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XRF analysis of heavy metals contents in oak wood (*Quercur robur* L.)

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Abstract: *XRF analysis of heavy metals contents in oak wood (Quercur robur* L.). The aim of this study was to determine an amount of adsorbed metals ions from water solutions by oak (*Quercus robur* L.) shavings. This paper focuses on XRF analysis of metal contents in examined samples. Necessary material was obtained from damaged flooring strips. Samples were soaked with standard water solutions of lead (II) nitrate, cadmium nitrate and mercury (II) chloride. After 7 days wood shavings were dried and reduced to ashes in muffle furnace. Content of adsorbed metal was marked (XRF) and classified depending on percentage concentration of metal ions in solutions.

Keywords: heavy metal content, XRF spectrometer, wood shavings

INTRODUCTION

Nowadays, one of the most serious problems, which could affect not only people but also plants, are the environmental pollutants. Metals such as zinc, copper, cadmium, lead and mercury can be found in industrial wastewater or soil. It is due to fact that heavy metals are not biodegradable. To the factors, which have an impact on increased amount of the environmental pollutants, may include metal plating facilities, mining operations, pesticides and tanneries. (Fu, Wang, 2011).

There are three direct ways how heavy metals can entry into trees. First of all, metal compounds can be transferred from the soil via the roots. Secondly, air pollutions can move into leaves or conifer needles. Finally, lots of toxic substances may be in contact with bark and penetrate into the wood. (Lepp, 1975)

One of the useful methods, that helps researchers determine amount of heavy metal content in wood bark, is biomonitoring. Biological materials are examined in order to mark the content of hazardous substances. Data interpretation shows how many pollutants are in the air and how pollutants spread through the environment. According to Pańczyk et al. (2018) wood bark can contain metals as nickel, copper, zinc, cadmium and lead. Absorbed metal value depends on various factors such as bark porosity or anisotropic structure of chosen samples. As a consequence, the range of results can be seen clearly.

It is a public knowledge that wood ashes can be used for liming soils. Probably the majority of gardeners have never thought about heavy metals in them. The performed analysis showed, that the heavy metals content in ashes was low but exceeded limits for waste materials. Although, examined samples exhibit good physical and chemical properties. As a results they can be used to lime medium and heavy soils. (Symanowicz et al, 2018)

Around the world lots of scientist try to face the problem of increased amount of metal ions in several types of wastewater. There were attempts to remove metal ions by cashew nut shell (Coelho et al., 2014), wood sawdust (Šćiban et al., 2006), modified sugarcane bagasse (Pereira et al., 2009) and *Moringa stenopetala* bark (Kebede et al., 2018). There were used different measuring techniques. Some of the values were determined by FAAS (Flame atomic absorption spectroscopy), FTIR (Fourier-transform infrared spectroscopy) or TGA (Thermogravimetric analysis). Results were obtained by using AAS (Atomic Absorption Spectrometry) too. It seems that there are lots of methods to analyze metal content in wood.

*It must be emphasized that presented data is analyzed in terms of impulse counts not quantitatively.

However, it must be emphasized that some of them require laborious stage of preparation and performed analysis may be time-consuming. That is why there is a noticeable need to elaborate another method, that gives results faster and without unnecessary preparation of samples.

In this paper was made an attempt to state if X-ray fluorescence technique (XRF) is suitable to check an amount of adsorbed metal by oak (*Quercus robur* L.) shavings. Considering anisotropic wood anatomy, there were chosen two different types of matrix in order to check their effectiveness (Zielenkiewicz, 2010).

MATERIALS AND METHOD

Samples of oak were obtained from old flooring strips. Orbital sander was used to remove varnish from wood. Pure material was turned into shavings. This procedure was necessary to increase the adsorbing area of wood. Material was divided into 3 fractions by sieves and medium part (0,43- 0,75mm) was selected. In order to homogenise the availability of pores by levelling the humidity, the chips were boiled in distilled water for 2 hours (Szadkowski et al, 2015). Absolute humidity was determined as arithmetic average for two separated measurements. The achieved value oscillated around 168%.

Conical flasks were filled with ca. 1g of previously prepared wet material. Standard solutions of lead (II) nitrate, cadmium nitrate and mercury (II) chloride were prepared. Percentage contents of metals ions in solutions were determined on maximum tolerance of metal concentration in wastewater in Poland (Dz. U. 2014 poz. 1800). Additionally, three more solutions for each salt were made, corresponding to different metal concentration.

Table 1. Metals concentrations in standard 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

Each flask was filled with approximately 30 cm^3 of liquid. One of those was filled with distilled water. After 168 hours of soaking wood shavings were filtered by the use of vacuum flask and dried for 24 hours. Samples mass was examined. In order to reduce wood shavings into ashes, samples were put into ceramic crucible and after that into muffle furnace (8 hours at 600°C). Mass of ashes was determined.

Ashes were examined using XRF. During analysis two types of XRF calibration were used. Method A consisted of one-stage measurement of elements in the material for 200 seconds point, lamp settings (voltage 45.00 kV, current 0.150 mA). Method B consisted of measuring the fragments in two stages. During the initial measurement for a period of 100 seconds, the apparatus was set (voltage 45.00 kV, current 0.150 mA), while in the second stage the samples were lighted for a period of 200 seconds with a lamp (voltage 25.00 kV, current 0.350 mA. Equipment target settings in both methods was 1.00 mm. Each result was determined as arithmetic average for three “scan points”. The chosen points were examined and gave impulse counts, which are characteristic for each element (Zielenkiewicz, 2010). Three series of measurements were made.

RESULTS AND DISCUSSION

Table 2 shows real mass of taken wood shavings samples for each concentration of prepared solution depending on chosen metal.

*It must be emphasized that presented data is analyzed in terms of impulse counts not quantitatively.

Table 2. Mass of wet wood shavings with 168% humidity, for each standard solution

metal	metal concentration in solution [mg/l]	wood shavings mass [g]
Hg	0,1	1,04
	0,01	1,05
	0,001	1,01
	0,0001	1,03
Cd	0,2	1,01
	0,02	1,02
	0,002	1,05
	0,0002	1,00
Pb	0,1	1,01
	0,01	1,05
	0,001	1,03
	0,0001	1,01
native sample		1,00

The average impulse counts for ashed samples depending on used method are presented in the tab. 3.

Table 3. The average of impulse counts for examined metal depending on chosen method

metal	metal concentration in solution [mg/l]	Impulse counts *		
		method "A" 200 s	method "B"	
			300s	600s
Hg	0,1	0,00	175,52	163,14
	0,01	0,00	114,92	116,31
	0,001	0,00	220,75	209,07
	0,0001	0,00	199,65	190,05
Cd	0,2	3,81	0,00	0,00
	0,02	58,15	0,00	0,00
	0,002	323,00	0,00	0,00
	0,0002	2039,30	0,00	0,00
Pb	0,1	631,07	1628,24	2065,90
	0,01	1211,63	6684,27	6627,07
	0,001	5774,30	33593,00	34232,00
	0,0001	29453,00	141835,33	138952,00
Hg	native sample	0,00	348,05	326,98
Cd		4,12	0,00	0,00
Pb		72,57	633,36	626,19

Differences between obtained results are easily noticeable. The dependence for mercury was not found for method "A". This same results were obtained for cadmium after method "B" examination. Those results show clearly, how important is correctly chosen method during XRF analysis. What is more, correlations between Cd and method "A" as well as between Pb and methods "A" and "B" show inverse proportionality. The higher metal concentration in standard water solution, the lower amount of impulses. Those questions need to be further analyzed.

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For lead and cadmium content in oak chips, a greater increase in the presence of these metals in the tested material is observed with solutions of lower concentration. The increase in cadmium content at 0.0002 mg/l metal concentration in liquids is over five hundred times greater than for 0,2 mg/l concentration. (Method A), for the content of determined lead, the increase in the content of this metal is more than forty-six fold greater for a concentration of 0,0001 mg/l than 0,1 mg/l (method A). The increase in mercury content in wood chips after exposure to liquid contaminated with this metal is greater at lower concentrations. The largest value is observed at a concentration of 0,0001 mg/l and is almost 126% higher than for a liquid taken as a 0,1 mg/l mercury concentration (method B 300 s).

The results obtained may be related to chip penetration through the solution. Solutions with a higher metal concentration can cause closing plugs in wood chips, which means that the deposit has a smaller surface for the adsorption of metallic contaminants.

CONCLUSIONS

1. This research confirmed that XRF analysis method is effective in examining metal concentration but it needs to be optimized.
2. There is a need for a deeper analysis of the issue in order to find the reason why there are no results for mercury and cadmium.
3. Correlations between metal concentration in standards solutions and impulse counts should be determined by increased amount of examined samples.
4. The increase in heavy metal content in the oak chip deposit is associated with their concentration in model liquids
5. Oak shavings better capture heavy metals from liquids in which their concentration is lower.

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Streszczenie*: Analiza zawartości metali ciężkich w dębinie (Quercus robul* L.*) metodą fluorescencji rentgenowskiej XRF*. Celem niniejszych badań było sprawdzenie adsorpcji wybranych metali ciężkich tj. kadm, rtęć i ołów z modelowych roztworów, za pomocą drewna dębu (*Quercus robul* L.). Materiał do badań został pozyskany z recyklingu tj. z uprzednio oczyszczonych desek parkietowych. Aby zwiększyć powierzchnię adsorpcji próbek, drewno zostało rozdrobnione na wióry. Przygotowano po 4 stężenia roztworów dla każdego związku metalu. Wykorzystane zostały: azotan kadmu (II), azotan ołowiu oraz chlorek rtęci (II). Każda z próbek wiórów (ok.1 gram) nasiąkała przez ok. 168 godzin w danym roztworze. Następnie materiał został wysuszony, spopielony i finalnie przebadany za pomocą metody spektrometrii XRF (korzystającej z metody fluorescencji rentgenowskiej). Wykorzystano dwa sposoby kalibracji urządzenia oraz trzy różne czasy naświetlania punktu pomiarowego. Otrzymane wyniki zostały przeanalizowane pod kątem osiągniętej ilości zliczeń.

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