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# Removal of Copper from Water Solutions by Adsorption on Spruce Sawdust <sup>†</sup>

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**Abstract:** Pollution of water by toxic elements is one of the major factors of concern for human health, as well as for environmental quality, and draws a large amount of scientific attention. New and cheaper methods of wastewater treatment are increasing the quality of the environment and reducing the negative impacts on fauna, flora, and human beings. The sorption technique is considered a cost effective method for effectively removing heavy metals. During the past few years, there have been increasing studies dedicated to using low-cost adsorbents like bark, tannin-rich materials, lignin, chitosan peat moss, and sawdust. The presented paper describes the adsorption behavior of spruce wood sawdust. In order to determine its applicability for wastewater treatment, copper removal from model solutions was studied.

**Keywords:** adsorption; aquatic solutions; spruce sawdust; copper

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## 1. Introduction

Different human activities on Earth have resulted in serious pollution of the air, land, and water. Water pollution has caused a shortage in aquatic resources due to drought and the misuse and production of large volumes of wastewater. The accumulation of heavy metals has negative effects on the health of flora, fauna, and human alike. Inorganic pollutants most commonly appearing in wastewater are nickel, zinc, silver, lead, iron, chromium, copper, arsenic, cadmium, and uranium, and these have been intensively investigated from the point of view of persistence and toxicity.

Copper can be found in high concentrations because it is usually used in many industrial sectors like metal finishing, electroplating, plastics, and etching. It is recognized as one of the most widespread heavy metal contaminants in the environment. Water contaminated with copper must be treated before being discharged into the environment because of its toxic properties, even at low concentrations [1–3].

In order to increase the use of more eco-friendly and economical water treatment methods, there has been increased research interest into developing new adsorbents that can be used for this purpose. Adsorption, in comparison to other methods like chemical precipitation, electrochemical technologies, ion exchange, membrane filtration, and others, is cheaper, more flexible, more effective; has greater simplicity of design, ease of operation, and insensitivity to toxic pollutants; and results in a high quality purified product. Sorption methods have come to the forefront due to their efficiency in the removal of pollutants from water or wastewater that are too stable to be removed by biological processes [4,5].

In recent years, low cost adsorbents showing potential as efficient wastewater treatment materials have been reported, including aquatic plants, discarded tea leaves, bark, peat moss, lignin,

and sawdust. Sawdust is an agricultural waste material that is available in large quantities, has a low cost, and is easily regenerated after use [6–8].

The aim of this research was to investigate the application of spruce wood sawdust for the removal of heavy metal ions from aquatic solutions. Copper was selected as a model ion due to its being a common pollutant introduced into natural water by various types of industrial wastewater. Spruce sawdust was also characterized by FTIR in order to determine the changes caused by adsorption/ionexchange process.

## 2. Materials and Methods

### 2.1. Adsorbent

Locally acquired spruce sawdust was used in the sorption experiment. In the experiment, only sawdust with a particle size below 2 mm was used. One gram of dry spruce sawdust was mixed with 100 mL water solutions.

### 2.2. Experiment Procedures

The water solutions with concentrations of 10 mg/L of Cu(II) were prepared by the dissolution of measured amounts of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in distilled water.

Wooden sawdust was analysed by FTIR on a Bruker Alpha Platinum-ATR spectrometer (Bruker Optics, Ettingen, Germany). A total of 24 scans were carried out in the range of 4000–400  $\text{cm}^{-1}$ .

The first experiment focused on the interaction between the sorbent and sorbate after 24 h. The sawdust was initially mixed with the model solution and left at room temperature for the duration of the experiment. We then performed a kinetic study, with the contact time between sorbent and sorbate being 5, 10, 15, 30, 45, 60, and 120 min, respectively. During these timeframes, spruce sawdust was intensively mixed with the model solution.

In the filtrates, the concentration of copper was determined via the colorimetric method (Colorimeter DR890, Hach Lange, Germany) with an appropriate reagent. Changes in pH were measured using a pH meter (Mettler Toledo FG2, Schwerzenbach, Switzerland).

The sorption efficiency percentage was calculated using the following equation:

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

where  $c_0$  is the initial concentration of appropriate ions (mg/L), and  $c_e$  is the equilibrium concentration of ions (mg/L).

## 3. Results and Discussion

### 3.1. Infrared Spectra

The FTIR method was used to determine active sites existing in the surface structure of the sawdust [8]. The IR spectrum of spruce sawdust is shown in Figure 1. The main components of sawdust are lignin, cellulose, and hemicelluloses. A broad band in the region of 3336  $\text{cm}^{-1}$  represents the presence of hydroxyl groups ( $-\text{OH}$ ), and the valence vibration related to aromatic C–H is shown on the spectrum at 2883  $\text{cm}^{-1}$ . The aromatic functions of lignin are characterized by infrared absorption bands, which is characteristic of the C=C vibrations of the aromatic skeleton of lignin at the 1648  $\text{cm}^{-1}$  region. Other bands corresponding to lignin (carbonyls (C=O), alcohols, and ethers) were observed at 1508, 1451, and 1316  $\text{cm}^{-1}$ , respectively. Wavenumbers at 1422, 1367, 1316, 1260, 1026, and 895  $\text{cm}^{-1}$  belong to cellulose. The functional groups of aromatics were observed at 895  $\text{cm}^{-1}$  [9,10].

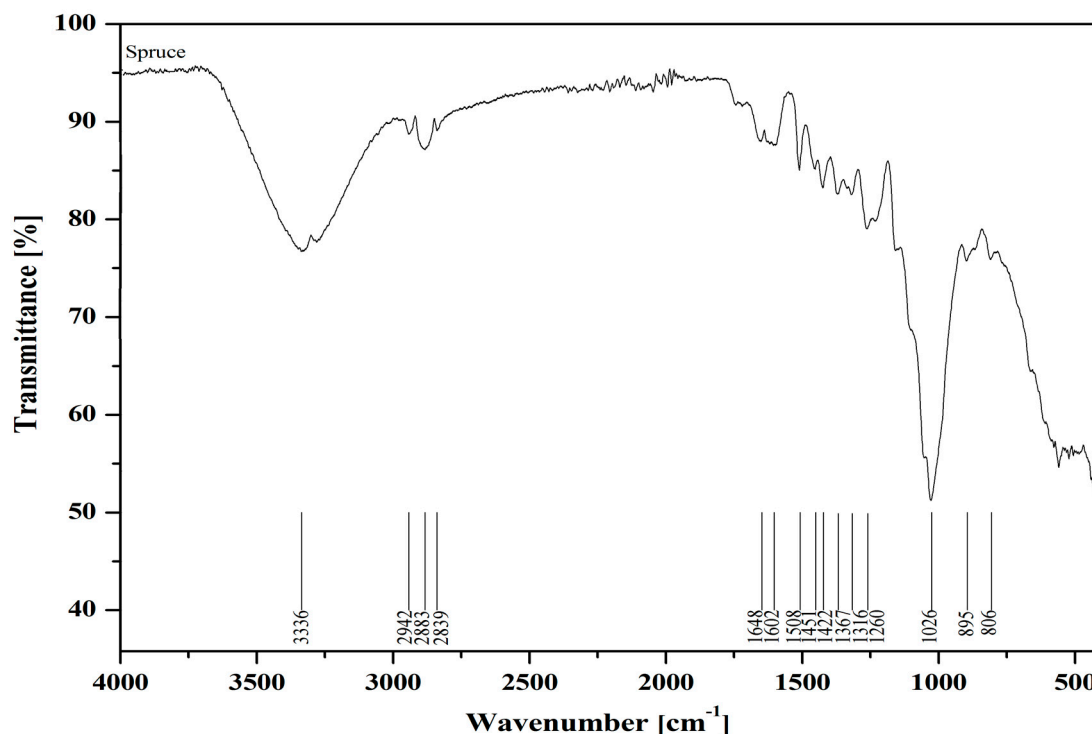


Figure 1. Infrared spectra of spruce sawdust.

### 3.2. Sorption Experiments

In the 24 h experiment, the efficiency of spruce sawdust for Cu(II) removal was at about 85%, and resulted in a pH of 5.3. The results of the kinetic study of the sorption experiments are presented in Figure 2. Larous et al. [11] revealed that copper adsorption by sawdust is dependent on the solution pH, temperature, agitation speed, initial concentration, contact time, liquid to solid ratio, ionic strength, etc. A significant result was first observed at 10 min, when the sorption efficiency achieved more than 80%. The highest efficiency of Cu(II) sorption ( $\approx 90\%$ ) was reached after 60 min. Change in pH due to ion exchange between metal ions in model solutions and functional groups of spruce wood sawdust is the major mechanism of retention of copper by sawdust.

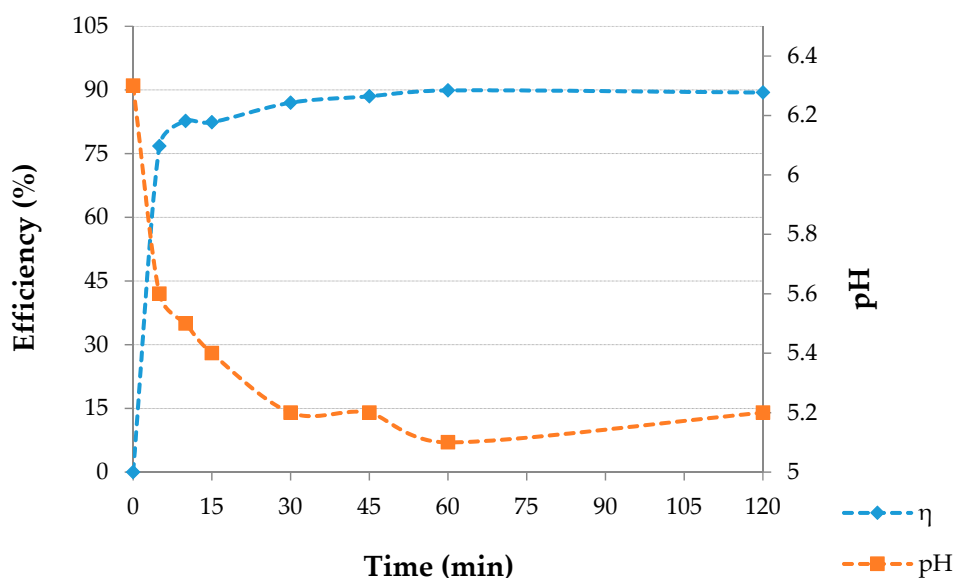


Figure 2. Dependence of sorption efficiency  $\eta$  and changes of pH on time during experiment.

#### 4. Conclusions

The current international trend to obtain higher environmental standards favors the usage of cheap and environmentally friendly systems for treatment of effluents. Inexpensive, readily available materials like wood sawdust can be used for the removal of heavy metal ions from water.

FTIR analyses of spruce sawdust confirmed the presence of functional groups that are able to bind copper ions.

In all experiments, Cu (II) removal was more than 75%. After 5 min, most of copper ions were removed; the time after this point was characterized by slow changes in removal efficiency and can be considered as relatively constant. Changes in pH values demonstrated the processes of adsorption and ion exchange; for example, after a 24 h experiment, the pH changed from 6.3 to 5.3.

The sorption experiments have demonstrated the potential for wood sawdust as a means to remove heavy metal ions from water solutions. The results from our experiments therefore provide promising perspectives for the utilization of sawdust for reducing metal pollution.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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