STUDY OF SORPTION PROPERTIES OF VARIOUS WOOD SAWDUST FOR SULPHATE REMOMAL

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Abstract

Sulphates are present in effluents of many industries, especially hydrometallurgy due to the widespread use of sulfuric acid in many processes and they are also the main anions in acid mine drainages that are product of sulphide oxidation. Sulphates are the contaminant with negative impact on water environment, therefore it should be removed from wastewater using an adequate process of treatment. Sulphates containing wastewaters or mine drainages are usually treated by a combination of operations including acidity neutralization, lime (or limestone) precipitation, reverse osmosis, electro-dialysis and adsorption. The selection of the treatment process of such effluents is a function of many factors such as chemical availability, local regulations and process economics. Recent research has shown that biosorption by low cost biomass can also be an effective alternative.

The paper deals with the sulphate removal from model solutions (initial concentration of sulphate ions 15 and 75 $mg.L^{-1}$, respectively) by the natural biosorbents – wood sawdusts. Hornbeam sawdust had over 99 % efficiency for sulphate removal from model solution with initial concentration 15 $mg.L^{-1}$.

Key words

Sulphate, wood sawdust, sorption

To cite this paper: *Demcak, S., Balintova, M., Pavlikova, P. (2016).* Study od sorption properties of various wood sawdust for sulphate remomal, *In conference proceedings of People, Buildings and Environment 2016, an international scientific conference, vol. 4, Luhačovice, Czech Republic, pp. 206-211, ISSN: 1805-6784.*

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1 INTRODUCTION

Industrial wastewaters can contain high concentrations of sulphate. There are various methods of sulphate removal e.g. reverse osmosis, ion exchange, precipitation by lime, cements, and salts of barium and the biological removal process [1]. The soluble salts of barium are most commonly used for precipitation of sulphate from aquatic acidic solutions to the insoluble product barium sulphate $BaSO_4$[2].

Sulphate is one of the least toxic anions with a lethal dose for humans of 45 g in form of potassium or zinc salt [3]. In such cases, it is questionable whether the toxicity is associated with the sulphate or the counter ion. For example, a minimum lethal dose of magnesium sulphate for human is 200 $mg.kg^{-1}$. People consuming drinking water containing sulphate in concentrations exceeding 600 $mg.L^{-1}$ (e.g. mineral and healing waters) commonly experience cathartic effects for problems with a stomach ache. Problem with long-term taking of sulphate is dehydration and has also been reported as a common side effect following the ingestion of large amounts of magnesium or sodium sulphate [4-7].

In the case of Slovakia the allowable concentration of sulphate in purified wastewaters is under 250 $mg.L^{-1}$ - Government Regulation No. 269/2010. Specific producer of sulphate in Slovakia wastewater is mine industry due to the content of heavy metals including sulphate. AMD is discharged into the river without treatment and have negative impact on aquatic environment [1, 8].

A perspective tends to removal of inorganic pollutants from wastewater shave use of a natural organic sorbents material as wooden sawdust, peat, bark, roots, rice husk, bone gelatin mass, hemp hurds or their modification [9]. 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 [10, 11].

The aim of this article was the study of sorption properties of various wood sawdust's (hornbeam, poplar, spruce, cherry, oak, pine, and ash) for a sulphate removal from model solutions with initial concentrations15 and 75 $mg.L^{-1}$, respectively. Hornbeam wood sawdust removed over 99 % sulphate from model solution with initial concentration 15 $mg.L^{-1}$.

2 MATERIAL AND METHODS

Model solutions containing sulphate anions were prepared by dissolution of sulphate salts ($CuSO_4.5H_2O$, $ZnSO_4.7H_2O$, $FeSO_4.7H_2O$) in deionised water. A Colorimeter DR890 (HACH LANGE, Germany) with appropriate reagent was used to determine concentration of dissolved sulphate.

For sorption poplar, hornbeam, ash, oak, cherry, pine, and spruce wood sawdust were used. For the purpose of wood sawdust efficiencies investigation, batch adsorption experiments were carried out. 1 g of each type of wood sawdust was mixed with 100 mL of model solutions containing 15 $mg.L^{-1}$ and 75 $mg.L^{-1}$ of sulphate anion, respectively. After 24 hours reaction time, wood sawdust was removed by filtration through a laboratory filter paper for qualitative analysis, residual concentrations of appropriate ions were determined by colorimetric method and pH change was also measured by pH meter inoLabph 730 (WTW, Germany). Also the % removal was calculated using the following equation (1):

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

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

3 RESULTS AND DISCUSSION

Concentration of sulphate in solution after sorption experiments was determined (Fig. 1). Hornbeam decreased the concentration of sulphate at the value less than 0.5 $mg.L^{-1}$ in solution of $CuSO_4$ and $ZnSO_4$, representing the efficiency of 99.0 %. In solutions of $FeSO_4$ the sulphate by ash and cherry was removed with high efficiencies.

Changes of pH values in solutions were observed after sorption too (Tab. 1). Due to different properties of Cu(II), Zn(II), and Fe(II) cations binding on sulphate and different sawdust materials, the adsorption took place in a slightly different pH range for different metals. Shukla et al. [12] 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, sulphate anions may be bonded by anion exchange mechanism. Sorption of heavy metal cations in solutions by a hornbeam and poplar increases of value pH. Possibility of ion exchange between dissolved metal cations in and H^+ from sawdust (spruce, ash, pine, cherry, oak) was indicated by decreasing of pH.

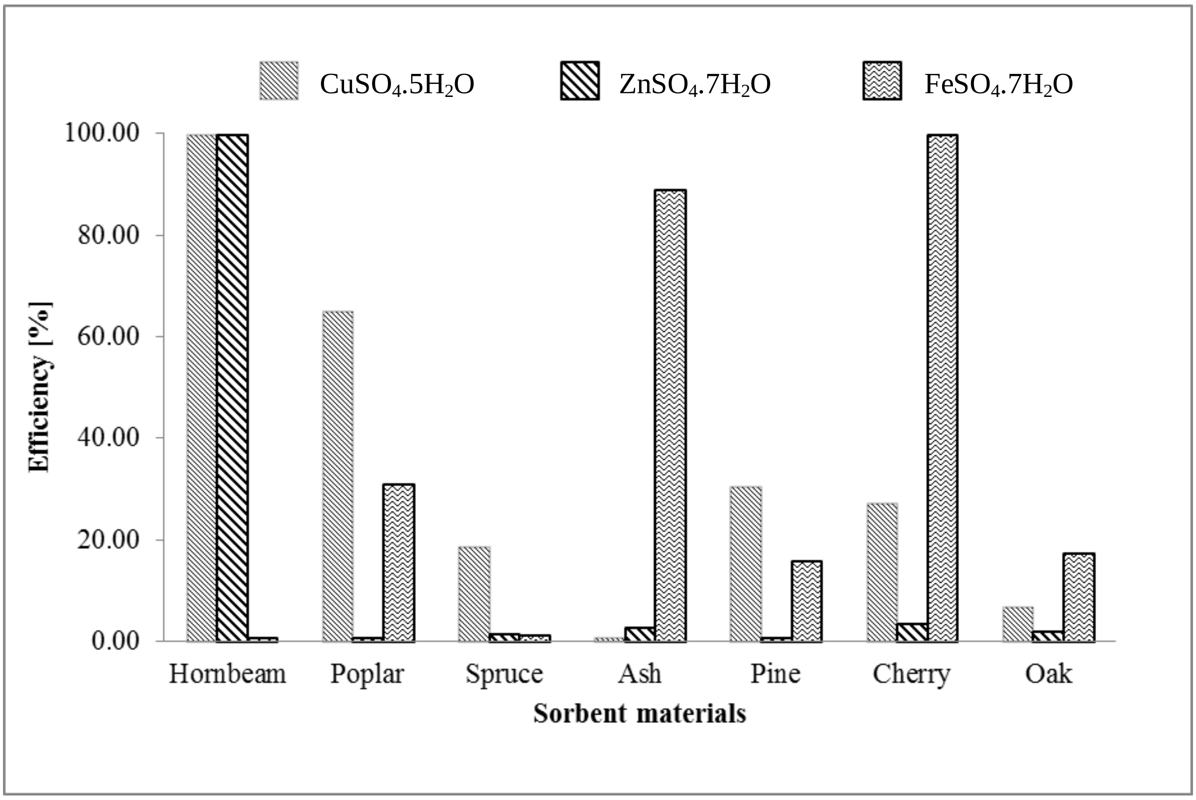

Fig. 1: Results of sorption experiments (initial concentrations of sulphate c_0=15 $mg.L^{-1}$)

Tab. 1: Changes of pH values after sorption experiments (initial concentrations of sulphate c_0=15 mg.L^{-1})

Model solution	Initial pH	Hornbeam	Poplar	Spruce	Ash	Pine	Cherry	Oak
$CuSO_4.5H_2O$	5.81	5.16	5.32	4.86	5.39	4.64	4.87	4.12
$ZnSO_4.7H_2O$	5.42	5.91	5.86	5.27	5.03	5.13	5.21	4.37
$FeSO_4.7H_2O$	5.43	5.48	5.67	5.03	5.75	4.79	4.96	3.74

This study was compared with determination of the efficiency of removal cations with five times higher concentrations. Figure 2 presents the efficiency of sulphate removal from these solutions. Surprisingly, the concentration of sulphates in these solutions remained practically unchanged. Only in case of $FeSO_4.7H_2O$ solution, Ash wood sawdust was removed sulphate with almost 20 % efficiency.

Also in this case changes of pH values in solutions were observed after sorption. Values of pH after sorption by sawdust, which are shown in Table 2, were decreased in all causes. We can suppose that oak sawdust from solution $FeSO_4.7H_2O$ shows intensive ion exchange with Fe^{2+} cations which is declared by a intensive decreasing at a pH= 3.0. More significant changes of pH were observed in sorption from solutions $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$ by oak sawdust too.

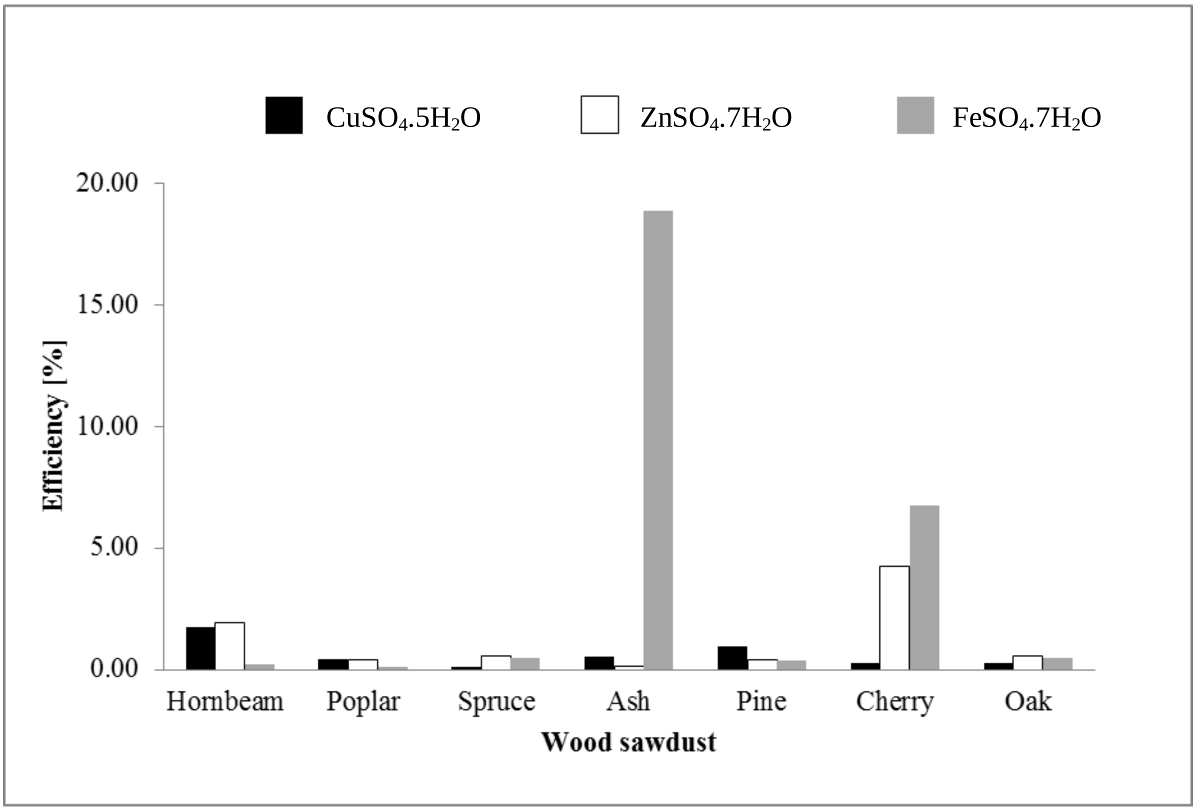

Fig. 2: Results of sorption experiments (initial concentrations of sulphate c_0=75 mg.L^{-1})

Tab. 2: Changes of pH values after sorption experiments (initial concentrations of sulphate c_0=75 mg.L^{-1})

Model solution	initial pH	Hornbeam	Poplar	Spruce	Ash	Pine	Cherry	Oak
$CuSO_4.5H_2O$	4.74	4.45	4.58	4.39	4.71	4.06	4.25	3.5
$ZnSO_4.7H_2O$	5.10	5.01	4.97	4.75	4.85	4.68	4.89	4.07
$FeSO_4.7H_2O$	4.79	4.51	4.79	4.68	4.17	4.79	4.03	3.02

4 CONCLUSIONS

The use of low cost natural sorbents as a replacement of industrial materials from solution is increasing in recent years. Natural materials or waste products from industry with a high capacity for sorption can be obtained, employed, and disposed of with a little cost. Sawdust, as a low-cost organic sorbent material, has been proven as a promising material for the removal of metals (Cu, Zn and Fe) from waste waters.

At lower concentrations of sulphate in zinc and copper solution hornbeam removed approximately 99.0 % of sulphates. The same efficiency had cherry at removal sulphate from iron solution.

Changes of values pH showed the processes of adsorption and ion exchange. In case of sulphate removal by oak sawdust (initial concentration 75 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 sulphate removal (initial concentration 75 mg.L^{-1}) by a hornbeam and poplar.

ACKNOWLEDGEMENT

This work has been supported by the Slovak Grant Agency for Science (Grant No. 1/0563/15).

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