

## Using of wooden sawdust for copper removal from waters

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### Abstract

The heavy metal removal from wastewater is very important due to their persistent character in aquatic environment. The use of wooden sawdust is emerging as a potential alternative to the existing conventional technologies for the removal of metal ions from aqueous solutions. The aim of this work is to study the Cu(II) removal of from water by unconventional waste products including the wooden sawdust of poplar, cherry, spruce and hornbeam. The FT-IR spectra of the studied wooden sawdust confirmed the presence of functional groups that have potential for heavy metal binding. The highest efficiency of Cu(II) removal was observed for poplar wooden sawdust at static (86 %) and dynamic (88 %) adsorption experiments. Data obtained by neutron activation analysis revealed that ion exchange is also a mechanism of metal removal by the selected wooden sawdust.

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## Introduction

The heavy metal ions are discharged to the aquatic environment by various branches of industries as mining, tanneries, batteries, paper industries, agrochemicals, etc. The heavy metals are toxic and accumulate in living bodies causing serious diseases and disorders (Celik and Demirbaş 2005; Singovszka *et al.* 2016). The toxic heavy metals such as Cr, Se, V, Cu, Co, Ni, Cd, Hg, As, Pb, and Zn can be considered as the most hazardous metals toxic for human even at low concentrations (Gardea-Torresdey *et al.* 1998). The most commonly used methods for removal of metal ions from wastewaters are chemical precipitation, ion exchange, chemical oxidation/reduction, reverse

osmosis, electro dialysis, ultra-filtration, etc. (Gardea-Torresdey *et al.* 1998; Zhang *et al.* 1998). However, these techniques have limitations such as less efficiency at low concentrations or production of secondary sludge, which furthers the disposal, is costly (Ahluwalia and Goyal 2005). Another technology suitable for treatment of wastewater is adsorption of heavy metals by activated carbon. However, the high cost of activated carbon and its loss during the regeneration restricts its wide application (Imamoglu and Tekir 2008). In last two decades is booming for the use of low cost organic materials for heavy metal ions removal. It started with the application of biomass and agricultural waste materials as peat, rice husk, leaves or seeds (Bailey *et al.* 1999; Vieira and

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**Table 1.** Examples of adsorption capacity of selected natural adsorbents.

Adsorbent	Adsorption capacity [mg.g <sup>-1</sup> ]					References
	Cu(II)	Zn(II)	Ni(II)	Pb(II)	Cd(II)	
Chitosan	222.0	75.0	164.0	16.4	8.5	(Bailey <i>et al.</i> 1999; Babel and Kurniawan 2003)
Zeolites	5.1	5.5	4.5	175.0	137.0	(Bailey <i>et al.</i> 1999; Babel and Kurniawan 2003)
Clays	1.2	52.9	–	4.3	11.4	(Bailey <i>et al.</i> 1999; Babel and Kurniawan 2003)
Peats	19.6	13.1	11.7	–	22.5	(Bailey <i>et al.</i> 1999; Babel and Kurniawan 2003)
Bark	0.7	0.8	–	400.0	32.0	(Bailey <i>et al.</i> 1999; Demcak <i>et al.</i> 2017b)
Sawdust	3.9	3.7	–	7.3	–	(Bailey <i>et al.</i> 1999; Holub <i>et al.</i> 2016)

Volesky 2000; Demcak *et al.* 2017a). The major advantages of adsorption on natural sorbents in comparison to conventional methods include low cost, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, regeneration of biosorbents, and possibility of metal recovery (Leng *et al.* 2015). The Table 1 represents the adsorption capacities of selected natural adsorbents for the heavy metals removal.

Wooden materials or wastes are cheap sorbent materials (Ngah and Hanafiah 2008; Ahmaruzzaman 2011). The benefits of application of wooden adsorbent materials (by-products or wastes) for heavy metals removal from wastewaters are determined by their high removal selectivity, good adsorption capacity and possibility of regeneration. In several studies (Shukla *et al.* 2002; Šćiban *et al.* 2007; Asadi *et al.* 2008) it has been reported that the wooden adsorbent materials such as straw, tree bark, peanut skins, wood sawdust, moss and peat are a suitable replacement of industrial produced sorbents with comparable efficiencies of pollutants removal. The wooden sawdust is a perspective low-costs adsorbent material for the removal of heavy metal ions, some types of acid, basic dyes, and other unwanted compounds from wastewaters (Demcak *et al.* 2017b). The efficiency of the wooden sawdust adsorption processes is also affected by the composition of the wastewater where the formation of complex compounds of metal cations with wood sawdust functional groups can take place resulting in the decrease or a failure of the heavy metals adsorption (Ahmad *et al.* 2009).

The adsorption properties of wooden sawdusts are influenced by their composition. The wooden

sawdust are mainly composed from lignin, cellulose and hemicellulose, carbohydrates, and phenolic compounds, which contain carboxyl, hydroxyl, sulphate, phosphate, and amino groups, the main metal binding (Gardea-Torresdey *et al.* 1990; Crini 2006). The application of wooden materials such as wooden sawdust for heavy metals removal brings many benefits for the protection of environment, where the contaminated water could be treated. It brings for the timber industry a new opportunity for the utilization of wooden sawdust as promised cheap adsorbents (Shukla *et al.* 2002).

The paper deals with a Cu(II) ions removal from model solutions by poplar, spruce, cherry and hornbeam wooden sawdust under static and dynamic conditions. The selected wooden sawdust were analysed by infrared spectrometry for characterization of functional groups, which can be responsible for metal binding. Efficiency of Cu(II) ions removal was analysed by colorimetric method and changes of pH values were also measured. Neutron activation analysis was used to determine the elemental composition of wooden sawdust (raw and Cu-loaded).

## Experimental

### *Sorbent-sorbate characterisation*

The wooden sawdust of poplar, spruce, cherry, and hornbeam species of locally available wood was sieved, and only the fractions with a particle size under 2.0 mm were used for the experiments. The model solution with initial concentrations of Cu(II) ions 10 mg.L<sup>-1</sup> was prepared by dissolving of CuSO<sub>4</sub>·5H<sub>2</sub>O in deionised water.

### Sorption experiment

The batch adsorption experiments were carried out in two modes (static and dynamic conditions). In both adsorption experiments, 1 g of dry wooden sawdust were mixed with 100 mL of model solutions (initial concentration of dissolved Cu(II) ions was 10 mg.L<sup>-1</sup>). In static conditions, the sorbent-sorbate interaction time was 1 day. To determine the contact time required for equilibrium sorption in dynamic condition the samples were analysed in different time intervals (5, 10, 15, 30, 45, 60 and 120 min). In all cases, at the end of the adsorption experiments, wooden sawdust was removed by filtration through a laboratory filter paper. Residual concentrations of Cu(II) ions present in solutions were determined by colorimetric method and pH changes was also measured. In both cases, the percentage efficiency of ion removal  $\eta$  removal was calculated using the following equation (Eq. 1):

$$\eta = \frac{(c_0 - c_e)}{c_0} \times 100 \%, \quad (1)$$

where  $c_0$  is the initial concentration of appropriate ions [mg.L<sup>-1</sup>] and  $c_e$  equilibrium concentration of ions [mg.L<sup>-1</sup>]. All adsorption experiments were carried out in triplicate under the batch conditions and results are given as arithmetic mean values.

### Apparatus and instrumentation

The IR measurements of the wooden sawdust were performed on a Bruker Alpha Platinum-ATR spectrometer (BRUKER OPTICS, Ettingen, Germany). A total of 24 scans were performed on each sample in the range of 4,000 to 400 cm<sup>-1</sup>. Concentrations of the Cu(II) in solution were determined using the colorimetric method with a Colorimeter DR890, (HACH LANGE, Germany) and the appropriate reagent. The input pH value of model solution was measured by pH meter inoLab pH 730 (WTW, Germany).

The elemental composition of raw and Cu-loaded wooden sawdust was determined by neutron activation analysis (NAA) at the pulsed fast reactor IBR-2 of the Frank Laboratory of Neutron Physics, JINR, Dubna, Russia. For NAA analysis samples of approximately 0.3 g, dried at 40 °C to constant weight, were packed in polyethylene foil bags for

short-term irradiation or in aluminium cups for long-term irradiation. A total of 5 elements: Na, Mg, K, Ca, and Ba were determined. More details concerning the irradiation time and gamma spectra processing can be found in (Frontasyeva 2011). The difference between the certified and measured content of elements of the certified material varied between 1 and 10 %.

## Results and Discussion

### Infrared spectra of wooden sawdust

The functional groups present in natural materials as alcoholic, carbonyl, phenolic, amide and amino, sulfhydryl groups etc. have affinity for heavy metal ions to form metal complexes or chelates. The mechanism of biosorption process includes chemisorption, complexation, adsorption on surface, diffusion through pores and ion exchange (Sud *et al.* 2008). The functional groups of poplar, spruce, cherry, and hornbeam were determined using FTIR spectroscopy (Fig. 1). The metal adsorption capacity of wooden sawdust is influenced with the presence of surface structures of -OH (3,650 – 3,000 cm<sup>-1</sup> and 1,700 – 1,600 cm<sup>-1</sup>), -COOH (1,750 – 1,350 cm<sup>-1</sup> and 1,250 – 1,000 cm<sup>-1</sup>), and -NH<sub>x</sub> (3,337 cm<sup>-1</sup>) functional groups that are present in organic materials (Ricordel *et al.* 2001). According to the literature (Kidalova *et al.* 2015), the structure of wooden sawdust is primarily formed by cellulose, hemicellulose, and lignin. The detailed FT-IR spectra of wooden sawdust

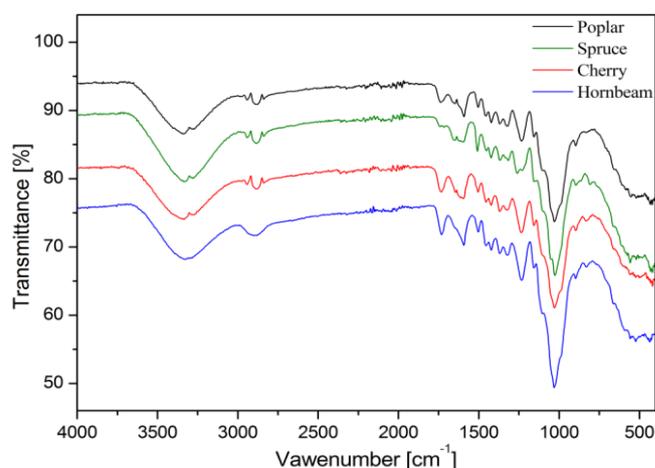


Fig. 1. Infrared spectra of selected wooden sawdust.

characterisation and the band assignments are available in the literature (Ricordel *et al.* 2001; Schwanninger *et al.* 2004; Stevulova *et al.* 2014; Ghosh *et al.* 2015; Kidalova *et al.* 2015; Zhang *et al.* 2015).

#### Static adsorption study

The results of Cu(II) removal from the model solution with initial concentration 10 mg.L<sup>-1</sup> by the selected wooden sawdust are shown in Table 2. The poplar, spruce, cherry, and hornbeam wooden sawdust exhibit a very good efficiency for Cu(II) removal. The best absorption property was revealed for the poplar wooden sawdust with efficiency about 86 %. It is comparable to the results of research Šćiban *et al.* (2007). They found that 2 g of poplar wooden sawdust in 100 mL of contaminated water is efficient for removal of the most of the dissolved Cu(II).

**Table 2.** Results of static adsorption experiments with the selected wooden sawdust ( $c_0(\text{Cu(II)}) = 10 \text{ mg.L}^{-1}$ ).

Sorbent	Cu(II) Initial pH = 5.8		pH
	$c_e$ [mg.L <sup>-1</sup> ]	$\eta$ [%]	
Poplar	1.42	85.8	5.2
Spruce	1.90	81.0	4.9
Cherry	2.30	77.0	4.9
Hornbeam	2.72	72.8	5.2

The adsorption experiments were accompanied by decreasing of pH values in solutions. The monitoring of the pH changes in the solutions during adsorption is an important controlling parameter that could be used to describe the heavy metals removal mechanisms. Since pH affects the surface charge of the adsorbent, the degree of ionization and speciation of sorbate during adsorption (Rahman and Islam 2009). Shukla *et al.* (2002) observed that at decreasing of pH values, the positively charged metal ion species can compete with H<sup>+</sup> and be absorbed at the surface of the sawdust through the ion exchange mechanism. On the other hand, some heavy metals may cause the releasing of OH<sup>-</sup> instead of H<sup>+</sup> when they are adsorbed by sawdust materials, and

therefore result in an increase in pH. Decrease of pH in studied systems indicate on ion exchange of Cu(II) and H<sup>+</sup> ions.

#### Kinetic adsorption study

The poplar wooden sawdust exhibited under static conditions the best adsorption properties. From this reason these sawdust was used for detailed study under dynamic adsorption mode. The efficiency of Cu(II) removal and pH changes over the experimental time are shown in Table 3. Obtained data show high rate of Cu(II) removal from model solution after 5 min of sorbent-sorbate interaction (approximately 88 %). The rest of the adsorption experiment can be considered as a relative settled with slower changes of removal efficiency. From this result we could suppose that the removal of Cu(II) ions might occur as a two-stage process. At the beginning of the sorbent-sorbate interaction, the increase in pH is accompanied with ion-exchange. In the second stage, the adsorption of metals ions takes place at stabilised pH values. The maximum efficiency of Cu(II) removal from model solution (98 %) was achieved after 30 min.

Changes of pH values in solutions were also observed. A significant change of pH value was revealed at the beginning of dynamic experiment. Holub *et al.* (2013) observed that an intensive pH change is caused by the high initial concentration of heavy metals in solution that are involved in the intensive ion exchange with the adsorbent. The change of pH was recorded after 5 min of the adsorption where pH values increase from 5.8 to 6.1. It could be caused by the mechanism of ion exchange between Cu(II) and chemical elements in the poplar wooden sawdust. After the completion of the ion exchange, the pH began to decrease gradually to the approximately input values.

#### Neutron activation analysis of wooden sawdust

The NAA data obtained for raw and Cu-loaded wooden sawdust are presented in Table 4. Obtained results reveal the decrease of content of all determined elements in Cu-loaded wooden sawdust showing that ion exchange is one of the

**Table 3.** Results of metal sorption efficiencies  $\eta$  and changes of pH values over the experimental time at dynamic.

Time	[min]	0	5	10	15	30	45	60	120
$c_e$	[mg.L <sup>-1</sup> ]	10.0	1.22	0.88	0.72	0.24	0.68	0.50	1.12
$\eta$	[%]	0.0	87.8	91.2	92.8	97.6	93.2	95.0	88.8
pH		5.8	6.1	5.9	5.8	5.7	5.7	5.7	5.7

mechanisms of copper biosorption. Thus, the amount of potassium (K) in the Cu-loaded wooden sawdust after the 24-hour adsorption experiments decreased under the detection limit. The most pronounced decrease of calcium (Ca) content, approximately 10 times, was observed for spruce

Cu-loaded sawdust. Significant decrease of sodium (Na) content was observed for spruce and hornbeam wooden sawdust, while of magnesium (Mg) for spruce and cherry wooden sawdust. The content of barium almost in the same degree for all studied sorbents was decreased.

**Table 4.** Chemical composition of natural wooden sawdust and Cu-loaded wooden sawdust (selected elements).

Element	Average content of elements in adsorbents [mg.kg <sup>-1</sup> ]				
	Na	Mg	K	Ca	Ba
Poplar	12.5±0.9	264±18.5	1,790±286	1,810±181	32.1±1.6
Poplar_Cu(II)	12.3±0.9	174±12.2	< 151.0*	1,520±152	24.5±1.23
Spruce	5.8±0.4	497±34.8	287±45.9	5,210±521	5.4±0.54
Spruce_Cu(II)	1.8±0.1	37.4±2.62	< 63.0*	495±49.5	4.0±0.40
Cherry	21.2±1.5	175±12.3	606±97	1,040±104	6.5±0.52
Cherry_Cu(II)	15±1.1	8.7±0.61	< 232.0*	697±69.7	3.7±0.29
Hornbeam	48.6±3.4	376±26.3	1,570±267	4,350±435	30.2±1.51
Hornbeam_Cu(II)	11.3±0.8	220±15.4	< 214.0*	2,660±266	26.4±1.32

\* Values under detection limits

## Conclusions

The wooden materials as sawdust, in their natural form or after some physical or chemical modification, are promising by-products that can be used in the removal of metal ions. The FT-IR analysis of the wooden sawdust confirmed the presence of the functional groups that are able to bind heavy metal ions as was also confirmed by static adsorption experiments with efficiencies of Cu(II) ions removal approximately 85 %.

At dynamic conditions approximately 88 % of Cu(II) ions were removed by the poplar wooden sawdust after 5 min of sorbent-sorbate interaction. The maximum removal efficiency approximately 98 % of Cu(II) was observed after 30 min. The changes of pH were recorded after 5 min of adsorption that was caused by the ion exchange between Cu(II) in model solutions and chemical elements in poplar wood sawdust. The neutron activation analysis revealed a decrease

of concentration of the certain elements (K, Na, Mg, Ba, and Ca) after the adsorption, indicating that ion exchange is one of the mechanisms of heavy metals removal by wooden natural sorbents.

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## Conflict of Interest

The authors declare that they have no conflict of interest.

## References

- Ahluwalia SS, Goyal D (2005) Removal of heavy metals by waste tea leaves from aqueous solution. *Eng. Life Sci.* 5: 158-162.
- Ahmad A, Rafatullah M, Sulaima O, Ibrahim MH, Chii YY, Siddique BM (2009) Removal of Cu(II)

- and Pb(II) ions from aqueous solutions by adsorption on sawdust of Meranti wood. *Desalination* 247: 636-646.
- Ahmaruzzaman M (2011) Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Adv. Colloid Interface Sci.* 166: 36-59.
- Asadi F, Shariatmadari H, Mirghaffari N (2008) Modification of rice hull and sawdust sorptive characteristics for remove heavy metals from synthetic solutions and wastewater. *J. Hazard. Mater.* 154: 451-458.
- Babel S, Kurniawan TA (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: A review. *J. Hazard. Mater.* 97: 219-243.
- Bailey SE, Olin T J, Bricka RM, Adrian DD (1999) A review of potentially low-cost sorbents for heavy metals. *Water Res.* 33: 2469-2479.
- Celik A, Demirbaş A (2005) Removal of heavy metal ions from aqueous solutions via adsorption onto modified lignin from pulping wastes. *Energ. Source.* 27: 1167-1177.
- Crini G (2006) Non-conventional low-cost adsorbents for dye removal: A review. *Bioresour. Technol.* 97: 1061-1085.
- Demcak S, Balintova M, Demcakova M (2017a) Study of heavy metals removal from model solutions by wooden materials. *In IOP Conference Series: Earth and Environmental Science*, vol. 92, IOP Publishing, p. 1-5.
- Demcak S, Balintova M, Hurakova M, Frontasyeva MV, Zinicovscaia I, Yushin N (2017b) Utilization of poplar wood sawdust for heavy metals removal from model solutions. *Nova Biotechnol. Chim.* 16: 26-31.
- Frontasyeva MV (2011) Neutron activation analysis in the life sciences. *Phys. Part. Nucl.* 42: 332-378.
- Gardea-Torresdey JL, Becker-Hapak MK, Hosea JM, Darnall DW (1990) Effect of chemical modification of algal carboxyl groups on metal ion binding. *Environ. Sci. Technol.* 24: 1372-1378.
- Gardea-Torresdey JL, Gonzalez JH, Tiemann KJ, Rodriguez O, Gamez G (1998) Phytofiltration of hazardous cadmium, chromium, lead and zinc ions by biomass of *Medicago sativa* (Alfalfa). *J. Hazard. Mater.* 57: 29-39.
- Ghosh S, Dhole K, Tripathy MK, Kumar R, Sharma RS (2015) FTIR spectroscopy in the characterization of the mixture of nuclear grade cation and anion exchange resins. *J. Radioanal. Nucl. Chem.* 304: 917-923.
- Holub M, Balintova M, Demcak S, Pavlikova P (2016) Application of waste materials as potential biosorbents for Cu (II) and Zn (II) removal. *Chem. Technol.* 67: 40-45.
- Holub M, Balintova M, Pavlikova P (2013) Removal of metal ions from acidic solutions using peat – a low cost sorbent. *In Proceedings of the 13<sup>th</sup> International Conference of Environmental Science and Technology*, Athens, Greece, September 5-7, p. 1-6.
- Imamoglu M, Tekir O (2008) Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks. *Desalination* 228: 108-113.
- Kidalova, L, Stevulova, N, Terpakova, E (2015) Influence of water absorption on the selected properties of hemp hurds composites. *Pollack Periodica* 10: 123-132.
- Leng L, Yuan X, Zeng G, Shao J, Chen X, Wu Z, Peng X (2015) Surface characterization of rice husk bio-char produced by liquefaction and application for cationic dye (Malachite green) adsorption. *Fuel* 155: 77-85.
- Ngah WW, Hanafiah MAKM (2008) Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresour. Technol.* 99: 3935-3948.
- Rahman MS, Islam MR (2009) Effects of pH on isotherms modeling for Cu (II) ions adsorption using maple wood sawdust. *Chem. Eng. J.* 149: 273-280.
- Ricordel S, Taha S, Cisse I, Dorange G (2001) Heavy metals removal by adsorption onto peanut husks carbon: characterization, kinetic study and modeling. *Separ. Purif. Technol.* 24: 389-401.
- Schwanninger M, Rodrigues JC, Pereira H, Hinterstoisser B (2004) Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose. *Vib. Spectros.* 36: 23-40.
- Šćiban M, Radetić B, Kevrešan Ž, Klačnja M (2007) Adsorption of heavy metals from electroplating wastewater by wood sawdust. *Bioresour. Technol.* 98: 402-409.
- Shukla A, Zhang YH, Dubey P, Margrave JL, Shukla SS (2002) The role of sawdust in the removal of unwanted materials from water. *J. Hazard. Mater.* 95: 137-152.
- Singovszka E, Balintova M, Holub M (2016) Heavy metal contamination and its indexing approach for sediment in Smolnik creek (Slovakia). *Clean Technol. Environ. Policy* 18: 305-313.
- Stevulova N, Cigasova J, Estokova A, Terpakova E, Geffert A, Kacik F, Singovszka E, Holub M (2014) Properties characterization of chemically modified hemp hurds. *Materials* 7: 8131-8150.
- Sud D, Mahajan G, Kaur MP (2008) Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review. *Bioresour. Technol.* 99: 6017-6027.
- Vieira RH, Volesky B (2000) Biosorption: a solution to pollution? *Internat. Microbiol.* 3: 17-24.
- Zhang LI, Zhao LI, Yu Y, Chen C (1998) Removal of lead from aqueous solution by non-living *Rhizopus nigricans*. *Water Res.* 32: 1437-1444.
- Zhang P, Dong SJ, Ma HH, Zhang BX, Wang YF, Hu XM (2015) Fractionation of corn stover into cellulose, hemicellulose and lignin using a series of ionic liquids. *Ind. Crops Prod.* 76: 688-696.