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Analysis of adsorption of heavy metals from water solutions by wood of selected domestic species using X-Ray Fluorescence (XRF)

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Abstract: *Analysis of adsorption of heavy metals from water solutions by wood of selected domestic species using X-Ray Fluorescence (XRF).*The aim of this study was to analyze the absorption of three specific heavy metals from model water solution by wood species from domestic Polish forests. This paper focuses on XRF method to determine metal content in samples. European aspen (*Populus tremula* L.) and Black locust (*Robinia pseudoacacia* L.) have been chosen. Firstly, shavings were prepared and soaked with standard solutions of lead (II) nitrate, cadmium nitrate and mercury (II) chloride for 7 days. Then, the material was dried and reduced to ashes using muffle furnace. Finally, content of absorbed metal was marked (XRF) and analyzed with a view to initial contents of metal ions in standard solutions. It was established, that the higher the concentration of mercury in standard solution is, the higher impulse counts is obtained for European aspen. This reversal of the dependence is noticeable for second analyzed species.

Keywords: X-Ray Fluorescence Spectroscopy, wood shaving, adsorption, heavy metals

INTRODUCTION

Heavy metals are omnipresent in the environment around us. Metal compounds penetrate the soil and move to the plants. Not only soil but also the air or food may contain toxic substances. The most important elements during penetration process are the root system and the leaf blades (Ociepa-Kubicka and Ociepa, 2012). The amount of absorbed metal depends on metal's type, the forms in which they occur and from the plant species. There were lots of analyses which were focused on metals content in frequently used food products. In China 47 % of examined tea leaves had higher concentration of Pb than acceptable level (Jin et al. 2005). Furthermore, Polish carrots and celeriac, from Rzeszów allotment gardens, contained more cadmium than it was permitted (Właśniewski and Hajduk, 2012).

Cadmium belongs to the most toxic chemical elements. It concerns not only peoples but also plants. When cadmium gets into the soil, it will stay there for more than 250 years. This element is accumulated in plants roots and is easily moved to all the cells. In consequence, it disturbs natural processes in the plant. In the human body, cadmium has an impact on lungs or kidneys (Gruca-Królikowska and Wacławek, 2006). Lead is present in industrial products such as batteries, welding or components based on metal alloy (Schwantes et al.2018). People may have a contact with it through gasoline, pottery or lead based painting. Discussed element is highly poisonous and it interacts with the nervous system, the brain and the kidneys. Moreover, it may cause anemia (Wani at al. 2015). Mercury, as both of previous listed elements, is a toxic heavy metal common appearing in nature. The most popular exposing factors are: contaminated fish, dental amalgam and mining. A low-level exposure causes weakness or weigh loss (Bernhoft, 2011).

The dilemma of the most efficient method to remove metals form wastewaters is publicly known and often is being discussed by scientist from all over the world. Especially, the subject is undertaken more often in the context of ecology. Lots of attempts have been made to face contamination problem for instance by Božić et al. (2009) using sawdust of

linden (*Tilia*), poplar *(Samsun clone)* and beech *(Fanus sylvatica),* using pulp and Kraft lignin (Ščiban and Klašnja, 2004) as well as with the use of cashew nut shell *(Anacardium occidentale L.)* (Coelho et al. 2014) or even tried to separate metal complexes from fresh water (Hiraide, 1992).

Every mentioned paper showed, there is a huge need to develop new efficient method to analyze and remove metal's contaminations and indicate the effectiveness of wood and listed organic products as adsorbents.

In Poland, 30.8% of the land area is being covered with forests which is similar to the global afforestation rate of 30.6% (Forest Europe, 2015). What is more, almost 24% of forest resources are hardwood forest. In order to analyze adsorption properties of Polish wood, two species were chosen – European aspen (*Populus tremula* L.*)* and black locust *(Robinia pseudoacacia L.).*

The Black locust has been known in Poland for more than 200 years now and it is the dominant species in around 0.1% of domestic stands. The area, where the species is present, equals 3.0% or 6.2% counted by number of trees dominated by Black locust (Fig.1). Discussed species is a melliferous plant and its wood is appropriate for biomass production because of energy properties (Wojda et al. 2015). Therefore, robinia is second Polish tree best serving during honey production process. When the weather allows, honeybees can use up almost all nectar produced from the trees, but it needs to be done gradually. In black locust's flowers they may find substantial content of the nectar and this affects their work efficiency (Jabłoński and Kołtowski, 1993).

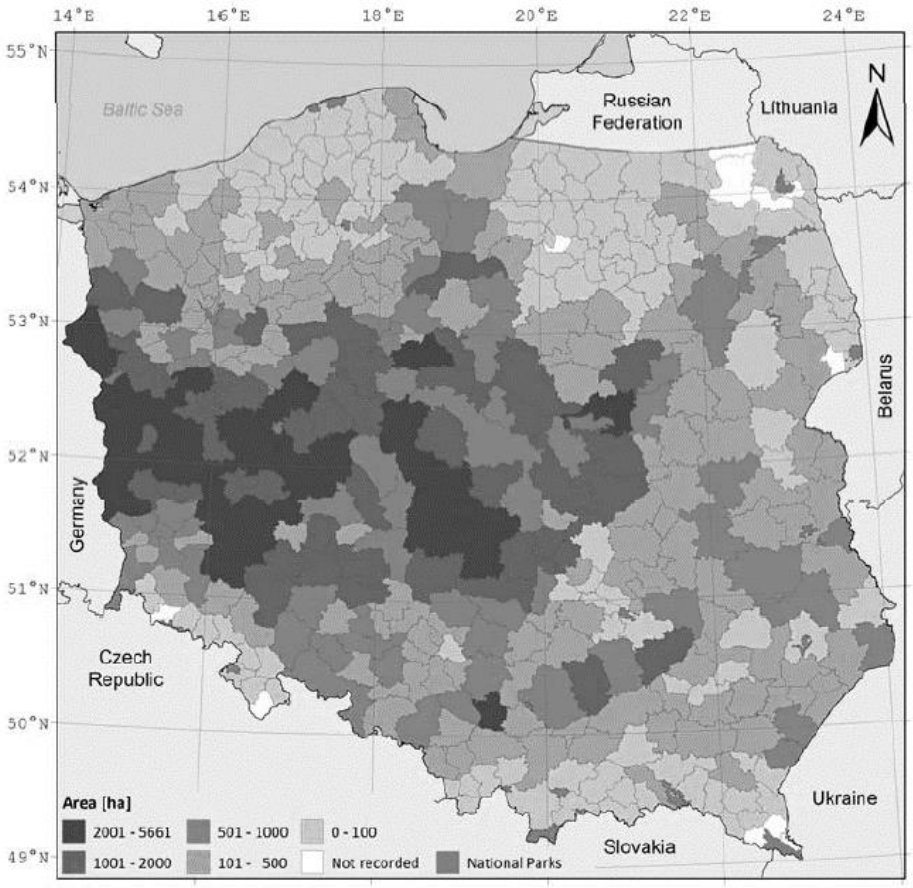

Figure 1. Area of occurrence of the black locust in Poland (in all layers and with whatever share of the forests on State Forest's land) (Wojda et al. 2015)

The second species – *Populus termula* L. – is present not only in Europe but also in Asia. Around 0.8% area of domestic forest is being covered by aspen. Which makes European aspen the sixth most common broadleaved species in Poland (GDLP, 2018). Moreover, it is broadly known that it is a fast-growing tree with low-temperature resistance. It may stand a various habitat conditions and cover disturbed areas for instance after wind-throw or fire (Cardullo and Rigo, 2016). Just like the previous discussed species, aspen is often use for biomass production. The wood is mostly processed during paper and veneer production.

MATERIALS

Samples of wood shavings were produced from two different domestic species. European aspen (*Populus tremula)* and black locust *(Robinia pseudoacacia L.)* were chosen for this experiment. Timber parts were turned into shavings using power drill, and subsequently, the material was ground into smaller particles. This action was taken to upsurge the absorbing area of wood. Material was sieved to standardize the size of the shavings, and the medium fraction (0.43-0.75 mm) was used for further analysis. Subsequently, selected fraction was heating (approximately 80°C) in distilled water for 2 hours. The ratio of wood shavings to water was 1:12.5. As others have highlighted (Szadkowski et al. 2015) boiling homogenizes pores' availability by leveling the humidity.

The next step was to determine the absolute humidity of the boiled material. European aspen shavings were divided into two parts. First one was used immediately after treatment and the second one was stored for 2 weeks in room temperature in order to stabilize the moisture content. What is more, during drying of wood shaving the permeable of mesopores and micropores decrease significantly (Szadkowski et al. 2015). This issue must be mentioned, because it may have an impact on further results. Before beginning of the main analysis, two samples of each species were collected, dried and weighted to calculate the moisture content as arithmetic mean. The results were as follows: 292% for European aspen I (full-saturated with water before analysis was started), 10% for European aspen II (unsaturated with water before analysis was started) and 120% for black locust.

Standard water solutions were prepared by dissolving lead (II) nitrate, cadmium nitrate and mercury (II) chloride. Concentration of appropriate solutions were selected on the basis of maximum tolerance of metal concentration in wastewater in Poland (Dz. U. 2014 poz. 1800). Finally, 12 solutions were prepared, four for every salt. Each one of them had different concentration of metal ions. Exact values were shown below (Table 1).

Table 1. Concentration of metals in standard water solutions

metal	metal content [mg/l]			
Hg	0.1	0.01	0.001	0.0001
Cd	0.2	0.02	0.002	0.0002
Pb	0.1	0.01	0.001	0.0001

From every prepared solutions approximately 30 cm^3 of liquid was taken. Conical flasks were filled with a predetermined amount (Table 2) of wet wood shavings and then the solutions were added. Native sample was also prepared and was filled with distilled water. The material was soaking for 168 hours in room temperature without access to natural light. After this time, it was drained using vacuum flask and dried for 24 hours at a temperature of 105°C. In order to prepare the samples for further testing stage, dried shavings were reduced into ashes by the use of muffle furnace. The combustion process lasted 8 hours at temperature of 600°C.

The last part of the study was based on X-ray fluorescence (XRF) analysis. Sample was treated with high-energy X-rays which caused excitation of the particles. Consequently,

fluorescent X-rays from examined sample were emitted. Each of the elementary substances emits a specific return beam. This resulted in an impulse counts characteristic for each element (Zielenkiewicz, 2010). This phenomenon allows to determine an amount of metal absorbed by wood shavings during sorption. Two different methods of analysis were chosen. First one (Method A) was based on one-stage measurement of particles inside tested sample for 200 seconds. Second one (Method B) examined the material in two stages, during which the apparatus settings were changed. The measurements begun with lamp settings: voltage 45.00 kV and current 0.150 mA (Method A and first stage on Method B for 100 seconds) and finished for voltage 25.00 kV and current 0.350 mA (second stage of Method B) for 200 seconds. The final values were based on an arithmetic mean of three scan points specified for every examined sample. XRF method is dedicated to mark the content of specified element in metal alloys. This type of analysis works rightly because of homogeneous structure of the samples.

Finally, the increase of specific heavy metal content was determined. Graphs were created to show how the impulse counts have changed depending on wood species and chosen method of examination. Mostly, logarithmic scale was used to show clearly the obtained results.

RESULTS

Mass of wet wood shavings used in series I, II and III were presented in Tables below (Table 2).

Table 2. Masses of samples taken for each standard solution

Metal	Metal concentration in solution [mg/l]	Wood shavings mass /g		
		European aspen I (*Populus tremula)*	European aspen II *(Populus tremula)*	Black locust III (*Robinia pseudoacacia L.)*
Hg	0.1	1.00	1.05	1.12
	0.01	0.99	1.08	1.00
	0.001	1.06	1.02	0.88
	0.0001	1.03	1.01	0.94
Cd	0.2	1.00	1.04	0.90
	0.02	1.05	1.01	0.84
	0.002	1.04	1.02	0.91
	0.0002	1.07	1.03	0.95
Pb	0.1	1.00	1.07	0.84
	0.01	1.06	1.03	0.99
	0.001	1.00	1.03	0.91
	0.0001	1.02	1.01	0.89
native sample		0.0001	1.05	1.07

Table 3 shows obtained results for European aspen I. The values for mercury are similar. What is important, there is no significant difference between results for Method “B” 300 s and 600 s. Maximum values for lead do not exceed 100000 counts (Method ”B”) and 25000 counts (Method “A”). Method “B” has not detected cadmium.

Table 3. Results for European aspen I (XRF)

Metal	Metal concentration in solution [mg/l]	Impulse counts		
		Method "A"	Method "B"	
		200 s	300 s	600 s
Pb	0.1	23315.00 ± 588.00	98976.50 ± 15037.56	86427.00 ± 15258.67
	0.01	13252.00 ± 1953.00	13088.40 ± 6762.67	54578.67 ± 10687.11
	0.001	1452.97± 111.84	55776.67 ± 9224.44	6594.63 ± 7158.24
	0.0001	147.81 ± 12.33	1270.3 ± 134.7	5901.93 ± 361.38
Hg	0.1	N/D*	279.60 ± 101.02	308.52 ± 1.09
	0.01	N/D*	209.85 ± 6.82	189.38 ± 9.26
	0.001	N/D*	257.38 ± 44.86	245.54 ± 52.58
	0.0001	N/D*	286.49 ± 27.93	269.02 ± 43.26
Cd	0.2	2302.27 ± 738.11	N/D*	N/D*
	0.02	724.22 ± 89.55	N/D*	N/D*
	0.002	107.89 ± 58.32	N/D*	N/D*
	0.0002	17.31 ± 9.97	N/D*	N/D*
Pb	native sample	27.16 ± 8.63	264.90 ± 9.70	266.34 ± 6.79
Hg		N/D*	298.01 ± 9.77	201.70 ± 5.13
Cd		3.40 ± 1.22	N/D*	N/D*

* Not detected.

Results for European aspen II (Table 4) are higher than obtained for previous series. It is easily noticeable that drier material absorbed more metal ions than moister. Presumably, deaeration of wood during boiling process may be responsible for such wide variation of the obtained results.

Table 4. Results for European aspen II (XRF)

Metal	Metal concentration in solution [mg/l]	Impulse counts		
		Method "A"	Method "B"	
		200 s	300 s	600 s
Pb	0.1	879658.33 ± 185512.22	3543093.33 ± 761092.89	7059773.67 ± 1514187.11
	0.01	255397.67 ± 42050.22	995291.00± 151228.67	1993062.33 ± 303936.44
	0.001	55048.67 ± 14663.11	223238.33 ± 43232.89	430017.00 ± 74965.33
	0.0001	28347.67 ± 11822.89	144045.67 ± 40916.89	278096.00 ± 83012.67
Hg	0.1	N/D*	16828.00 ± 3001.00	31259.00 ± 5681.00
	0.01	N/D*	3134.00 ± 2186.00	8546.00 ± 2224.00
	0.001	N/D*	5498.00 ± 451.00	10550.00 ± 523.00
	0.0001	N/D*	7190.67 ± 2580.89	14141.50 ± 8948.50
Cd	0.2	46862.00 ± 7674.67	N/D*	N/D*
	0.02	8213.33 ± 1508.44	N/D*	N/D*
	0.002	4432.00 ± 592.67	N/D*	N/D*
	0.0002	523.00 ± 126.67	N/D*	N/D*
Pb	native sample	23244.00 ± 4853.11	112064.00 ± 13465.00	242797.00 ± 35488.89
Hg		N/D*	218.00 ± 122.00	5348.50 ± 4205.56
Cd		249.50 ± 76.00	N/D*	N/D*

* Not detected.

Table 5 shows black locust results. Obtained values are in reversal dependence than was shown before (Table 3 and Table 4).

Table 5. Results for black locust III (XRF)

Metal	Metal concentration in solution [mg/l]	Impulse counts		
		Method "A" 200 s	Method "B"	
			300 s	600 s
Pb	0.1	464.90 ± 30.31	2237.30 ± 187.27	2246.70 ± 176.27
	0.01	514.95 ± 371.26	2226.00 ± 1031.20	2235.27 ± 1076.22
	0.001	8580.27± 3327.82	36952.00 ± 13623.33	37089.33 ± 13867.11
	0.0001	58004.50 ± 24889.33	239785.00 ± 15095.00	235252.00 ± 16486.00
Hg	0.1	N/D*	477.09 ± 31.40	463.53 ± 24.00
	0.01	N/D*	357.38 ± 17.54	346.85 ± 11.71
	0.001	N/D*	218.09 ± 5.78	215.98 ± 4.17
	0.0001	N/D*	295.93 ± 53.98	293.51 ± 33.54
Cd	0.2	4.00 ± 0.27	N/D*	N/D*
	0.02	42.80 ± 3.40	N/D*	N/D*
	0.002	426.45 ± 48.72	N/D*	N/D*
	0.0002	3306.40± 202.07	N/D*	N/D*
Pb	native sample	34.37 ± 7.34	386.27 ± 55.37	376.01 ± 50.84
Hg		N/D*	307.38 ± 15.50	305.66 ± 10.92
Cd		1.47 ± 0.59	N/D*	N/D*

* Not detected.

Lead is the only element that was marked for every chosen method. The highest values were referred for Method "B" regardless of scanning time. Figure (Fig2) shows a change in lead content relative to native sample. The results for black locust were similar. The exposure time did not affect the results (Fig2).

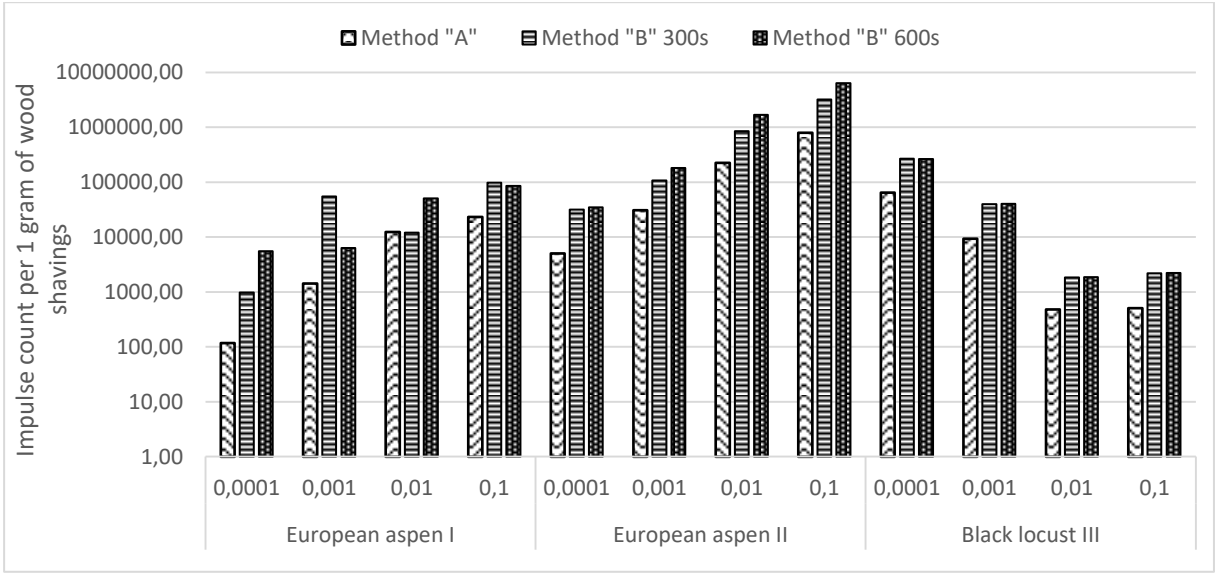

Figure. 2. Growth of Pb content per 1 gram of wood shavings

Due to the impulse counts' values obtained for cadmium, the logarithmic scale was replaced with numerical scale (Fig2). Using the previous one would make the results impossible to

show. Obtained values for some of the tested ashes were lower than gained for native sample. It means that negative growth occurred. This phenomenon is possible and it was highlighted (Mohan et al. 2007) for cadmium between 30th and 40th hour of equilibrium time. That study has been made on an oak wood. The cited analysis included the results only for 50 hours of adsorption. Most likely this dependence could be repeated after much longer period of sorption. Figure (Fig3) shows a change in cadmium content relative to the native sample.

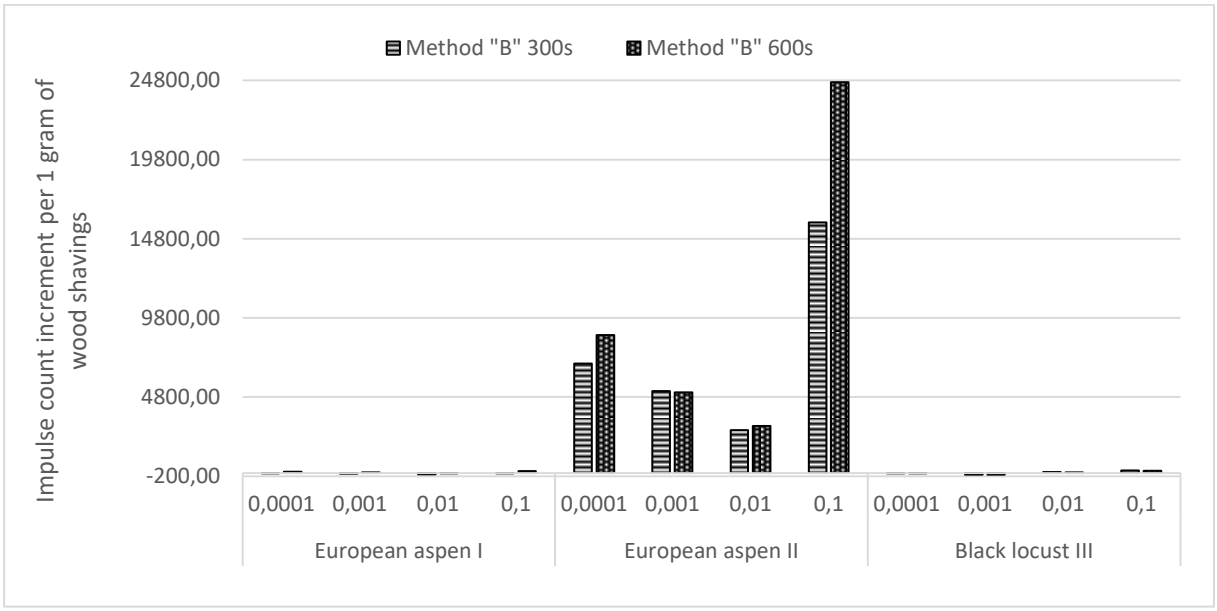

Figure. 3. Growth of Cd content per 1 gram of wood shavings

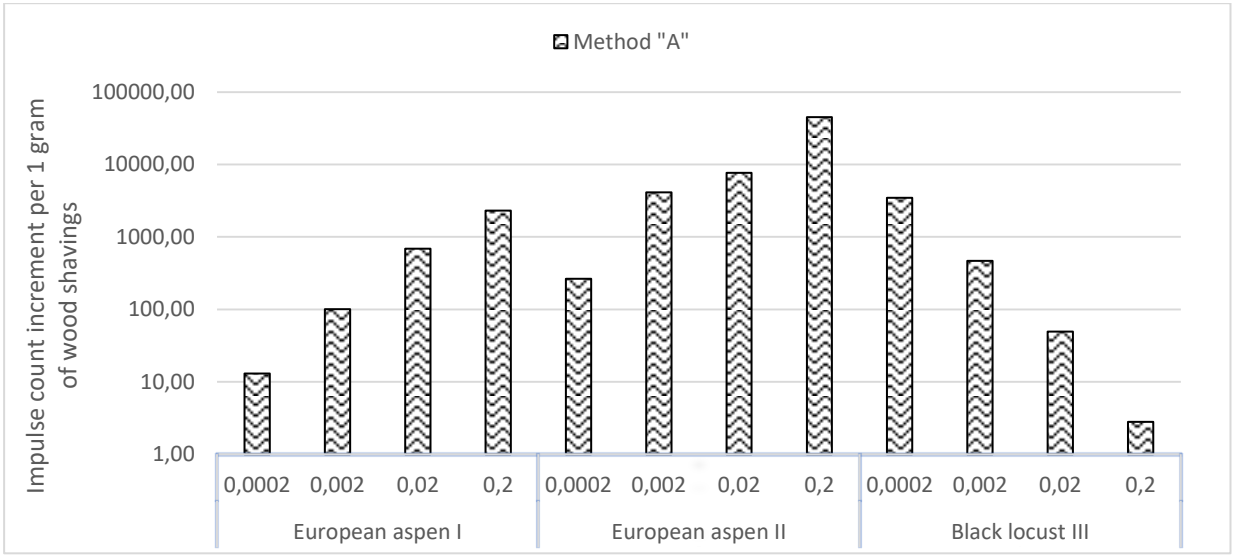

Figure. 4. Growth of Hg content per 1 gram of wood shavings

The higher the concentration of mercury in standard solution, the higher impulse counts obtained for European aspen. This reversal of the dependence is noticeable for second analysed species. It means that the higher the concentration of mercury in standard solution is, the lower amount of impulse counts is obtained for black locust (Fig4).

CONCLUSIONS

1. XRF analysis is suitable for determining metal content in wood.
2. Obtained results show the differences of absorbed metals' level and its may contribute to more advanced research.
3. The results show how important are adsorption and desorption of heavy metals in context of wood.
4. The higher moisture content in European aspen wood, the lower amount of impulse counts obtained during XRF examinations.
5. The increase of exposure time (Method "B") insignificantly affects increase impulse counts. In case of Black locust, no changes in impulse counts for lead and mercury were noticed.
6. The higher the concentration of mercury in standard solution is, the higher impulse counts is obtained for European aspen. This reversal of the dependence is noticeable for second analyzed species.
7. The higher the concentration of lead in standard solution is, the lower impulse counts is obtained for Black locust. This reversal of the dependence is noticeable for second analyzed species.
8. The higher the concentration of cadmium in standard solution is, the higher impulse counts is obtained for European aspen. This reversal of the dependence is noticeable for second analyzed species.

REFERENCES

1. BERNHOFT R. A., (2011), Mercury Toxicity and Treatment: A Review of the Literature, Incorporating Environmental Health in Clinical Medicine, 2011
2. BOŽIĆ D., STANKOVIĆ V., GORGIEVSKI M., BOGDANOVIĆ G., KOVAČEVIĆ R., (2009), Adsorption of heavy metal ions by sawdust of deciduous trees, Journal of Hazardous Materials, 171, 2009, 684–692
3. CAUDULLO, G., DE RIGO, D., (2016), Populus tremula in Europe: distribution, habitat, usage and threats. In: San-Miguel-Ayanz, J., de Rigo, D., Caudullo, G., Houston Durrant, T., Mauri, A. (Eds.), European Atlas of Forest Tree Species. Publ. Off. EU, Luxembourg,
4. COELHO G.F., GONÇALVES JR. A.C., TARLEY C.R.T., CASARIN J., NACKE H., FRANCZISKOWSKI M.A., (2014), Removal of metal ions Cd (II), Pb (II), and Cr (III) from water by the cashew nut Shell *Anacardium occidental* L.Ecological Engineering, 514-525
5. FOREST EUROPE, 2015: State of Europe's Forests 2015
6. GENERALNA DYREKCJA LASÓW PAŃSTWOWYCH, (2018), Rocznik statystyczny Rzeczpospolitej Polskiej, GUS
7. GRUCA-KRÓLIKOWSKA S., WACŁAWEK W., (2006), Metale w środowisku; cz. II. Wpływ metali ciężkich na rośliny, Chemia-Dydaktyka-Ekologia-Metrologia, 11, 2006, 41-54
8. HIRAIDE M., (1992), Heavy metals complexed with humic substances in fresh water, Analytical Sciences, 8, 1992, 453-459
9. JABŁOŃSKI B., KOŁTOWSKI Z., (1993), Badania wartości pszczelarskiej robinii akcjowej (*Robinia pseudoacacia L.*), Pszczelnicze Zeszyty Naukowe, XXXVII
10. JIN C.W., ZHENG S.J., HE Y.F., ZHOU G.D., ZHOU Z.X.,(2015), Lead contamination in tea garden soils and factors affecting its bioavailability, Chemosphere 2005, 59, 1151-1159

11. MOHAN D., PITTMAN C. Jr., BRICKA A., SMITH F., YANCEY B., MOHAMMAD J., STEELE P., ALEXANDRE-FRANCO M., GÓMEZ-SERRANO V., GONG H., (2007). Sorption of arsenic, cadmium, and lead by chars produced form fast pyrolysis of wood and bark during bio-oil production, Journal of Colloid and Interface Science 310, 2007, 57-73
12. OCIEPA-KUBICKA A., OCIEPA E., (2012), Toksyczne oddziaływanie metali ciężkich na rośliny, zwierzęta i ludzi, Inżynieria i Ochrona Środowiska, 15, 2012, 169-180
13. Rozporządzenie ministra środowiska w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego, Dz. U. (2014), poz. 1800, 16-17, 23
14. ŠCIBAN M., KLAŠNJA M., (2004), Wood sawdust and wood originate materials as absorbents for heavy metal ions, Holz Roh Werkst, 62:69-73
15. SCHWANTES D., GONÇALVES A. C. JR., CAMPAGNOLO M. A., TEIXEIRA TARLEY C. R., DRAGUNSKI D. C., DE VARENNES A., KINKAS DOS SANTOS SILVA A., CONRADI E. JR., (2018), Chemical modifications on Pinus bark for adsorption of toxic metals, Journal of Environmental Chemical Engineering, 6, 2018, 1271-1278
16. SZADKOWSKI J., RADOMSKI A., SZADKOWSKA D., ZAKRZEWSKI A., RĘBOKWSKI D., MARCHWICKA M., LEWANDOWSKA A., (2015), The changes in available mesopores distribution of white poplar (*Populus Alba L.)* wood during cyclic drying, Episteme 26, 399-407
17. WANI AL., ARA A., USMANI J. A., (2015), Lead toxicity: a review, Interdiscip Toxicol, 8(2), 55-64
18. WOJDA T., KLISZT M., JASTRZĘBOWSKI S., MIONSKOWSKI M., SZYP-BOROWSKA I., SZCZYGIEŁ K., (2015), The geographical distribution of the black locust (*Robinia pseudoacacia L.)* in Poland and its role on non-forest land, Papers on Global Change, 22, 101-103
19. WŁAŚNIEWSKI S., HAJDUK E., (2012), Akumulacja kadmu w glebach i wybranych warzywach uprawianych w ogrodach działkowych Rzeszowa, Roczniki Gleboznawcze, LXIII,55-60
20. ZIELENKIEWICZ T, (2010); Method development of the XRF analysis of metal content in scots pine wood (*Pinus Sylvestris* L.), Ann. WULS-SGGW, For and Wood Technol. 72, 2010, 514-521

Streszczenie: *Badanie adsorpcji metali ciężkich z modelowych roztworów wodnych przez drewno wybranych gatunków krajowych za pomocą Spektrometrii Fluorescencji Rentgenowskiej (XRF)*. Celem wykonanych badań było sprawdzenie poziomu adsorpcji wytypowanych metali ciężkich tj. ołowiu, kadmu oraz rtęci, przez dwa gatunki rodzime topolę (*Populus tremula* L.) oraz robinię akacjową *(Robinia pseudoacacia* L.). W fazie przygotowawczej materiał został znacznie rozdrobniony i rozdzielony na kilka frakcji. Działanie to miało na celu zwiększenie powierzchni adsorpcji badanego drewna. Azotan kadmu (II), azotan ołowiu oraz chlorek rtęci (II) zostały rozpuszczone w destylowanej wodzie w takich proporcjach, aby stworzyć po cztery roztwory – każdy o innym stężeniu. Wybrana frakcja wiórów została poddana obróbce termicznej w wodzie destylowanej w celu usunięcia zawartego powietrza. Następnie frakcję podzielono na próbki 1 gramowe. Drewno nasiąkało w modelowych roztworach przez ok. 168 godzin. Finalnie zostało ono odsączone, wysuszone i spopielone w piecu muflowym. Tak przygotowane próbki zostały poddane badaniu z wykorzystaniem spektrometrii fluorescencji rentgenowskiej (XRF). Urządzenie analizowało

zawartość metali w pyle za pomocą dwóch różnych programów i trzech czasów naświetlania. Otrzymane wartości analizowano pod kątem ilościowym a nie jakościowym.

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