatively stable forms, i.e. Fe-ox-hydroxides and residuum. It seems that because of very high iron content in the studied acidic wastes, its considerable portion are not extractable in the reducible fraction but in residuum. Hence the relative high portion of stable Zn was found also in the residuum, probably combined with Fe-oxides.

Concentration of metals in plants

Results of metal concentrations in birch and willow leaves growing on settlers are present in Figure 2 and Table 2. Concentrations of selected metals were compared to standard concentrations of metals in various plants, according Kabata-Pendias & Pendias (1999). Results have shown that Zn concentration in all birch and willow samples were elevated when compared with standard values. According to Pendias & Pendias (1999) upper toxic level of Zn in various plants is reported to be between range 100–400 mg/kg, and normal or sufficient level ranges between 25–150 mg/kg. In all investigated leaves from the settlers Zn concentrations were found to exceed the excessive or toxic concentration and ranged from 156 mg/kg to 431 mg/kg in birch leaves and 181–679 mg/kg in willow leaves. Particularly high Zn bioavailability was observed in one willow sample, where its concentration was found to be 679 mg/kg, exceeding threshold value over four times. However as indicated by Kabata-Pendias & Pendias (1999), most plant species and genotypes have great tolerance to excessive amount of Zn and its phytotoxicity is reported relatively often, especially for acid soils. An excess of Zn lead to reduction in Fe concentration in plants. Moreover, Fe could decrease Zn absorption and its toxicity, probably because of the competition between Zn^{2+} and Fe^{2+} ions in the uptake processes. Concentrations of other metals Cu, Mn, Pb in all investigated leaves from birch and willow were not elevated when compared with threshold values in Table 2 meeting sufficient or normal level accepted for the plants.

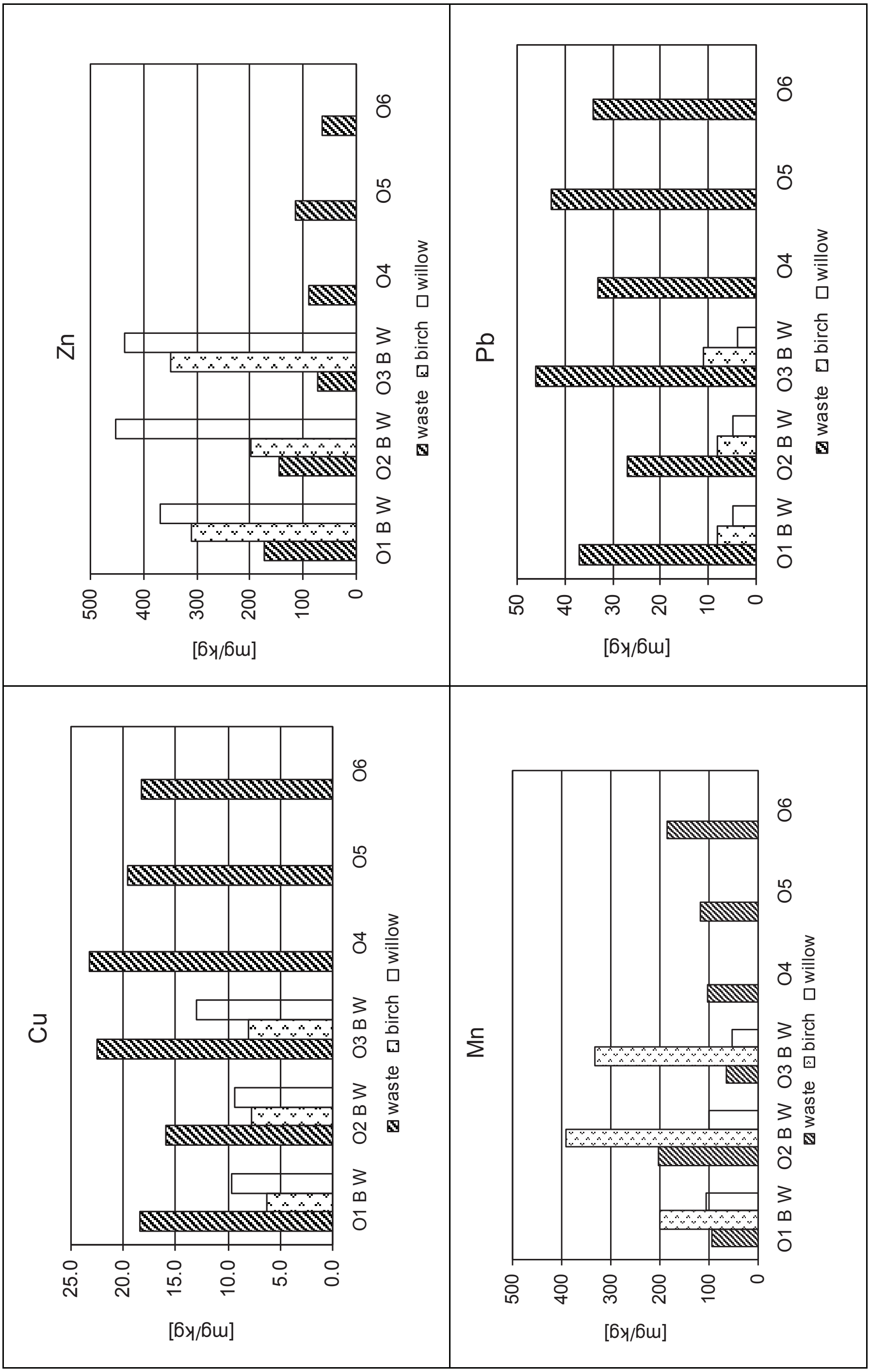

Fig. 2. Comparison of metal concentration in waste with metal intake by birch and willow leaves

Table 2

Concentration of metals in willow and birch leaves (collected from June to October)

Sample	Metal concentration in birch and willow leaves [mg/kg]			
	Mn	Zn	Cu	Pb
W1 VI	51	181	12	1
W1 VII	173	416	11	2
W1 VIII	66	322	8	6
W1 IX	93	475	8	8
W1 X	145	446	9	10
Mean	106	368	10	5
W2 VI	102	328	12	2
W2 VII	86	286	9	3
W2 VIII	49	304	11	7
W2 IX	129	618	8	6
W2 X	134	721	8	10
Mean	100	451	9	5
W3 VI	46	252	17	1
W3 VII	46	325	15	1
W3 VIII	60	485	12	5
W3 IX	60	679	12	6
W3 X	50	418	7	7
Mean	52	432	13	4
B1 VI	171	252	6	4
B1VII	93	218	7	5
B1 VIII	183	254	7	7
B1 IX	253	398	6	11
B1 X	295	427	6	12
Mean	199	310	6	8
B2 VI	276	161	7	5
B2 VII	246	156	6	6
B2 VIII	255	148	5	7
B2 X	790	329	8	13

Table 2 cont.

Mean	392	198	7	8
B3 VI	299	407	9	5
B3 VII	390	374	8	8
B3 VIII	266	220	7	10
B3 IX	308	307	8	11
B3 X	391	431	9	21
Mean	331	348	8	11
Physiological concentration in plants [mg/kg]*	30–300	25–150	5–30	5–10
Toxic concentration in plants [mg/kg]*	400–1000	100–400	20–100	30–300

* According to Kabata-Pendias & Pendias (1999)
W1, W2, W3 – willow from 1^{st}, 2^{nd}, 3^{rd} sampling points
B, B2, B3 – birch from 1^{st}, 2^{nd}, 3^{rd} sampling points
VI–X – month in which leave samples were collected

Moreover there was a great variation observed in metal concentrations in leaves of both trees in relation to the month in which samples were collected. Higher concentrations of metals in leaves were detected in October and November than in summer months, which was probably related to greated amount of precipitation during these periods.

CONCLUSIONS

Research results indicate that low pH of investigated waste and high concentration of sulfate anions can be potentially harmfull for trees growing on the settlers. However, an analysis revealed that high iron content control heavy metals mobilization. Furthermore, sorption of heavy metals is evoked by the presence of iron ox-hydroxides, which posses relatively high specific surface area, sorption capacity as well as good buffer capacity. Both birch and willow trees growing on the settlers revealed high tolerance to adverse living conditions caused by metal stress and low pH of the waste. Ability of these trees' leaves to accumulate metals from wastes is high. Both birch and willow are accumulating an elevated concentration of metals, especially Zn, which was detected at toxic levels. The results therefore confirm the reports of other authors e.g. Pulford & Watson (2003), Chaney (1998) and Dickinson (2000) about the suitability of birch and willow trees in phytoremediation of contaminated sites.

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