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Utilization of poplar wood sawdust for heavy metals removal from model solutions

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Abstract

Some kinds of natural organic materials have a potential for removal of heavy metal ions from wastewater. It is well known that cellulosic waste materials or by-products can be used as cheap adsorbents in chemical treatment process. In this paper, poplar wood sawdust were used for removal of Cu(II), Zn(II) and Fe(II) ions from model solutions with using the static and dynamic adsorption experiments. Infrared spectrometry of poplar wood sawdust confirmed the presence of the functional groups which correspond with hemicelluloses, cellulose and lignin. At static adsorption was achieved approximately of 80 % efficiency for all treated model solutions. Similar efficiency of the adsorption processes was reached after 5 min at dynamic condition. The highest efficiency of Cu(II) removal (98 %) was observed after 30 min of dynamic adsorption. Changes of pH values confirmed a mechanism of ion exchange on the beginning of the adsorption process.

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Introduction

Heavy metals and their compounds are excessively released into the water bodies by a wide range of industrial activities such as: metal plating, mining activities, smelting, battery manufacture, tanneries, and many other branches of industries (Ngah and Hanafiah 2008; Saifulnizam and Jaafar 2010). In comparison with organic contaminants, heavy metals are non-biodegradable and they can be accumulated in living organisms, causing various diseases and disorders. For these reasons, heavy metals must be removed from wastewater before their discharge into the aquatic environment (Ahmaruzzaman 2011). Nowadays, organic materials from plant wastes or by-product are often used instead of the costly conventional methods of metal ions removal from wastewater (Ngah and Hanafiah 2008; Fu and Wang 2011; Nayak *et al.* 2017).

Physico-chemical processes based on adsorption on natural organic materials are cheap and effective techniques for metals removal from wastewater. According to Bailey *et al.* (1999), low-costs organic sorbents widely abundant in nature can be used as cheap alternative to industrially produced sorbents.

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Wooden materials or wastes are cheap sorbent materials (Ngah and Hanafiah 2008; Ahmaruzzaman 2011). The benefits of application of wooden by-products or wastes for wastewater treatment are determined by their high removal selectivity, good adsorption capacity and possibility of regeneration. The use of original and untreated wooden materials or wastes such as straw, tree bark, peanut skins, wood sawdust, moss and peat has been reported for pollutants removal in several studies (Shukla *et al.* 2002; Šćiban *et al.* 2007; Asadi *et al.* 2008). Wood sawdust, a low-costs adsorbent, is perspective for removing metal ions, some types of acid and basic dyes as well as other unwanted compounds from wastewaters (Singh *et al.* 1993). The efficiency of the adsorption processes strongly depends on the composition of the wastewater (Keränen *et al.* 2016). Ahmad *et al.* (2009) showed formation of complex compounds of metal cations with wood sawdust functional groups. Lignin, cellulose and hemicellulose, carbohydrates, and phenolic compounds, which contain carboxyl, hydroxyl, sulphate, phosphate, and amino groups, are the main metal binding sites (Gardea-Torresdey *et al.* 1990; Crini 2006). The application of wood sawdust for removal of pollutants brings many benefits for the protection of environment and timber industry. Contaminated water could be treated, and a new market would be opened for the sawdust (Shukla *et al.* 2002).

The aim of the present research was to study the sorption properties of poplar wood sawdust for copper, zinc and iron removal from model solutions. Poplar sawdust was analysed by infrared spectrometry for characterization of functional groups, which can be responsible for metal binding. Efficiency of heavy metals removal was analysed by colorimetric method and changes of pH values.

Experimental

Wood sample

The sawdust of poplar, species of locally available wood, was sieved, and the fraction with particle size max. 2.0 mm was used for experiments. 1 g of dry poplar sawdust was weighted and used for adsorption experiments. IR spectrum of poplar sawdust was studied for characterization of present functional groups, which can be responsible for metal binding. FTIR measurements of poplar sawdust were carried out on Bruker Alpha Platinum-ATR spectrometer (Bruker Optics, Ettingen, Germany). A total of 24 scans were performed on sample in the range of 4,000–400 cm^{-1}.

Adsorbate solutions

Adsorbate solutions of Cu(II), Zn(II) and Fe(II) (initial concentration c_0=10 $mg.L^{-1}$) were prepared by dissolving $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$ and $FeSO_4 \cdot 7H_2O$, respectively in deionised water. Concentrations of appropriate ions were determined by colorimetric method (Colorimeter DR890, Hach Lange, Germany) with appropriate reagents to determine concentration of dissolved cooper, zinc, and iron. Copper in the sample reacts with a reagent (bicinchoninic acid) to form a purple coloured complex in proportion to the copper concentration. Zinc reacts in the sample complex with cyanide. Adding cyclohexanone selectively releases zinc. The zinc then reacts with the 2-carboxy-2'-hydroxy-5'-sulfoforamazyl benzene (zincon) and forms a blue colour that is proportional to the zinc concentration. The 1,10-phenanthroline indicator reacts with iron ion in the sample to form an orange colour in proportion to the iron concentration. Input pH values were also measured by pH meter inoLab pH 730 (WTW, Germany).

Adsorption studies

Batch adsorption experiments were carried out on static and dynamic conditions of experimental setup. In both experiments, 1 g of dry poplar sawdust was mixed with 100 mL of model solutions containing 10 $mg.L^{-1}$ of copper, zinc, and iron respectively. In static conditions, the sorbent-sorbate interaction time was 24 h. To determine the contact time required for equilibrium sorption in dynamic condition the samples were removed at different time intervals 5, 10, 15, 30, 45, 60 and 120 min,

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respectively. After the end of experiments, wood sawdust was removed by filtration through a laboratory filter paper. Residual concentrations of appropriate ions were determined by colorimetric method and pH change was also measured.
In both cases, the efficiency of ion removal η (in %) removal was calculated using the following equation (Eq. 1):

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

where c_0 is the initial concentration of appropriate ions (mg.L^{-1}) and c_e equilibrium concentration of ions (mg.L^{-1}). All adsorption experiments were carried out in triplicate under the batch conditions and results are given as arithmetic mean values.

Results and Discussion

Poplar sawdust infrared spectrum

The aim of the present research was to study the sorption properties of poplar wood. Metal adsorption capacity is influenced strongly by the surface structures of C–O and C–OH functional groups which are present in organic materials (Ricordel *et al.* 2001). Functional groups in poplar wood sawdust were determined using FTIR spectroscopy. The IR spectrum of poplar sawdust is shown in Fig. 1. According to literature (Kidalova *et al.* 2015) we can suppose that the structure of wooden sawdust is mainly formed by cellulose, hemicellulose, and lignin. Strong broad OH stretching (3,650–3,000 cm^{-1}) and C–H stretching of methyl and methylene groups (2,950–2,800 cm^{-1}) are present (Fig. 1), possibly due to the presence of –OH functional groups or could be absorbed also from atmospheric damp. For comparison, typical for hemicelluloses is the stretching band at 1,736 cm^{-1} caused by presence of C=O from the acetyl groups. Infrared spectra of lignin in wooden sorbent materials (Zhang *et al.* 2015) revealed characteristic bands at 1,503 and 1,454 cm^{-1} (correspond to aromatic skeletal vibrations of lignin) and at 1,320 cm^{-1} (syringyl and guaiacyl condensed lignin). Deformations detected in a range of 1,421 to 895 cm^{-1} wavenumber appertain to cellulose that can occur in two forms (crystalline and/or amorphous). Functional groups of aromatics, carboxylic acids and alkyl halides were described at 829 cm^{-1} (Schwanninger *et al.* 2004).

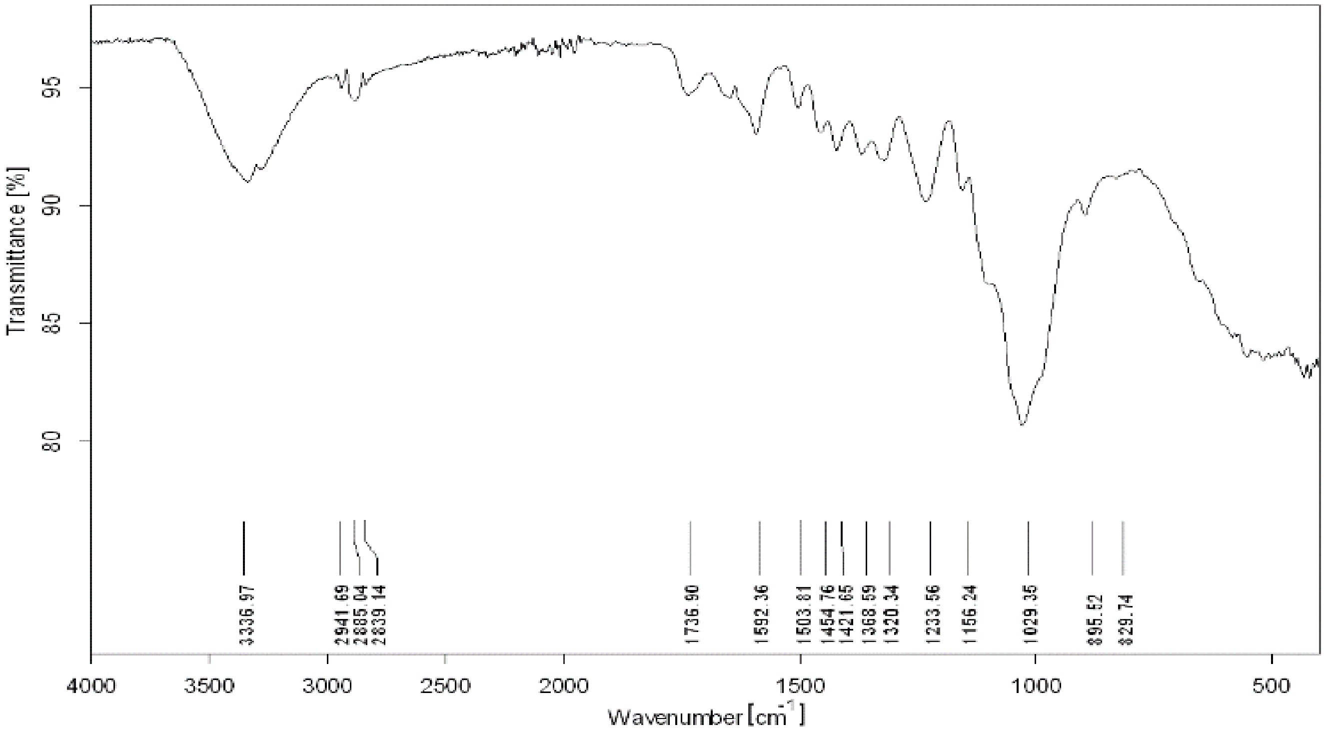

Fig.1. Infrared spectrum of poplar wood sawdust.

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Adsorption study of poplar wood sawdust – Static conditions

Results of sorption experiments under static conditions for solutions with cation concentrations 10 mg.L^{-1} are shown in Table 1. The data suggest that poplar sawdust has a very good efficiency of removal of studied metal ions. The most efficient sorption was for copper with efficiency of 85.8 %. For zinc and iron the efficiencies were 74 % and 78 % (respectively). Previously, Šćiban *et al.* (2007) have suggested that 20 g.L^{-1} of poplar sawdust is efficient for removal of most of the Cu(II) ions.

Sorption is accompanied by changes of pH values in solutions. The pH of the solutions is an important controlling parameter in the adsorption process, since pH affects the surface charge of the adsorbent, the degree of ionization and speciation of sorbate during adsorption (Rahman and Islam 2009). At lower pH, the positively charged metal ion species may compete with H^+ and be absorbed at the surface of the sawdust by ion exchange mechanism. At elevated, mainly neutral pH, metal cations may be absorbed by hydrogen bonding mechanism along with ion exchange. Due to different properties of the metals Cu(II), Zn(II), and Fe(II), the adsorption took place at slightly different pH values (respectively). Sorption of Cu(II) by poplar sawdust increases the pH of the solution. Possibility of ion exchange between dissolved Zn(II) and Fe(II) metal cations and H^+ from poplar sawdust was indicated by decreasing of pH.

Table 1. Results of static sorption experiments with poplar sawdust (initial concentration of cations in solutions c_0=10 mg.L^{-1}).

Ion	Input values		Adsorption experiments		
	c_0 [mg.L^{-1}]	pH	c_e [mg.L^{-1}]	η [%]	pH
Cu^{2+}	10.0	5.8	1.4	85.5	5.3
Zn^{2+}	10.0	5.4	2.6	74.0	5.8
Fe^{2+}	10.0	5.4	2.2	78.0	5.7

η – efficiency of ion removal,
c_0 – initial concentration of ions,
c_e – equilibrium concentration of ions.

Adsorption study of poplar wood sawdust – Dynamic conditions

Sorption efficiency and changes of pH values over time are shown in Fig. 2. Using the poplar sawdust for absorption experiment in model solutions with dissolved ions Cu(II), Zn(II), Fe(II), the curve indicates the rapid progress of sorption. After 5 min of sorbent-sorbate interaction, approximately 80 % of metal cations were removed from the solution.

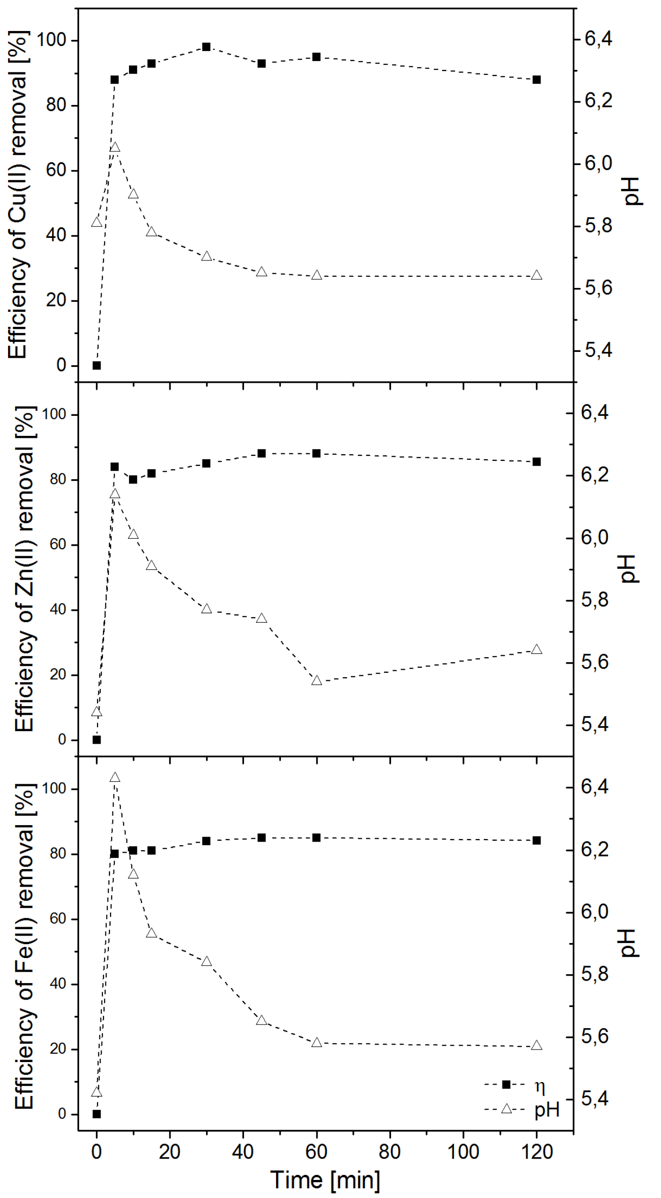

Fig. 2. Comparison of metal sorption efficiencies η (black squares) and changes of pH values (empty triangles) over the experimental time.

The residual time of experiment can be considered as a relative settled with slower changes of removal

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efficiency. Values of Cu(II), Zn(II), and Fe(II) sorption show that ion removal might occur in two-steps staring with ion exchange and subsequent adsorption. The highest efficiency of Cu(II) removal from model solution (98 %) was obtained after 30 minutes. On the other hand, the highest efficiency of Zn(II) (88 %) and Fe(II) (85 %) removal were reached both after 45 min.

Changes of pH values in solutions were observed after adsorption indicating to physical and chemical processes resulting in heavy metal ions removal from aqueous solutions. As shown in Fig. 2, use of poplar sawdust in dynamic conditions is connected with decrease (in case of Cu^{2+}) or increase (Zn^{2+} and Fe^{2+}) of pH values in the tested samples. Such a significant change of pH value has previously been observed at high initial concentration of dissolved heavy metals as a result of intensive ion exchange (Holub *et al.* 2013).

In all cases, changes of pH values were recorded after minutes of the adsorption. The most notable pH change was in case of Fe(II) removal (from 5.4 to 6.4). During intensive increase of pH, metal cations were absorbed by mechanism of ion exchange by hydrogen bonding, while with the decreasing metal ion concentrations the ion exchange is not so dominant and does not affect the pH (Petrilakova *et al.* 2014). After completion of the ion exchange, the pH began to decrease gradually in all cases in our system to nearly input values (Fig. 2).

Conclusions

Poplar sawdust was proved as a suitable product for removal of selected metals from solutions. The function groups of poplar sawdust were characterized by infrared spectra that confirmed the presence of hemicelluloses, cellulose and lignin.

At static adsorption experiment the poplar wood sawdust exerted good capability to remove copper, zinc, and iron ions with efficiency of ~ 80 %. Changes of pH at static conditions point to adsorption and ion exchange.

At dynamic conditions the sorption processes for all model solutions reached 80 % efficiency already after 5 min. The highest removal efficiency of Cu(II) (98 %) was observed after 30 min, and of both zinc (88 %) and iron (85 %) after 45 min. Significant changes of pH were recorded after 5 min of adsorption as a consequence of ion exchange between metal ions in model solutions and functional groups of poplar wood sawdust.

The adsorption experiments showed that the poplar wood sawdust is suitable for metal removal from model acidic solutions and also provides promising perspective for use in purification of metals from wastewaters.

Acknowledgements

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