The Utilization of Cherry Wood Sawdust for Heavy Metals Removal from Wastewaters

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Abstract. The presence of inorganic pollutants such as heavy metal ions in industrial effluents is a worldwide issue for the environment. These pollutants are not only hazardous in exceeding concentrations but due to the property of accumulation in living organisms it is urgent to look for the plausible solutions for their reducing and treatment from wastewaters.

In this study, cherry wooden sawdust were used for removal Cu(II), Zn(II) and Fe(II) ions from model solutions with using the static and kinetic adsorption experiments. Infrared spectrometry of cherry wooden sawdust confirmed the presence of the functional groups which correspond with hemicelluloses, cellulose and lignin. At static adsorption was achieved approximately of 70% efficiency for all treated model solutions that is comparable with the efficiency of the adsorption processes reached after 5 min at kinetic experiments. The highest efficiency of Fe(II) removal (89%) was observed after 120 min of intensively shaking at frequency of 100 rpm. The mechanism of ion exchange on the beginning adsorption process by the changes of pH values was indicated.

Keywords: Wastewater treatment · Heavy metals · Adsorption · Wooden sawdust

1 Introduction

Water pollution by the heavy metals is a result of the industrial activities as mining, mineral processing and metallurgical operations. The heavy metals present in the wastewater are persistent, non-biodegradable in nature, accumulate in living organisms and thus they are entering the food chain, where are causing serious health diseases and disorders (Demcak et al. 2017a; Singovszka et al. 2016). From these reasons, treatment of heavy metals from the industrial wastewaters is necessarily before their discharging into the aquatic environment. The most commonly used methods for heavy metals removal from contaminated water includes chemical precipitation, ion exchange, membrane filtration, reverse osmosis, and electro dialysis (Fu and Wang 2011; Ngah and Hanafiah 2008). These methods are effective, on the other hand are costly, produce large volumes of toxic sludge and require high energy input. They are associated with the generation of toxic sludge, disposal of which renders it expensive and non-ecofriendly in nature (Tripathi and Ranjan 2015). Based on these facts, the safe and economical treatment of heavy metals from the wastewater in the last decades was

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investigated. Use of adsorption has emerged out to be better alternative to conventional methods of water treatment (Rahmani et al. 2009; Shah et al. 2009). It was observed that natural low-costs adsorbents, due to their wide abundance in nature can be used as cheap alternative to industrially produced sorbents (Bailey et al. 1999).

The adsorption by nonconventional materials is a highly effective method because it is a simple and cost effective method for recovering and eliminating heavy metal ions from wastewaters (Dehghani et al. 2016; Siti et al. 2013). The natural adsorbent should have high selectivity to facilitate quick separations, favorable transport and kinetic characteristics, stability (thermal, mechanical, chemical), regeneration capacity and low solubility in the liquid in contact to ensure the competitive for the commercial (Tripathi and Ranjan 2015). The mostly used low-cost natural adsorbents with the above parameters are agricultural waste (rice husk, plant bark, waste tea, and walnut shel), industrial by-products (fly ash, blast furnace sludge, lignin, bark, and sawdust), natural materials (zeolites, clay, peat moss and chitin) or modified biopolymers (Tripathi and Ranjan 2015; Crini 2006; Bailey et al. 1999). In addition, the main benefit of adsorption over the conventional methods is an absence of generation of sludge and its subsequent storage.

The wooden by-products or wastes as wooden sawdust are promising adsorbent materials due to their cheap costs production, processing and possibility of their regeneration (Ahmaruzzaman 2011). The wooden sawdust are perspective for removing metal ions, some types of acid and basic dyes, and other unwanted compounds from contaminated waters but the adsorption efficiency closely depends also on the composition of the wastewater (Balintova et al. 2016b; Keränen et al. 2016). The wooden sawdust are forming of complex compounds of metal cations with sorbent functional groups that are the main metal binding sites (Crini 2006; Gardea-Torresdey et al. 1990). The use of non-conventional adsorbents as wooden sawdust may contribute to the sustainability of the environment and offer a lot of promising benefits for commercial purpose in the future (Ghaedi and Mosallanejad 2013).

The present study deals with the sorption properties of cherry wooden sawdust for copper, zinc and iron removal from model solutions. Cherry sawdust was analysed by infrared spectrometry for characterization of functional groups, which can be responsible for the heavy metals binding. Efficiency of heavy metals removal was analysed by colorimetric method and changes of pH values were also measured.

2 Materials and Methods

As the adsorbent material was used the locally available wooden sawdust of cherry trees that was dried and sieved. For the adsorption experiments the fractions with a particle size under 2.0 mm were used. The FTIR 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^{-1}.

The single component model solution with initial concentrations of Cu(II), Zn(II) and Fe(II) $10 mg \cdot L^{-1}$ respectively was prepared by dissolving of appropriate sulphate salts in deionised water. The initial and residuals concentrations of the Cu(II), Zn(II) and Fe(II) were determined using the colorimetric method with a Colorimeter DR890, (HACH LANGE, Germany) and the appropriate reagent and pH values of model solutions by pH meter inoLab pH 730 (WTW, Germany) were also measured.

The batch adsorption experiments were carried out in static and kinetic conditions. In both adsorption experiments, 1 g of cherry wooden sawdust was mixed with 100 mL of model solutions. In static mode, the sorbent-sorbate interaction time was 1 day. In the kinetic mode, to determine the contact time required for equilibrium adsorption the samples were analysed in different time intervals (5, 10, 15, 30, 45, 60 and 120 min). In both modes, at the end of the adsorption experiments, the cherry wooden sawdust was removed by filtration through a laboratory filter paper. The residual concentrations of heavy metals ions in solutions were determined by colorimetric method and pH changes were also tracked. The efficiency of ion removal η was calculated using the following equation (Eq. 1):

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

where η is efficiency of ion removal (%), c_0 is the initial concentration of appropriate ions (mg.L^{-1}) and c_e in an equilibrium concentration of ions (mg $\cdot$ L^{-1}).

3 Results and Discussion

3.1 The FTIR Cherry Sawdust Characterisation

The heavy metal removal by the wooden materials from waters is influenced by various factors. Important role has the surface structures hydroxyl, carboxyl, carbonyl, amine, and amino functional groups that are present in organic materials that are capable to bind metal ions (Ricordel et al. 2001). The structure of sawdust is primarily formed by cellulose, hemicellulose, and lignin (Kidalova et al. 2015). The functional groups of cherry wooden sawdust were determined using FTIR spectroscopy that the IR spectrum is shown in Fig. 1. The FTIR spectroscopy reveal several major intense bands that can be divided into the following three significant areas of wavenumbers: 3,650 to 3,000 cm^{-1} (-OH and -NH functional groups), 3,000 to 2,800 cm^{-1} (symmetric and asymmetric vibrations of CH_3 functional groups), and 1,750 to 800 cm^{-1} (C = O, -OH, -COOH, -NH_x, and haloalkanes functional groups) (Demcak et al. 2017b; Balintova et al. 2016a; Zhang et al. 2015; Schwanninger et al. 2004).

3.2 Static Adsorption Study

The results of the static absorption experiments for model solutions with cation concentrations of 10 mg.L^{-1} are shown in Table 1. The cherry wooden sawdust used in the absorption experiments was able to remove copper, zinc and iron ions from the solution. The best efficiency (89.4%) of ion removal was observed for Fe(II) adsorption. Results correspond to research of Shukla et al. (2002) and observed that wooden sawdust as a promising adsorbent for heavy metal removal from wastewater.

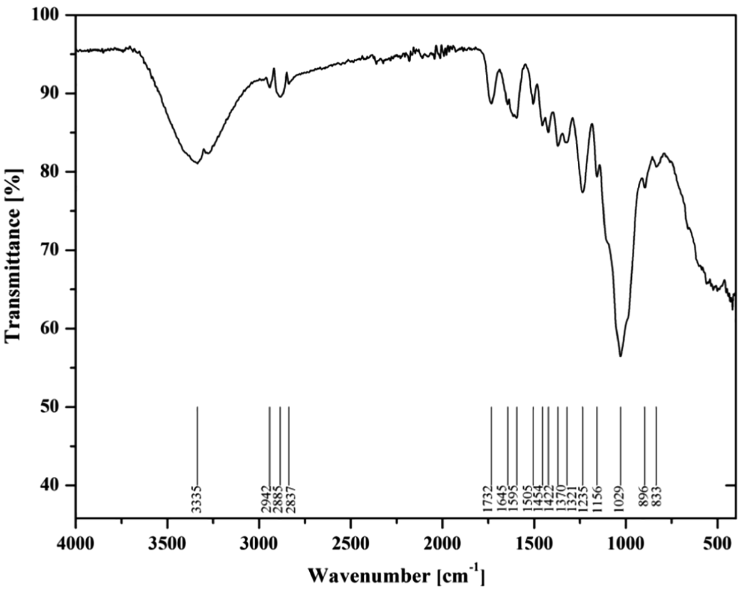

Fig. 1. Infrared spectrum of cherry wooden sawdust

They observed that selected wooden sawdust are potentially more economical than the common heavy metal removal processes.

Table 1. Results of static sorption experiments with cherry wooden sawdust

Ion	Input values		Adsorption experiments		
	c_0 [mg · L^{-1}]	pH	c_e [mg · L^{-1}]	η [%]	pH
Cu(II)	10.0	6.3	3.47	65.3	5.2
Zn(II)	10.0	6.2	2.57	74.3	5.3
Fe(II)	10.0	5.9	1.06	89.4	5.0

The pH monitoring is an important parameter in the characterisation of adsorption processes. Due to the different input pH values of the model solutions, the adsorption took place in different pH ranges. In all causes decrease of pH values was observed. Decrease of pH values is due to the higher concentration of H^+ ions present in the reaction mixture which compete with the dissolved metal ions for the adsorption sites at wooden sawdust (Yu et al. 2003).

3.3 Kinetic Adsorption Study

Based on results from static adsorption condition, the cherry sawdust was used for detailed study under dynamic adsorption mode. The efficiency of Cu(II), Zn(II), and Fe (II) removal and pH changes over the experimental time are shown in Figs. 2, 3 and 4. The curves indicate the rapid progress of ion removal in 5 min of sorbent-sorbate interaction accompanied by a decrease pH values, where approximately 70% (Cu(II) and Zn(II)) and 84% (Fe(II)) ions were removed from the solution. The residual time of experiment can be considered as a relative settled with slower growth of ions removal efficiency. Based on these results can be supposed that the ions removal might be interpreted as a two-stage process consisting of ion-exchange (at the beginning interaction) and adsorption (in rest of interaction). After 45 min was obtained the maximum efficiency of Zn(II) removal from model solution 78.7%. In 120 min were reached the highest efficiency of Cu(II) (84.9%) and Fe(II) (88.6%) removal.

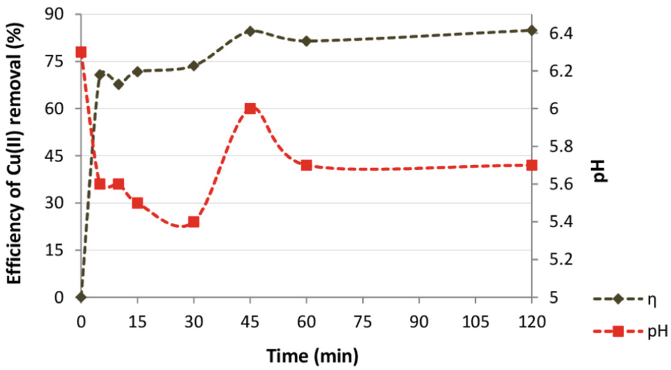

Fig. 2. Comparison of Cu(II) sorption efficiencies and changes of pH values over the experimental time

Changes of pH values in solutions were also observed. A significant change of pH value was revealed in case of Cu(II) removal. 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 45 min of the adsorption where pH values increase from 5.4 to 6.0. It could be caused by the mechanism of ion exchange between Cu(II) and chemical elements in the cherry sawdust. After the completion of the ion exchange, the pH began to decrease gradually.

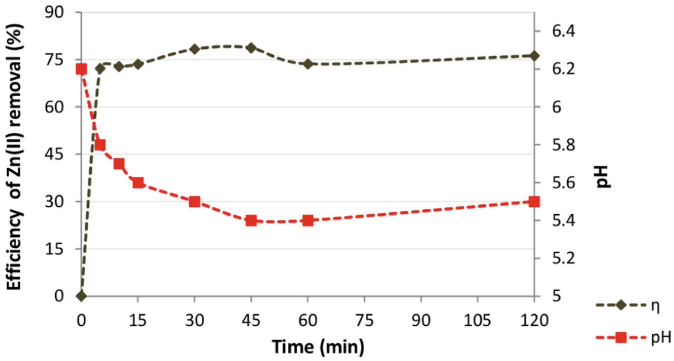

Fig. 3. Comparison of Zn(II) sorption efficiencies and changes of pH values over the experimental time

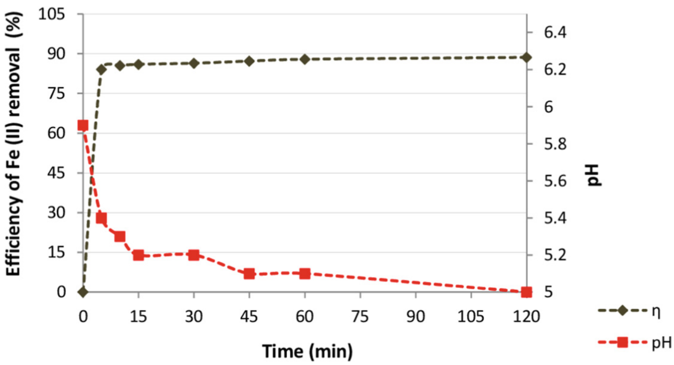

Fig. 4. Comparison of Fe(II) sorption efficiencies and changes of pH values over the experimental time

4 Conclusions

Sawdust appears to be a promising adsorbent for removal of Cu(II), Zn(II) and Fe(II) from model solution. Sawdust is economical sorbent because of its low cost, easy availability, renewability and high affinity for heavy metals. Thus, this process is more economical than current process technology.

The Fourier transform infrared spectroscopy (FT-IR) spectra of cherry sawdust can proved the functional groups, like; -OH, C = O and $-NH_x$ which are responsible for metal binding and suggested the main mechanisms involved in the removal of heavy metals ions might be the ionic exchange and complexation.

The adsorption of Cu(II), Zn(II) and Fe(II) is dependent on its contact time and pH of the water. The static adsorption study proved that the efficiency of Cu(II), Zn(II) and Fe(II) removal was height than 65% during experiment. The best efficiency (89%) was observed for iron removal from model solution. The kinetic adsorption study, was determined the rapid progress of ion removal in 5 min of beginning of experiment accompanied by a decrease pH values, where approximately 70% (for Cu(II) and Zn(II)) and 84% (for Fe (II)) ions were removed from the aquatic solution. Changes of pH are due to adsorption and ion exchange.

From the obtained results, the use of wooden sawdust has benefits to the environment because these materials are value sorbents, and are suitable for wastewater purification.

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