Study of heavy metals removal from model solutions by wooden materials

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Abstract. The paper deals with the heavy metals removal by wooden material. The adsorption experiments were carried out using of wood sawdust and bark from poplar tree for the removal of copper and zinc cations from model solutions with initial concentration of 10 mg.L⁻¹. The FTIR was used for functional groups determination not for analysis of hemicelluloses, cellulose and lignin in structure of wood sawdust and bark were studied by infrared spectrometry. Poplar sawdust efficiency for Cu(II) and Zn(II) removal from aquatic model solutions reached approximately 80.0%. Changes of pH values were also observed in model solutions that were probably caused by ion exchange between the ions of sorbents and the ions in solutions.

1. Introduction

The increasing of anthropogenic activities in last decades had the negative impact on all parts of the environment, mainly on aquatic environment. Industrial waters are specific, because contains of contaminants that may destroy waste water treatment process [1]. Heavy metal ions are contained as pollutants in wastewaters which must be removed primarily, due to their mobility in natural aquatic ecosystems and due to their toxicity because they are stable and persistent environmental contaminants since they cannot be degraded and destroyed. These metal ions can be harmful or toxic to living organisms in water and also they can be caused a serious public health problem for human health [2, 3]. Processes of finding of the new and cheap ways for treatment of wastewaters contaminated by heavy metals can increase the quality of the environment in the affected localities and thus prevent adverse effects on living organisms [4]. The most commonly used technique for the heavy metals removal from aqueous solutions is chemical precipitation, membrane filtration, electro extraction, ion exchange and sorption [5, 6].

The process of adsorption by sorbents implies that adsorbents bind molecules by physical attractive forces, ion exchange, and chemical binding. It is advisable that the adsorbent is available in large quantities, easily regenerable, and cheap [7]. The application of bio-sorption in environmental treatment of wastewaters contaminated by heavy metals has become a significant research area in the past 10 years [8]. Physic-chemical processes based on adsorption on natural organic materials are cheap and effective techniques for metals removal from wastewater [9]. Adsorbent materials derived from low-cost agricultural wastes or by-products from timber industries can be used for the effective removal and recovery of heavy metal ions from wastewater streams [8, 10-12]. The major advantages
of bio-sorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive bio-sorbent materials. Bio-sorption of heavy metals using wooden materials from aqueous solutions is a relatively new process which has been proven very promising in the removal of contaminants from aqueous effluents. The sorption capacity of wooden materials with content of lignocelluloses for metal ions is generally described as adsorption. The major advantages of wooden materials as adsorbents over conventional treatment methods include: low-cost, high efficiency, minimization of chemical and/or biological sludge, regeneration of bio-sorbent, no additional nutrient requirement and possibility of metal recovery [13]. For the overall understanding of the sorption process, it is necessary to characterize and determine the properties of the used adsorbents.

In this study the removal of Cu(II) and Zn(II) metal ions by using poplar wood sawdust and bark were investigated. For characterization of functional groups, which can be responsible for metal binding the wood sawdust and bark of poplar were analysed by infrared spectrometry.

2. Material and methods

The sawdust and bark of poplar, species of locally available wood, was dried and sieved, and the fraction with particle size max. 2.0 mm (sawdust) and max. 8.0 mm (bark) was used for adsorption experiments. 1 g of each dry adsorbent was mixed with 100 mL of each model solution prepared by dissolving of their appropriate sulphate salts in deionised water, include initial metal concentrations. Batch adsorption experiments were carried out on static conditions. The sorbent-sorbate interaction time was 24 h. After the end of experiments, poplar wood sawdust and bark were removed by filtration through a laboratory filter paper. Concentrations of appropriate ions were determined by colorimetric method (Colorimeter DR890, Hach Lange, Germany) with appropriate reagents to determine concentration of dissolved copper, and zinc. The pH values of solutions were also measured by pH meter inoLab pH 730 (WTW, Germany). In both cases, the efficiency of ion removal η (in %) was calculated using the following equation (equation (1)):

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

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.

IR spectra of dried poplar sawdust and bark were studied for characterization of present functional groups, which can be responsible for metal binding. Infrared spectrometry of poplar sawdust was carried out on Bruker Alpha Platinum-ATR spectrometer (Bruker Optics, Ettlingen, Germany). A total of 24 scans were performed on sample in the range of 4,000–400 cm$^{-1}$.

3. Results and discussion

3.1. Infrared spectra of polar sawdust and bark

The important role of FTIR spectroscopy is related to the characterization of sorbents, or to describe of functional groups which are involved to the mechanism of sorption processes. Metal ions adsorption capacity is strongly influenced by the surface structures of C–O and C–OH functional groups which are present in natural wooden organic materials [14]. Functional groups in poplar wood sawdust and bark were determined using FTIR spectroscopy. The IR spectra of poplar sawdust and bark are shown in figure 1. Poplar sawdust was detailed studied and characterized by Demcak et al. [3]. As can be seen from figure 1, the IR spectrum of the bark (the deadwood part of the wood pole) has a similar pattern to sawdust. A strong representation of hydroxyl functional groups is visible in both structures (3,650–3,000 cm$^{-1}$). There are no significant changes in the characteristic IR absorption bands of bark and sawdust indicating that the functional groups present of poplar on the surface (bark) and in the core (sawdust). The IR spectra of bark showed a strong band at 3,287 cm$^{-1}$ indicating the presence of
hydroxyl groups. The peaks at 2,918 and 2,890 cm\(^{-1}\) are due to the C–H stretching frequency and the peak at 1,622 cm\(^{-1}\) is due to C=O stretching mode of the primary and secondary amides (NH\(_2\)–C=O) [15]. The peak at 1,512 cm\(^{-1}\) is indicative of the N–H stretching of the primary and secondary amides, and the presence of amide or sulphamide band, respectively. The band at 1,317 cm\(^{-1}\) indicates a presence of carboxylic acids [16]. Weak band at 1,512 cm\(^{-1}\) is attributed to aromatic CC and two sharp peaks in area from 1,750 to 1,600 cm\(^{-1}\) which are characteristic of carbonyl group stretching were also observed. The strong C–O band at 1,022 cm\(^{-1}\) confirms the lignin structure of the bark [15].

![Infrared spectra of poplar wood sawdust and bark.](image)

**Figure 1.** Infrared spectra of poplar wood sawdust and bark.

### 3.2. Adsorption study of poplar sawdust and bark

The results of static sorption experiments are shown in table 1. Poplar sawdust used as a sorbent has shown a very good efficiency for the removal of studied metal ions. The efficiency which were achieved by sawdust in sorption of Cu(II) and Zn(II) from solutions were over \(\eta = 80\%\). Changes of pH values were also measured in the solutions after adsorption experiments by sawdust. The pH of the solutions is an important parameter for the characterization of adsorption processes and has an influence on the surface charge of the adsorbent, the degree of ionization and the type of used sorbent [17]. The adsorption experiments in the case of the poplar sawdust significantly increased the pH of the solution and it indicating that the ion exchange mechanism was also occurred in the adsorption process [3].

In the case of polar bark, the efficiency Cu(II) and Zn(II) removal from model solutions \(\eta = 70.3\%\) and \(\eta = 79.5\%\). It was found that after experiments the pH of the analysed solutions was increased what indicates that also like in case of poplar sawdust adsorption the adsorption processes and ion exchange run simultaneously.

| Adsorbent | Initial concentration \(c_0 (\text{Cu}^{2+}) = 10\, \text{mg} \cdot \text{L}^{-1}\) at pH = 4.6 | Initial concentration \(c_0 (\text{Zn}^{2+}) = 10\, \text{mg} \cdot \text{L}^{-1}\) at pH = 4.7 |
|-----------|------------------------------------------|------------------------------------------|
| sawdust   | \(c_0 (\text{Cu}^{2+})\) [mg.L\(^{-1}\)]  | \(c_0 (\text{Zn}^{2+})\) [mg.L\(^{-1}\)]  |
|           | pH                                      | pH                                      |
| sawdust   | 1.58                                    | 1.92                                    |
| bark      | 2.97                                    | 2.05                                    |

\(c_0\) - initial concentration of metal ions in model solution
\(c_e\) - residual concentration of metal ions in solution after adsorption
4. Conclusion
Bio-sorption is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluents. Natural organic wooden materials are inexpensive and effective metal ion adsorbents from agro waste materials or by-products from timber industries to offer these adsorbents as replacements for existing commercial materials were investigated.

The higher sorption efficiency was achieved with sawdust. It could be caused due to their higher specific surface area and smaller fraction. For the using of bark as adsorption materials, it is certainly appropriate to milled it to a smaller fraction and thereby to increase the surface area of the absorbent. As a limitation of bark adsorbents, it is leaching of organic-dyes into the solution.

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