A study of sorption heavy metals by natural organic sorbents

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***Abstract*—** The use of low cost natural sorbents as a replacement of current costly methods heavy metals removal from solution is increasing in recent years. Natural organic materials or waste products from industry with a high capacity for heavy metals removal can be obtained, employed, and disposed of with a little cost.

The aim of this article is cooper, zinc and iron cations removal from acidic solutions by the peat and the various kinds of wood sawdust (poplar, hornbeam, spruce, pine, cherry, ash, and oak). The presence of hemicelluloses, cellulose and lignin in structure of natural sorbents was studied by infrared spectrometry. Peat and poplar wood sawdust had efficiency of metal cations removal from aquatic model solutions approximately of 80.0 %. Hornbeam and poplar wood sawdust had 45.0 % efficiency of Cu, Zn and Fe removal at five times higher concentration of these metal cations. Peat adsorbed more than 50 % of metal ions from solutions with higher concentration.

Keywords— Sorption, wood sawdust, peat, hemp hurds

I. Introduction

THE heavy metals or trace elements can often be found in industrial wastewater, and their discharge to the environment is a significant threat due to their acute toxicity to aquatic and terrestrial life [1]. Among the metals associated with these activities also belong cooper (Cu), zinc (Zn) and Iron (Fe). Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [2]. Toxic heavy metals are exposed to the natural eco-system and subsequently are accumulated in human bodies will occur through either direct intake or food chains. Therefore, heavy metals should be eliminated from the environment. Treatment processes for water streams contaminated with metals include chemical precipitation, membrane filtration, ion exchange, carbon absorption, adsorption, and coprecipitation with adsorption [3-5].

The common methods used for removal of heavy metals and trace elements from wastewaters are based on their adsorption onto insoluble compounds – sorbents. Synthetic sorbents usually are quite expensive. Therefore, the use of the natural sorbents and their modifications seems a prospective method to metals removal. Industrial wastes are one of the rich sources of low-cost adsorbents besides industrial by-products and natural materials [4].

A perspective tends to removal of heavy metals and trace elements from wastewaters have use of a natural organic sorbents material as wooden sawdust, peat, bark, roots, rice husk, and bone gelatin mass, hemp hurds or their modification. Due to presence of organic compounds bearing polar functional groups (e.g. alcohols, aldehydes, carboxylic acids, ketones, and phenolic hydroxides) have a natural organic sorbents high complex capacity [2, 6].

In many studies were determined that better results were obtained with materials containing high concentration of polyphenol (e.g., tannins, lignin, and humic substances) to capture metal ions [7]. Therefore, a peat has an important role in the removal of heavy metal ions from wastewater. Peat is a light brown to very dark organic material formed under waterlogged conditions from the partial decomposition of mosses and other bryophytes, sedges, grasses, shrubs, or trees [8]. Based on the nature of parent materials, peat is classified into four groups, namely moss peat, herbaceous peat, woody peat, and sedimentary peat. For the past two decades, different kinds of peat have been used especially as cost-effective adsorbents in the treatment of municipal and industrial wastewater. Peat has a high potential in environmental purification [9, 10].

The use of low-cost adsorbents like wood sawdust has been investigated as a replacement of current costly methods. Sawdust is mainly waste by-product of the timber industry that is either used as cooking fuel or a packing material; however, it can be used as a low-cost adsorbent of heavy metals, principally due to its lignocelluloses composition. Natural materials or waste products from certain industries with a high capacity for heavy metals can be obtained, employed, and disposed of with little cost [6]. Heavy metals are often discharged by a number of industries. This can lead into the contamination of freshwater and marine environment [4]. Heavy metals are not biodegradable and have accumulation potential, causing various diseases and disorders. It is well known that some metals are harmful to life, such as antimony, chromium, copper, lead, manganese, mercury, cadmium, etc. They are significantly toxic to human beings and ecological environments [2, 11, 12].

Paper deals with a study of sorption properties of peat and wood sawdust (hornbeam, poplar, pine, spruce, ash, cherry, and oak) for removal inorganic ions pollutions from model solutions (concentration of dissolved cooper, zinc, and iron ions 10 and 50 $mg.L^{-1}$, respectively). The sorbents were analysed by infrared spectrometry for characterization of functional groups. Efficiency of metal removal was analysed by colorimetric method.

II. MATERIAL AND METHODS

Model solutions containing heavy metals cations (copper, zinc and iron) were prepared by dissolution of their sulphate salts in deionised water. A Colorimeter DR890 (HACH LANGE, Germany) with appropriate reagents was used to determine concentration of dissolved cooper, zinc and iron.

For sorption experiments were used peat, with particle distribution between 2-8 mm, and various kind of wooden sawdust with fraction under 2 mm (poplar, hornbeam, ash, oak, cherry, pine, and spruce wood sawdust). For the purpose of natural wooden materials efficiencies investigation, batch adsorption experiments were carried out. 1 g of each type of natural sorbents was mixed with 100 mL of model solutions containing 10 $mg.L^{-1}$and 50 $mg.L^{-1}$of cooper, zinc and iron cations, respectively. After 24 hours reaction time, natural organic sorbents were removed by filtration through a laboratory filter paper for qualitative analysis, residual concentrations of appropriate cations were determined by colorimetric method and pH change was also measured by pH meter inoLabph 730 (WTW, Germany). Also the efficiency of metal removal was calculated using the following equation:

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

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

Differences in FTIR measurements of all wood sawdust were carried out by Bruker Alpha Platinum-ATR spectrometer (BRUKER OPTICS, Ettingen, Germany). A total of 24 scans were performed on each sample in the range of 4000–400 cm^{-1}.

III. RESULTS AND DISCUSSION

A. *Infrared spectra of sorbents*

The IR spectra of wooden sawdust show similar structure (Fig. 1). The structure of wooden sawdust is mainly consistent by hemicellulose, cellulose, and lignin [13]. In Fig. 1 can be seen the strong broad OH stretching (3300–4000 cm^{-1}), C–H stretching of methyl and methylene groups (3000 - 2800 cm^{-1}). The strong broad OH stretching at this area can be caused by the presence of water or moisture too. For hemicelluloses are typical the stretching band at 1731 cm^{-1} (presence of C=O from the acetyl groups) [14]. For pine sawdust was observed the characteristic band at 1690 cm^{-1} which represents the occurrence of α, β–unsaturated aldehydes, ketones. Infrared spectra of lignin were observed by Zhang et al. [15]. The characteristic bands of lignin were confirmed at 1503 and 1452 cm^{-1}wavenumber (aromatic skeletal vibrations of lignin) and at 1320 cm^{-1} (syringyl and guaiacyl condensed lignin). Wavenumbers at 1422, 1367, 1315, 1153, 1024 and 894 cm^{-1} appertain to cellulose that occurs in two forms and this in crystalline (at 1315 cm^{-1}) and in amorphous (at 894 cm^{-1}). Functional groups of aromatics, carboxylic acids, alkyl halides were found at 828 cm^{-1}. At 554 cm^{-1} were determined alkyl halides (C–Cl and C–Br stretch) too [14,16].

An infrared spectrum of peat is shown on Fig. 2. Intensive deformation at area 3700 - 3300cm^{-1} represents the strong broad OH stretching. Functional groups of aliphatic C-H, CH_2, C-H_3 stretching was found at 2950 – 2850 cm^{-1}. At 1640 - 1725 cm^{-1} were determined C=O stretching of carboxylic acids. Aliphatic C-H deformation, OH deformations and C-O stretching of phenolic OH, C-H deformation of CH_3 groups and salts of carboxylic acids were measured at area 1470 - 1330 cm^{-1}. Presence of C-O stretching of esters, ethers and phenols was found at 1280 - 1140 cm^{-1}. Wavenumber at 1028 appertain to C-O stretching of alcoholic compounds, polysaccharides [7,17,18].

Comparison of infrared spectra wood sawdust and peat we can suppose sorption on surface hydroxyl groups and phenol groups.

Other authors found that sawdust was efficient for uptake of Cr(VI), but they used spruce sawdust instead of pine sawdust [19,20]. In these cases it was suggested that the adsorption occurred on the lignin or tannin molecules in the wood residue, lignin containing the same types of functional surface groups (hydroxyl groups and phenol groups) as tannin [21,22] and Johnson et al. [23] showed results regarding Cr sorption for various types of sawdust, indicating great variability, although there were no data for pine sawdust.

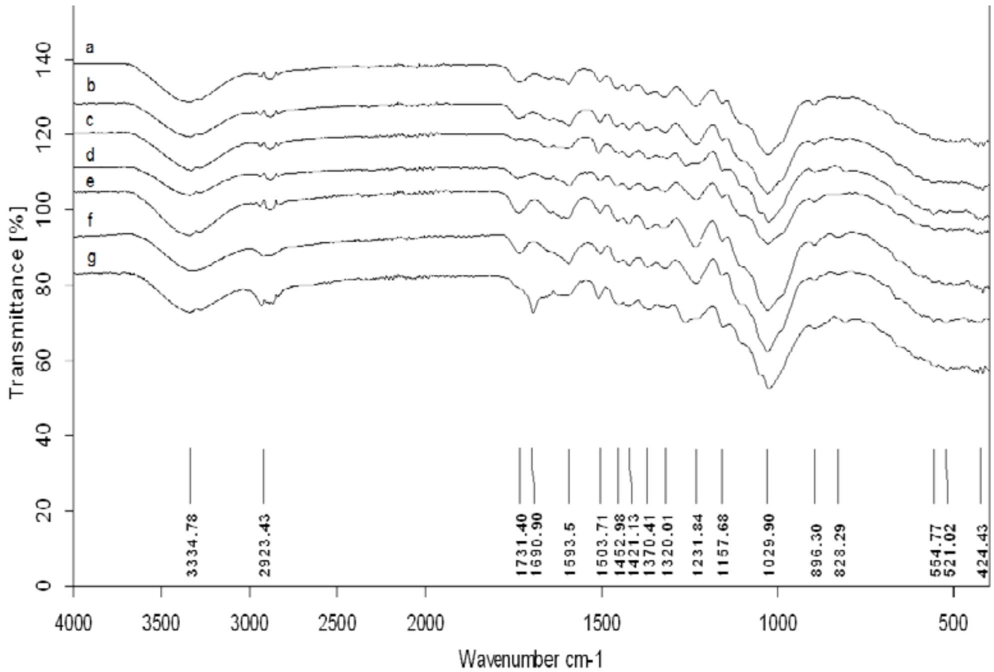

Fig. 1 Infrared spectra of wood sawdust: a-oak, b-ash, c-spruce, d-poplar, e-cherry, f-hornbeam and g-pine.

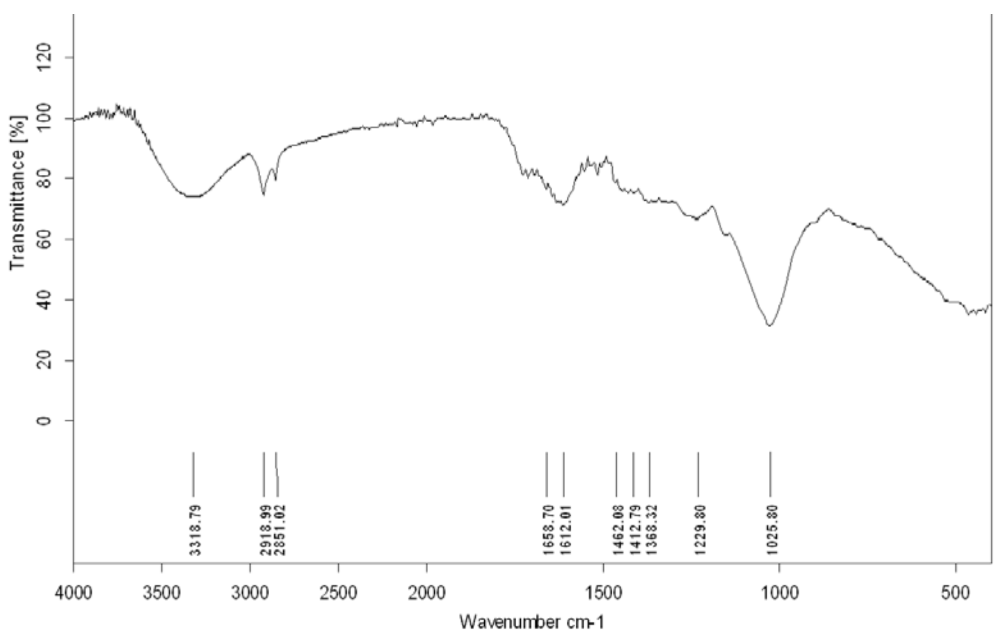

Fig. 2 Infrared spectrum of a wood peat.

B. *Sorption experiments*

The results of sorption experiments for solution with concentrations of 10 mg.L^{-1} cation are shown on Fig 3. All kinds of wood sawdust used for sorption were capable to removal the ions. Bulutand and Tez [24] investigated of metals removal by various sawdust adsorption as an appear to be a promising adsorbent for metals removal from wastewater with potentially more economical than current removal processes. Poplar and spruce exhibit the best effect on sorption from wood sawdust sorbent of copper from solution with efficiencies above of 80 %. Hornbeam, ash, pine, cherry and oak have efficiencies in the range of 50.0 - 75.0 %. For zinc removal the best wood sawdust was poplar (75.0 %), hornbeam and spruce (70.0 %). The other kinds of wood sawdust exhibit efficiencies from 30.0 % to 50.0 %. Poplar and spruce wood sawdust was also the best sorbent for iron removal with efficiencies above of 70.0 %. But ash has the lowest efficiency for iron removal (47.0 %). The peat showed potential to remove metal ions from aquatic solutions. For cooper and zinc removal had efficiency of removal above 70 % and in case of Fe(II) ions removed approximately 80 % .

Changes of pH values in solutions were observed after sorption too (Table 1). Due to different properties of Cu(II), Zn(II), and Fe(II) cations and different sawdust materials, the adsorption took place in a slightly different pH range for different metals. Shukla et al. [25] observed that In a certain pH range for a one specific metal cation may be one or more a of species present in a form (M, MOH^+, $M(OH)_2$, etc.) at a solution. At lower pH, the positive charged metal ion species may compete with H^+ and be absorbed at the surface of the sawdust by ion exchange mechanism. At elevated pH, mainly neutral, metal cations may be absorbed by hydrogen bonding mechanism along with ion exchange. Sorption of Zn(II) and Fe(II) by a hornbeam and poplar increase value of pH. Possibility of ion exchange between dissolved metal cations in and H^+ from sawdust (spruce, ash, pine, cherry, and oak) and a peat was indicated by decreasing of pH.

Fig. 3 Results of sorption experiments (initial concentrations of ions 10 $mg.L^{-1}$).

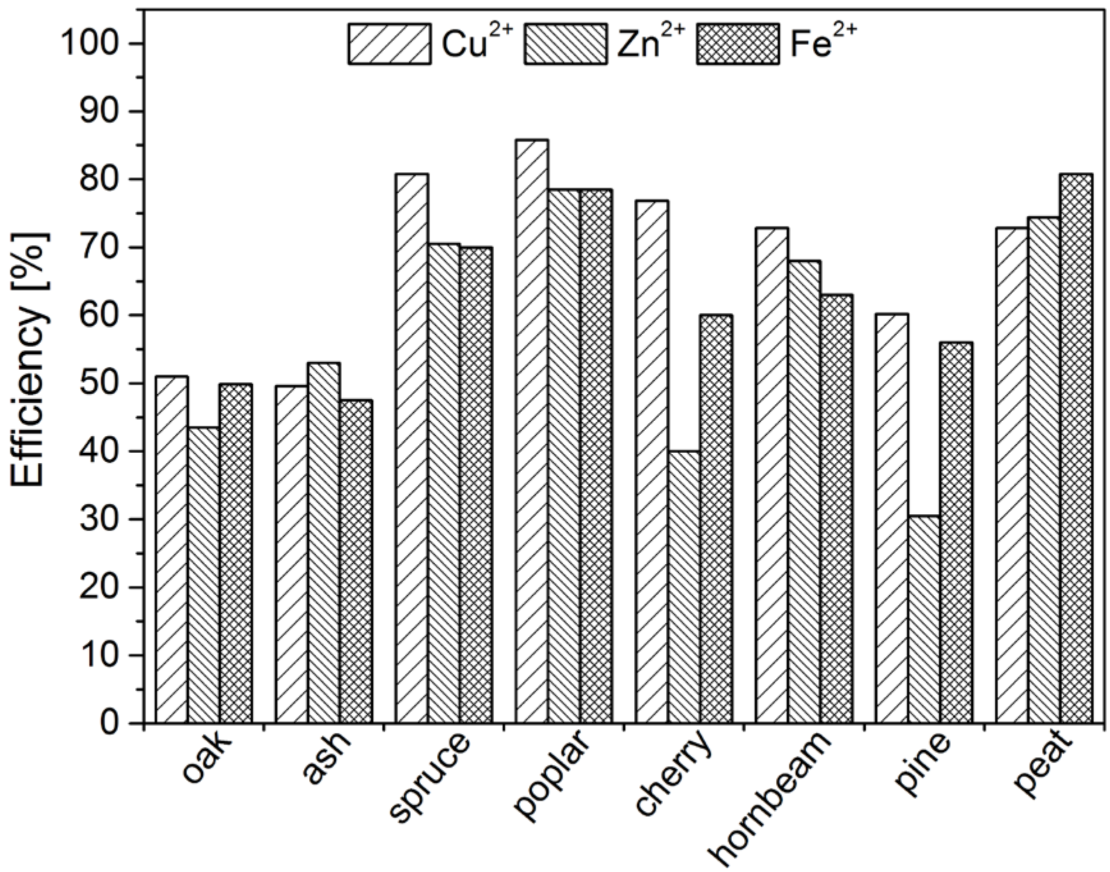

Table 1 Changes of pH values after sorption experiments (initial concentrations of ions 10 $mg.L^{-1}$).

cation	initial pH	oak	ash	spruce	poplar	cherry	hornbeam	pine	Peat
Cu^{2+}	5.81	4.12	5.39	4.86	5.32	4.87	5.16	4.64	4.21
Zn^{2+}	5.42	4.37	5.03	5.27	5.86	5.21	5.91	5.13	4.66
Fe^{2+}	5.43	3.74	5.75	5.03	5.67	4.96	5.48	4.79	4.89

This study was compared with determination of the efficiency of removal cations with five times higher concentrations. Fig. 4 presents the efficiency of metal cations removal from these solutions. Hornbeam and poplar have the best efficiency from wood sawdust (approximately 45.0 %) for copper, zinc and iron removal. Ash has the 40.0 % efficiency for zinc and iron removal. The lower values of cations removal from solutions can by caused by a lower sorption capacity of wood sawdust. The peat removed approximately 50 % Zn(II) and Fe(II) ions from solutions and 60 % of Cu(II) ions. Surprisingly, the concentration of sulphates in these solutions remained practically unchanged.

Also in this case changes of pH values in solutions were observed after sorption. Values of pH after sorption by sawdust were decreased in all causes. We can suppose that oak sawdust Fe(II) from solution shows intensive ion exchange which is declared by intensive decreasing at a pH=3.0. More significant changes of pH was observed in sorption of Cu(II) and Zn(II) from solutions by oak sawdust too. This can be attributed to the changes in counter ions associated with carboxylate and hydroxylate anions, indicating that acidic groups, carboxyl and hydroxyl, are the main functional groups in the biosorption of cadmium ions, which is in a good agreement with the pH analysis results, what was investigated by Albadarin et. al [26].

Fig. 4 Results from sorption experiments (initial concentrations of ions 50 mg.L^{-1}).

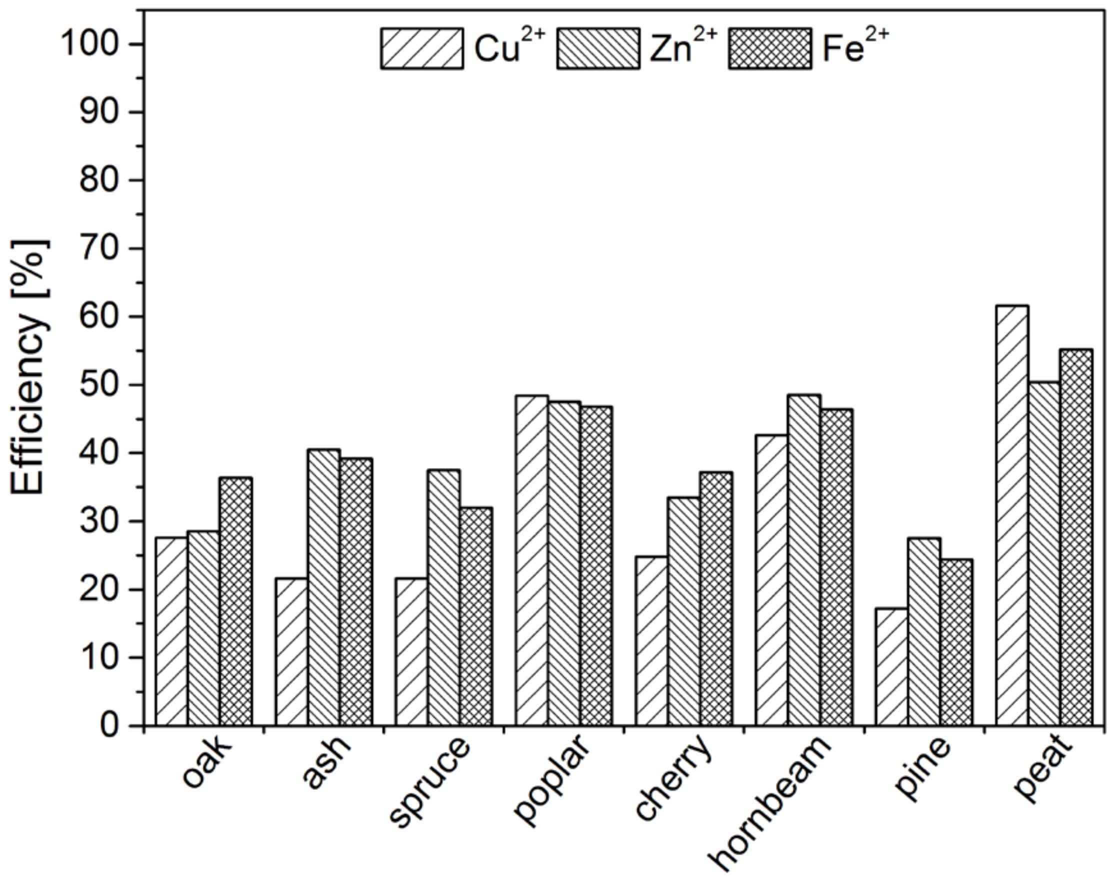

Table 2 Changes of pH values after sorption experiments (initial concentrations of ions 50 mg.L^{-1}).

cation	initial pH	oak	ash	spruce	poplar	cherry	hornbeam	pine	peat
Cu^{2+}	4.74	3.5	4.71	4.39	4.58	4.25	4.45	4.06	3.41
Zn^{2+}	5.10	4.07	4.85	4.75	4.97	4.89	5.01	4.68	3.76
Fe^{2+}	4.79	3.02	4.17	4.68	4.79	4.03	4.51	4.79	3.63

IV. CONCLUSION

Globally there is a tendency to develop simple, fast, cheap and effective natural materials for adsorption heavy metals. Nowadays have increasing tend using of natural material for removal pollutants from contaminated water. Peat and Sawdust, as a low-cost organic sorbent material, have been proven as a promising material for the removal of metals (Cu, Zn and Fe) from waste waters.

The function groups of sorbents were characterized by infrared spectra. For sawdust was confirmed the presence of hemicelluloses, cellulose and lignin (aromatic skeletal vibrations of lignin syringyl and guaiacyl condensed lignin). All kinds of wood sawdust exhibited the same behaviour. In case of pine wood sawdust was observed the α,β–unsaturated aldehydes, ketones with wavenumber at 1690 cm^{-1}. FTIR analysis of peat was confirmed presence of functional groups of aliphatic, phenolic salts of carboxylic acids esters, ethers phenols, and polysaccharides.

Wood sawdust has been shown as suitable product for removal metals from solutions. The best properties had poplar in solution with cations concentration of 10 mg.L^{-1} copper, zinc and iron and their removal exhibited efficiency about of 80.0 %. In case of five times higher metal cations concentration the best sorption properties had hornbeam and poplar.

Peat has comparable results of removal efficiency as poplar sawdust in case 10 mg.L^{-1} cation in solution. From solutions with concentration cation 50 $mg.L^{-1}$ a peat adsorbed more than 50 % cations from solutions.

Changes of values pH showed the processes of adsorbtion and ion exchange. In case removal Fe(II) by a oak sawdust (initial concentration 50 $mg.L^{-1}$) was decreased pH from 4.8 to 3.1, which was probably caused by an intensive ion exchange. Increased pH values were observed on zinc and iron removal by a hornbeam and poplar.

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