Study of zinc removal from water solutions using hornbeam wooden sawdust

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Abstract. The polluted water from an industry, in particular with heavy metals, aromatic molecules and dyes, is a serious environmental problem because their potential environment toxicity. Therefore, there is a need to develop methods that can remove toxic contaminates from wastewaters. The sorption process is one of the most popular methods for the environment treatment. Adsorption on low-cost materials is studying with great interest by researchers in last years. Hornbeam sawdust is a natural resource and an inexpensive material which can be used for water treatment. In this study, the hornbeam sawdust was used as for the removal of zinc from an aqueous solution. Fourier transform infrared spectroscopy (FTIR) was used to determine functional groups of sawdust. The pH decreased from 6.3 to 5.8 during 2 h and in case of 24-hours experiment on the value of 5.4. Hornbeam sawdust had efficiency of zinc removal from aquatic model solutions height than 75 % which means that there is significant potential for sawdust as a sorbent material for heavy metals removal from water.

1. Introduction
The problems of polluted wastewater are rising during the past decades because of urbanization, industrialization, and agricultural practices. The major source of the aquatic pollution is untreated wastewaters from the industries. This water has due to the defend kind of industries various composition and the combination of pollutant. The most common contaminants are pesticides, dyes, aromatic hydrocarbons, oils, heavy metals etc. and represent a risk in most countries [1-4].

In recent years, heavy metals in wastewaters present a major problem in the environment, because of its flexibility, accumulation, non-biodegradable and endurance. They are very dangerous to the living organisms and human’s health even at very low concentration [5, 6]. The zinc is applied in industrial activities like steel processing, mining and coal combustion. Though it is required by the humans in trace level zinc dose over 100 mg/day may lead to vomiting, skin inflammation, fever, anemia dysfunctions of respiratory track and brain. The main resources of zinc in water are electroplating industries, paper and pulp industries, steel making industries, and brass metal works [7, 8].

Despite the existence of many water treatment technologies as: chemical precipitation, ion exchange, different membrane techniques, coagulation, flocculation, ion exchange, flotation, chemical precipitation, electrochemical treatment, researches are still searching the unique methods of getting more economically and environmentally sustainable technology [9].

Over the last decade, bio-based wastewater treatment materials have received increased attention due to the global effort to increase environmental and cost effective purification processes. The biosorption is a cheap and fast separation method to heavy metals removal. The main sorption mechanism is ion exchange through the adhesion of positively charged metal ions on an adsorbent surface which consist of negatively charged polymeric functional groups.
The utilization of low-cost sorbents has been found as a perspective alternative to methods conventionally applied for metal removal. As biosorbents can be used lot of materials of natural origin: algae, microorganisms, coffee and tea grounds, yeasts, nut shells, citrus peels, rice husks, or sawdust [10, 8].

This paper presents the using of hornbeam wooden sawdust in removing zinc ions from aquatic solutions. Wooden sawdust is widely available and has a good mechanical stability and due to lignocellosic composition. Sorbent from hornbeam sawdust was analyzed by infrared spectrometry and efficiency of Zn(II) removal was measured by colorimetric method. The changes of pH were also determined.

2. Material and methods

2.1. Materials

The hornbeam wooden sawdust from local resources was sieved and in experiment only fraction less than 2 mm was used. The sawdust was analysed by infrared spectrometry by Bruker Alpha Platinum-ATR spectrometer (Bruker Optics, Ettingen, Germany). In the range of 4,000–400 cm\(^{-1}\) there were performed a total of 24 scans of hornbeam sawdust.

Aquatic solutions were prepared form appropriate amount of ZnSO\(_4\).7H\(_2\)O dissolved in distilled water. The concentration of Zn(II) in solution was 10 mg/L.

2.2. Experimental methods

To investigate the kinetic study 1 g of sawdust and 100 mL of model solutions was used. The sorption experiments last 5, 10, 15, 30, 45, 60 and 120 min, respectively. During this time the sorbent was intensively stirred in adsorbate.

In another experiment the same amount of sawdust and aquatic solutions was kept during 24 h in laboratory temperature.

After established time was sample filtered and in filtrate was measured by pH meter (Mettler Toledo FG2, Schwerzenbach, Switzerland) and concentration of zinc by colorimetric method (Colorimeter DR890, Hach Lange, Germany).

The efficiency of zinc removal was calculated using the following equation:

\[ \eta = \frac{(c_0 - c_e)}{c_0} \times 100, \]  

where \( \eta \) is the efficiency (%), \( c_0 \) is the initial concentration of appropriate ions (mg/L) and \( c_e \) equilibrium concentration of ions (mg/L).

3. Result and discussion

3.1. Infrared spectra

The FTIR spectra was measured due to determine the potential functional groups that involve in biosorption process of zinc onto sawdust (Figure 1).

Sawdust of different trees is a by-product of the timber industry, mainly composed of cellulose (45-50%) and lignin (23-30%). In their structure it contains functional groups such a non-negligible portion of lipids and waxes, bearing functional groups like alcohol, ketone and carboxylic groups which provide its metal binding capacity. These groups can be involved in complexation reactions with zinc cation and can be viewed as natural ion-exchange materials on the surface of sorbent [11, 12].

The strong broad band between 4,000 and 3,300 cm\(^{-1}\) can be assigned to hydroxyl groups and O–H bands stretching. In the band between 3,000-2,800 cm\(^{-1}\) indicate symmetric or asymmetric C–H stretching of methyl and methylene groups. It was observed in peak 1,731 cm\(^{-1}\) presence of stretching vibration of C=O bonds due to groups of hemicellulose. Lignin bands were indicated at 1,503, 1,454, and 1,321 cm\(^{-1}\). Cellulose can be seen in the band between 1,420 and 890 cm\(^{-1}\). Aromatics, carboxylic acids, alkyl halides were determined at 830 cm\(^{-1}\) [13].
3.2. Sorption experiments

The effect of contact time on the sorption of zinc at initial concentrations 10 mg/L by sawdust is shown in Figure 2. Bouziane et al. [14] determined that the most important factors to zinc sorption onto sawdust are initial concentration, sawdust mass and contact time.

Hornbeam shows high efficiency to zinc removal. In all experiment was more than 75% removal. The high efficiency was shown after 10 min.

The pH value is one of the most important factors influencing the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation, and in the adsorption processes the speciation and availability of heavy metals.

The effect of pH on the sorption of zinc on hornbeam sawdust can be determined with respect to the surface charge on the adsorbent material. Lower pH results in lower removal efficiency, due to high positive charge density on the surface sites adsorbent and electrostatic repulsion between metal ion and H⁺ ion will be high. On the other hand increasing pH means an enhancement of metal sorption because the electrostatic repulsion decreases and that show reduction of positive charge density of proton in the adsorbent’s sites [15].

![Figure 1. Infrared spectra of hornbeam wooden sawdust](image-url)
In 24-hours experiment was removal efficiency 90% at pH 5.4. Pragaty [16] published that 90% of zinc ion was removed after 120 min of contact time at pH 5. As was mentioned before, pH and contact time are very important parameters which can affect sorption process.

4. Conclusion
The sawdust obtained from the local sources is an inexpensive material which can be used as effective adsorbent for removal of zinc from aqueous solution.

Fourier transform infrared spectroscopy (FTIR) of sawdust indicated the functional groups, like; C–O, C=O and C–N 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. Efficiency of zinc removal was height than 75% during experiment. The highest efficiency (85 %) was after 10 min at pH 6.2. In 24-hour experiment was equilibrium concentration of ions 0.96 mg/L at pH 5.4. Changes of pH are due to adsorption and ion exchange. The hornbeam wooden sawdust could be used as an alternative economically and environmentally friendly sorbent for removal of Zn (II) from aqueous solutions.

5. References
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