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REMOVAL OF COPPER, ZINC AND IRON FROM WATER SOLUTIONS BY SPRUCE SAWDUST ADSORPTION

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ABSTRACT: The water pollution by toxic elements is one of the major problems threatening human health as well as the quality of the environment. Sorption is considered a cost-effective method that is able to effectively remove heavy metals. During past few years, researches have been researching usage of low-cost adsorbents like bark, lignin, chitosan peat moss and sawdust. This paper deals with the study of copper, zinc and iron adsorption by adsorption of spruce sawdust obtained as a by-product from locally used wood. Raw spruce sawdust was used to remove heavy metal ions from the model solutions with ion concentration of 10 mg/L during 24 hours or 5, 10, 15, 30, 45, 60, 120 min, respectively. Fourier-transform infrared spectroscopy was applied to determine functional groups of sawdust. Sorption efficiency was higher than 67% in short-time experiments and higher than 75% for one day experiments in all tested cations.

KEY WORDS: adsorption, model solutions, spruce sawdust, heavy metals

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Introduction

The pollution of air, soil, and water is a result of people's efforts to improve their lives. The industrial activities together with technology development lead to a release of large quantities of contaminants to the water. Among a wide range of pollutants contained in wastewater, metals are one of the most toxic substances. They do not biodegrade and due to their presence in streams and lakes living organisms accumulate such substances, causing health problems in animals, plants and human beings – the overall negative impact on the whole environment. Inorganic pollutants most frequently presented in wastewaters are copper, nickel, zinc, lead, iron, chromium and cadmium. These heavy metals were intensively investigated from the point of view of persistence and toxicity (Abdel-Raouf, 2016; Larous, 2012; Gogoi, 2018; Simón, 2019).

Copper can be found in high concentration because it is usually used in many industrial sectors like metal finishing, electroplating, plastics and etching. Copper is actually one of the most frequently occurring heavy metal contaminants in the environment. Water contaminated with copper must be treated before it is discharged to the environment because of its toxic properties even at low doses. High concentrations of copper can cause serious toxicological concerns because it can affect the brain, skin, liver and pancreas. This can lead to nausea, vomiting, headache, diarrhea, respiratory difficulties, liver and kidney failure (Al-Saydeh, 2017; Ageena, 2010; Larous, 2012).

Zinc is widely used in electroplating, galvanized pipes, iron, alloy and brass production and paper production. At trace amounts, zinc is an essential nutrient for certain biochemical and physiological functions of the organism. At concentrations beyond the permissible level (2.00 mg/L), zinc can lead to a malfunction of various systems in the human body and it can cause nausea, vomiting, epigastric pain, lethargy, fatigue, a short-term illness called "metallic smoke fever» and restlessness. Zinc is also poisonous to plants at high concentrations and can be damaging in soils because of its high mobility (Simón, 2019; Udomkitthaweewat, 2019).

Contamination of water with iron can either be geogenic or caused by industrial effluents and domestic waste. Although iron is essential for human and lack of it may lead to anaemia and health problems, its high levels may cause severe health problems in human beings such as vomiting, liver cancer, diabetes, cirrhosis of liver, heart diseases, infertility etc. The higher concentration of iron in water corrodes water pipe lines, changes colour of water, its taste, odour and leaves stains on clothes (Al-Shahrani, 2013; Kumar, 2017).

Due to all these reasons, the proper treatment of the wastewaters before its discharging to the environment is needed.

There are several methods of removing heavy metals from wastewaters, for example:

- precipitation – a simple process based on the fact that some metal salts are insoluble in water,
- ion – exchange method uses ions to exchange with metal ions in the water solutions,
- reverse osmosis method utilizes high pressure to filter out the metal ions trough a membrane (Simón, 2019; Ageena, 2010).

Due to increased interest in using eco-friendly and economical materials, researchers are now searching for new adsorbents that can be used for this purpose. The adsorption process (figure 1) has been considered as one of the most efficient methods with many advantages: low costs, higher flexibility, high efficiency, good selectivity, simplicity of design, ease of operation, insensitivity to toxic pollutants, high quality purified products and recyclability (Elkady, 2017; Balintova, 2016; Demcak, 2019).

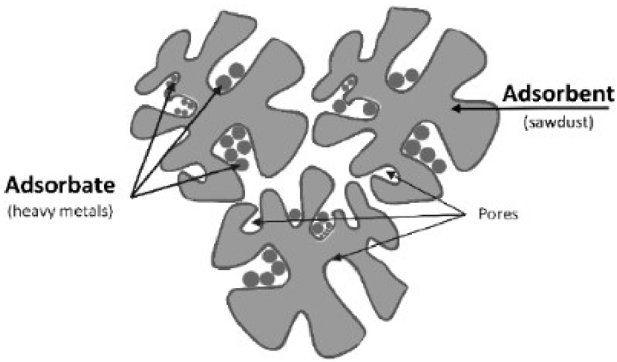

Figure 1. Realization of adsorption process using sawdust as adsorbent

Source: Ouafi, 2017, p. 117.

In recent years, extensive research has been done to identify new and cost-saving sorbents that could remove different heavy metal ions. The low-cost adsorbents including aquatic plants, waste tea leaves, bark, peat moss, lignin and sawdust have also been reported as efficient materials. Sawdust is one of the most appealing timber industry by-products that is available in large quantities, is cheap and easily regenerated after use (Memon, 2008; Thapak, 2015; Ince, 2017; El-Saied, 2017).

The aim of this research was to investigate application of spruce sawdust for Cu(II), Zn(II), and Fe(II) removal from aquatic solutions. Copper, zinc, and iron are metals found in nitrogen rich wastewaters (Zhang, 2019). Due to this reason these were selected as model ions to test spruce sawdust in the process of their removal from aquatic solutions. Spruce sawdust was also tested by FTIR method in order to determine the changes caused by adsorption/ion – exchange process.

Research methods

The spruce sawdust (particle size less than 2 mm) from local resources was used as a sorbent for the removal of selected heavy metals ions from aqueous solution without any pre-treatment. Wooden sawdust was analysed by FTIR on Bruker Alpha Platinum-ATR spectrometer (Bruker Optics, Ettingen, Germany). A total of 24 scans were carried out in the range of 4,000–400 cm^{-1}.

Dry spruce sawdust (1 g) was mixed with 100 mL of aquatic solutions. The water solutions with concentration 10 mg/L of Cu(II), Zn(II) and Fe(II) were prepared by dissolution of calculated amount of $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$ and $FeSO_4.7H_2O$ in deionised water.

The first experiment focused on interaction between sorbent and sorbate during 24 hours. The sawdust was initially mixed with the model solution and left at the room temperature (20±1°C) for the duration of the experiment.

The next step of the research was the study of kinetics, the contact time between sorbent and sorbate was 5, 10, 15, 30, 45, 60 and 120 min. During this time spruce sawdust was intensively mixed in the model solution at the room temperature (20±1°C).

After the experiments, the concentration of heavy metals in the filtrates was determined by colorimetric method (Colorimeter DR890, Hach Lange, Germany) with appropriate reagent. Changes of pH were measured by pH meter (Mettler Toledo FG2, Schwerzenbach, Switzerland). The percentage efficiency was calculated by following equations:

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

where:
η – sorption efficiency [%],
c_o – the initial concentration of appropriate ions [mg/L],
c_e – equilibrium concentration of ions [mg/L].

Results of the research

Infrared sprectra

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, 2001). FTIR method was used to determine active sites existing in the surface structure of sawdust (El-Saied, 2017). IR spectrum of spruce sawdust is shown in figure 2. The main components of sawdust are lignin, cellulose and hemicelluloses. A broad band of 3336 cm^{-1} represented presence of hydroxyl groups (–OH), the valence vibration related to aromatic C–H is shown on the spectrum at the 2883 cm^{-1}. The aromatic functions of lignin are characterized by infra-red absorption bands, which is characteristic of the C=C vibrations of the aromatic skeleton of lignin at the 1648 cm^{-1}. Another bands of lignin (carbonyls (C=O), alcohols and ethers) were observed at 1508, 1451, and at 1316 cm^{-1}. Wavenumbers at 1422, 1367, 1316, 1260, 1026 and 895 cm^{-1} belong to cellulose. The functional groups of aromatics were noticed at 895 cm^{-1} (Salamat, 2018; Schwanninger, 2004).

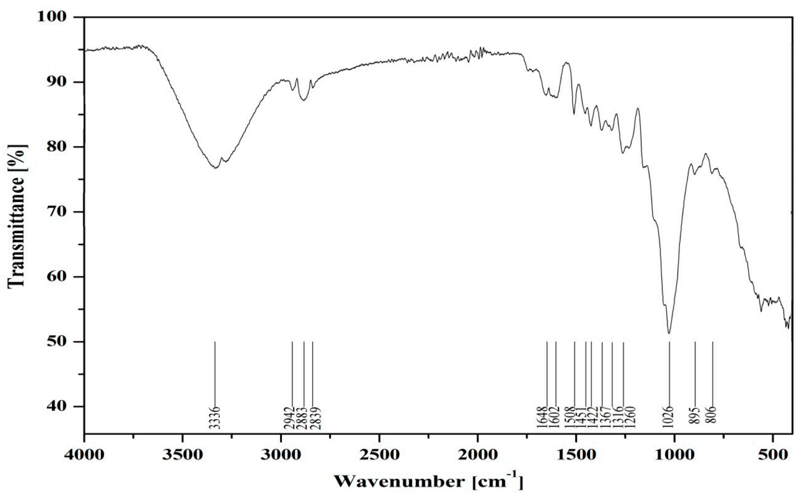

Figure 2. Infrared spectra of spruce wooden sawdust

Source: author's own work.

Sorption experiments – results of the 24 hours experiment

Results of the 24 hours experiment with initial concentration of cooper, zinc and iron ions 10 mg/L are shown in table 1. In all cases, the sorption efficiency reached more than 75%. The best removal efficiency was observed in the case of copper ions (more than 85%). The pH of the aqueous solution is an important controlling parameter in the adsorption process and thus the effect of pH has been studied as well (Balintova, 2011). Initial pH of the solutions was influenced only the type of chemicals used, so adsorption process was carried out at different pH ranges. In all cases, pH decreased when compared to the initial value. The decrease in pH values could be caused by the fight for adsorption between metal ions and H^+ (Demcak, 2019).

Table 1. Results of the 24 hours experiments

Heavy metal ion	Input value		Output value		Sorption efficiency [%]
	c_o [mg/L]	pH	c_e [mg/L]	pH	
Cu(II)	10.00	6.3	1.48	5.3	85.2
Zn(II)	10.00	6.2	1.92	5.4	80.8
Fe(II)	10.00	5.9	2.49	5.2	75.1

Source: author's own work.

Sorption experiments – short-term results

Results of the short-term experiments of copper removal from aquatic solutions are shown in figure 3. Larous et al. (2005) state that copper adsorption on sawdust depends on the solution's pH, temperature, agitation speed, initial concentration, contact duration, liquid to solid ratio, and ionic strength. A significant increase in sorption was observed at 10 minutes, when efficiency achieved more than 80%, the rest of the time is characterized by slow changes in removal efficiency which can be evaluated as relatively constant. The highest efficiency of Cu(II) (≈ 90%) was reached after 60 min. Changes of pH, due to ion exchange between metal ions in model solutions and functional groups of spruce wood sawdust, are the major mechanism of retention of copper by sawdust.

Figure 4 shows the results of zinc removal during the experiment (from 5 to 120 min). In all experiments, removal efficiency was higher than 73%. The result indicates that zinc removal decreases pH of the solutions in the range from 6.2 to 5.7. The maximum efficiency removal of Zn(II) was about 82% at pH 5.7. Pragati et al. (2015) used the ground sawdust to remove zinc from aquatic solutions. They found that the maximum level of zinc iones removal (at pH 5, during 120 min of contact time, and adsorbent dose 0.5g/100 mL) is about 90%.

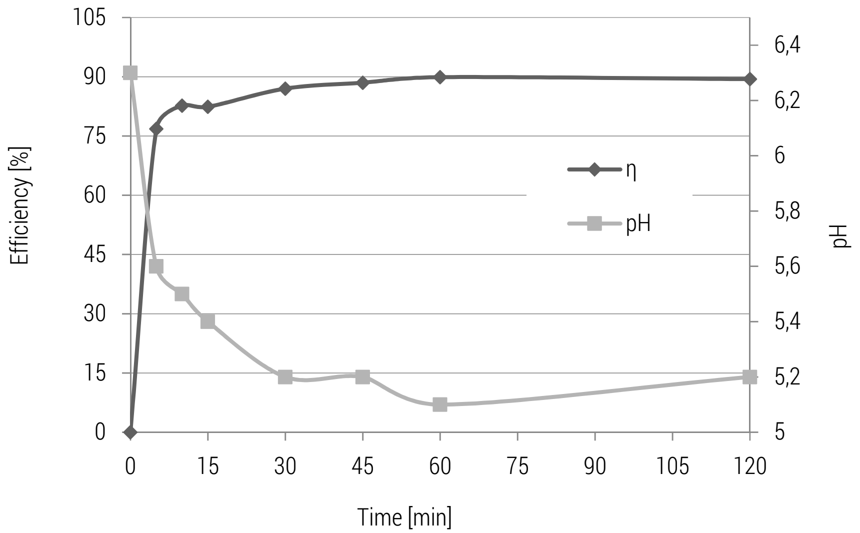

Figure 3. Dependence of sorption efficiency η and changes of pH over time when removing copper from aquatic solutions

Source: author's own work.

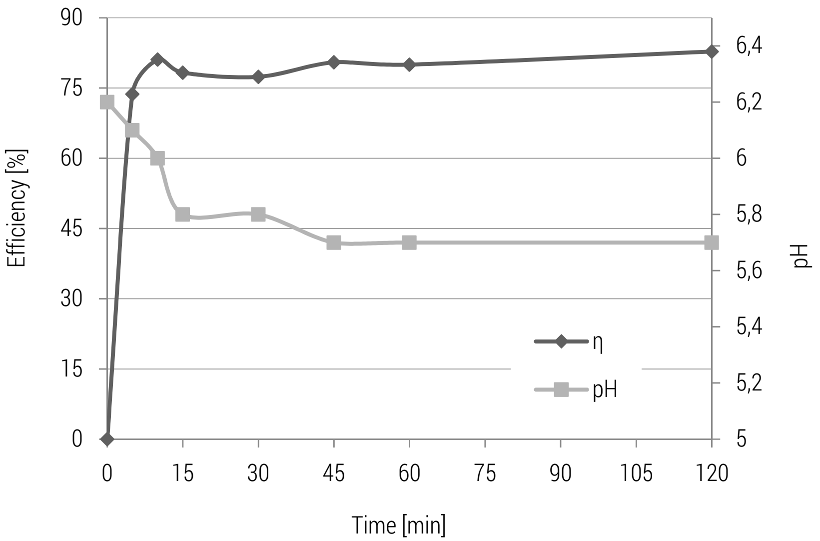

Figure 4. Dependence of sorption efficiency η and changes of pH on time during experiment on zinc removal from aquatic solutions

Source: author's own work.

The results of iron removal in short-term experiments indicated the removal efficiency higher than 67% (5 minutes), the highest efficiency was observed at 45 minutes at about 76% (figure 5). The value of pH was decreasing from 6.3 to 5.3 due to ion exchange. Senin et al. (2007) found that the maximum adsorption efficiency by sawdust was found to be 71.7% which corelates with the results of the experiment.

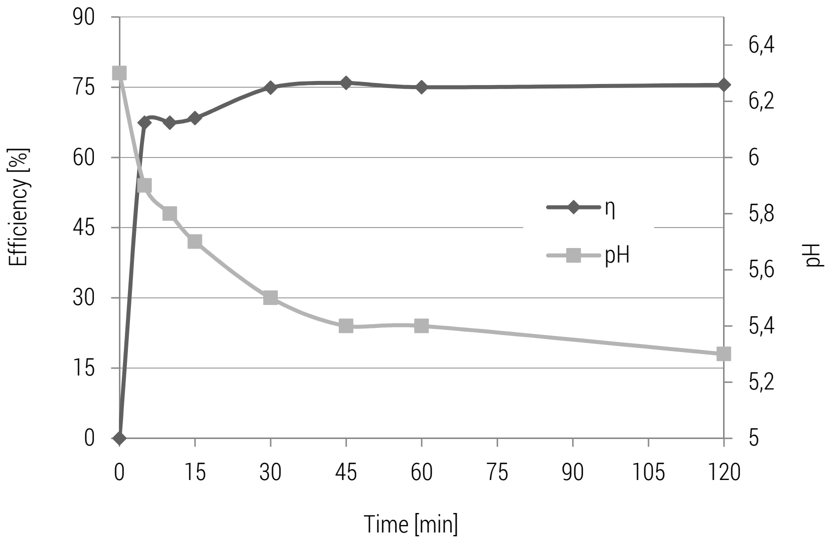

Figure 5. Dependence of sorption efficiency η and changes of pH on time during experiment on iron removal from aquatic solutions

Source: author's own work.

Conclusions

In terms of treatment of effluents, the current international tendency towards environmentally friendly standards and solutions favours cheap and harmless systems. Adsorption is one of the most effective techniques for removal of pollutants from aqueous solutions. Inexpensive and easily available materials like wood sawdust can be used as sorbent for purification of wastewaters.

The Fourier-transform infrared spectroscopy of spruce sawdust confirmed the presence of the functional groups that they are able to bind heavy metals ions.

Under the 24 hours experiments, the highest removal efficiency of ions was recorded for copper – more than 85%, and the lowest efficiency was recorded for iron ions – more than 75%.

In all experiments Cu(II), Zn(II) and Fe(II) removal rate was more that 67%. In case of copper, zinc and iron the equilibrium concentration of ions was highest at 60 minutes (1.01 mg/L) for Cu(II), 120 min (1.72 mg/L) for Yn(II) and 45 min (2.41 mg/L) for Fe(II). Changes in pH values in the processes of adsorption and ion exchange in all experiments shown a decreasing tendency.

The sorption experiments showed the huge potential of the spruce sawdust in removing heavy metals ions from water solutions. The results of the experiments are promising in terms of using sawdust to reduce pollution by heavy metals.

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The contribution of the authors

Zdenka Kovacova – 40% (carried out the experiments and contributed to the final version of the manuscript).

Stefan Demcak – 30% (conceived and planned the experiments, carried out the experiments and contributed to the final version of the manuscript).

Magdalena Balintova – 30% (conceived and planned the experiments, supervised the paper).

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