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Section: Water Engineering

Removal of inorganic compounds from acidic solutions by sorption

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Abstract

Manufacturing processes, primarily mining activities, often result in the production of effluents containing high amounts of inorganic pollutants e.g. heavy metals or sulphates. This category includes also low value pH waters with high content of heavy metals, known as acid mine drainage (AMD). Low value of pH of these waters is a result of hydrogen cations release into aqueous environment during the process of pyrite oxidation. Together with heaps and ponds belongs to the negative effects of mining activities in the form of environmental burdens.

According to Directive 2000/60/EC of the European Parliament it is necessary to ensure adequate water quality and protection of all water sources. In Slovak Republic, as the country with long mining traditions, now exist a few localities with existing AMD generation conditions (either in form of direct outflow from mine or leachate from tailing ponds).

Finding of the new and cheap options for treatment of these waters can increase the quality of the environment in these localities and thus prevent adverse effects on fauna, flora or human beings. A cost effective methods also include sorption techniques. Their main positives are high efficiency, low cost and high degree of modifiability and regenerability of the used sorbents.

This paper is focused on the utilization of natural sorbent for heavy metals removal from model sulphuric acid solutions (pH approx. 4). The adsorption properties of non-modified peat has been studied in order to determine its applicability for copper and zinc removal in treatment process of acid mine drainage (AMD). For purpose of the determination of the removal efficiencies of metals the experiments were performed under batch conditions using single and dual-component solutions under acidic conditions. The objectives of this work were to evaluate the effects of different parameters such as initial ion concentration, pH change or amount of the used sorbent on the sorption efficiency as an input data for further research of acid mine drainage treatment.

Keywords: sorption; copper; zinc; peat; acidic solutions.

Nomenclature

C_0	initial metal ion concentration (mg/L)
C_e	equilibrium metal ion concentration (mg/L)
q	adsorption capacity per unit mass of adsorbent (mg/g)
V	volume of the aqueous phase (L)
m	mass of the adsorbent (g)

1. Introduction

Heavy metal ions such as copper, zinc, chromium, cadmium or lead can often be found in industrial waste water, and their discharge to the environment gives alarm impact to their acute toxicity to aquatic and terrestrial life, including humans. For example excessive intake of copper (over 1.0 mg.L-1 in drinking water) is accumulated in the livers of human and animals, which results in hemochromatosis and gastrointestinal catarrh diseases [1]. It is especially toxic to fish, which are often in the first contact with polluting media.

The potential sources of toxic metal ions are, essentially, the industrial waste streams of metal cleaning and plating baths, paperboard and wood preservative-employing mills, the fertilizer industry, mining activities, etc. [2], [3].

Current metals removal technologies are result of a need by industry to achieve acceptable effluent quality standards set by the local governments. These conventional and emerging treatment methods for metals removal include precipitation, secondary co-precipitation, evaporative recovery, ion exchange, membrane separation, reductive electrolysis, differential precipitation, etc. [4–6].

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In industrial treatment technologies, precipitation has found wide application for metals removal. The fact that precipitation can only reduce the dissolved metal concentration to the solubility product level, create the motivation for change away from these metal control technologies. Another problem is treatment of wastewaters containing low concentrations of heavy metals, what makes in this case applications of common methods for removing of heavy metals either technically complicated or economically unfavorable. Precisely such problems are creating a space for new and innovative methods for treatment of heavy metals contaminated wastewater.

Adsorption or ion-exchange onto low-cost particulate materials such as peat now offers an attractive, inexpensive option for the removal of colloidal and dissolved metals [7].

Peat is a polar, highly porous material that has significant applications as an adsorbent for removal of different pollutants from aqueous solutions. The formation of peat is due to incomplete degradation of organic matter. There are several types of peat. Their quality depends on the conditions affecting the degree of decomposition and also the type of peat-forming plant community. Generally, organic matter has a high metal adsorption capacity and the cation exchange capacity (CEC) of soil is positively correlated with the content of soil organic matter [8]. The amount of adsorption sites on the peat surface is pH dependent due to dissociation of hydrogen ions from carboxylic and phenolic groups on the peat surface [9], [10]. The exact mechanism of metal ion binding to peat is not well understood. Various mechanisms including ion exchange, complexation and surface adsorption have been proposed by researchers [11].

The paper presents a study of the uptake efficiency of Zn^{2+} and Cu^{2+} from single and dual-component synthetic acidic solutions (pH approx. 4). As an adsorbent a treated and non-modified natural peat under batch conditions was chosen. The adsorption properties of peat has been studied in order to determine its applicability for copper and zinc removal in treatment process of acid mine drainage (AMD). The objectives of the experiments were to evaluate the effects of different parameters such as initial ion concentration, pH change or amount of the used sorbent on the sorption efficiency.

2. Material and methods

2.1. Adsorbent

As a sorption material commercial non-modified peat “PEATSORB” (provided by REO AMOS; Slovakia) was used. In experiments was used finer heterogeneous fraction which was prepared by sieving through a 2 mm sieve. After sieving, the separated fraction of peat was dried at 105 °C for 24 h and then allowed to cool in the desiccators before using in experimental set-up.

2.2. Adsorbates

Synthetic solutions of Cu^{2+} and Zn^{2+} were prepared from analytical grade $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$ respectively. Working solutions were prepared by further dilution to the desired initial concentration of appropriate heavy metal. The initial pH of each solution was adjusted to the required value ($pH \approx 4$) using 0.001 M sulphuric acid. It should be noted that sulphate anions are not forming precipitates or complexes with copper and zinc cations at the test conditions and are considered to be inert.

2.3. Apparatus and instrumentation

Concentrations of metal ions before and after the experiments were determined by colorimetric method using Colorimeter DR890 (HACH LANGE, Germany) with combination of appropriate reagent. pH values were determined by pH meter inoLab ph 730 (WTW, Germany) which was standardized using buffer solutions of different pH values (4.01, 7.00).

2.4. Batch adsorption experiments

For the purpose of peat removal efficiencies investigation, batch adsorption experiments were carried out. Peat was mixed with 100 mL of single-component solutions containing 50 mg/L and 110 mg/L of copper and zinc cations, respectively. Effect of sorbent amount on removal efficiencies was also investigated; therefore dose of peat was modulated as follows: 1.0, 3.0 and 5.0 g per 100 mL of solution. After 24 hours reaction time, peat was removed by filtration through a laboratory filter paper for qualitative analysis, residual concentration of appropriate metal ion was determined by colorimetric method and pH change was also measured.

Acid mine drainage normally contains mixture of metal cations (e.g. Zn^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Fe^{3+}, Cr^{3+} etc). Another test was performed to investigate the influence of the presence of another cation on the adsorption capacity of peat. Dual – component solutions containing concentrations of 50 mg/L and 110 mg/L of both types of cations (Cu^{2+} and Zn^{2+}) were made and mixed with natural peat for 24 hours. Experiments were performed by adding of 1.0, 3.0 and 5.0 g of peat and mixed with 100 mL of solution containing upper listed concentrations of metals.

After 24 hours reaction time, the peat was removed by filtration through a laboratory filter paper for qualitative analysis, residual concentrations of metal ions were determined and pH change was also measured.

All batch experiments were carried out at room temperature (23±0.2°C) in beakers under static conditions. Average of two replications was reported for each adsorption process.

The copper and zinc adsorption capacities were calculated by the following equation:

$$q = \frac{(C_0 - C_e)}{m} \; x \, V \tag{1}$$

The percentage adsorption (%) was calculated using the following equation:

$$\% \, Adsorption \; = \frac{(C_0 - C_e)}{C_0} \; x \, 100\% \tag{2}$$

3. Results

3.1. Single-component solutions efficiencies

The effects of the adsorbent dose on the uptake of heavy metal ions are shown in Table 1 and 2. It was observed that increase of dosage resulted to increasing of the amount of the heavy metals uptake, because of increasing of adsorption sites amount. From the result is also obvious, that copper cations are better adsorbed than zinc.

When the initial concentrations of Cu (II) solution are changed from 50 mg/L to 110 mg/L (comparison between Table 1 and 2) the absolute amount of Cu (II) ions adsorbed per unit of the peat increases from 3.44 mg/g (70.02% removal) to 5.92 mg/g (54.61% removal) at 21 °C, pH 4 and adsorbent dose 1g/100 mL. However, the percent of adsorption decreases with increasing concentration of Cu (II). The same trend applies also to zinc adsorption.

Table 1. The removal efficiencies of copper and zinc after 24 h of contact with 100 mL single-component solutions; initial concentration 50 mg/L, initial pH ≈ 4

	Removal efficiencies [%] at different adsorbent dose		
	1.0 g	3.0 g	5.0 g
Cu^{2+}	70.02	80.35	84.58
Zn^{2+}	60.06	74.43	81.02

Table 2. The removal efficiencies of copper and zinc after 24 h of contact with 100 mL single-component solutions; initial concentration 110 mg/L, initial pH ≈ 4

	Removal efficiencies [%] at different adsorbent dose		
	1.0 g	3.0 g	5.0 g
Cu^{2+}	54.61	76.89	81.79
Zn^{2+}	46.17	59.11	75

3.2. pH change

pH is one of the most important parameters controlling uptake of heavy metals from aqueous solutions. In all experiments, the initial pH of copper and zinc containing solution was adjusted to the desired value using 0.001 M H_2SO_4. Peat was added to the copper and zinc solution with adjusted pH and without maintaining the mixture at constant pH by sulphuric acid was noted that at the end of 24 h experiment the pH of all the solutions was decreased, see Figs 1 and 2.

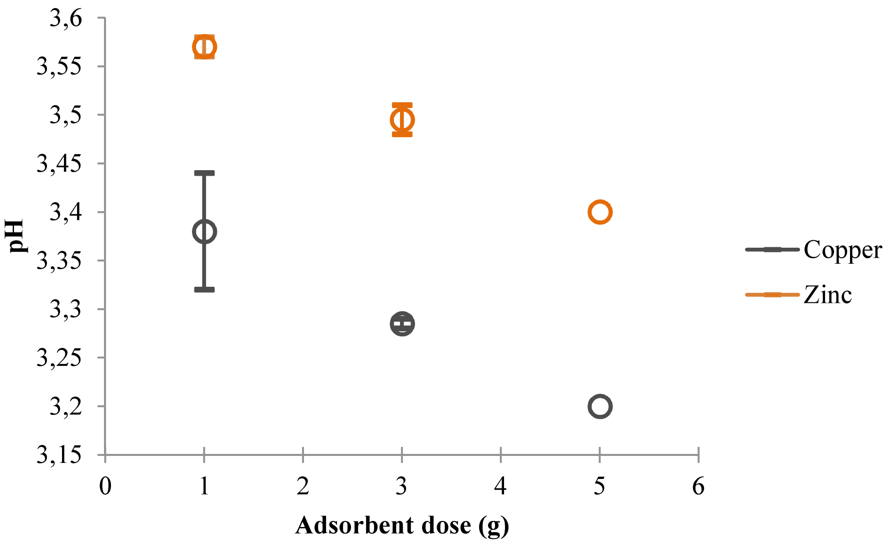


Fig. 1. pH values at the end of 24 h experiment at different adsorbent dose; single-component solutions, initial concentration 50 mg/L

This pH decreasing is due the mechanism of sorption process. According to data from literature ion-exchange is the most prevalent mechanism for heavy metal removal by peat. The humification of peat produces humic and fulvic acids. Metals react with the carboxylic and phenolic acid groups of the acids to release protons or, at sufficiently high pH, with their anion sites to displace an existing metal [12]. Studying nickel sorption Ho et al. observed that as the initial concentration of Ni increased, the equilibrium value of pH decreased [13]. This is accordance with the ion-exchange principles because as more nickel ions are adsorbed onto the peat, more hydrogen ions are released, thereby decreasing the pH.

Probably this phenomenon was observed also at the adsorption experiments of copper and zinc, as resulting from comparison between results in Figs 1 and 2, where stronger decreasing of equilibrium value of pH was caused by increasing of the initial concentration of metals. Therefore cations of copper and zinc can form complex compounds with surface functional groups of peat, such as aromatic carboxylates –COOH, and phenolic –OH through ion-exchange reactions, which lead to pH decreasing.

Another phenomenon that supports this theory is the adsorbent dose, whereas with increasing adsorbent dose decreases pH value.

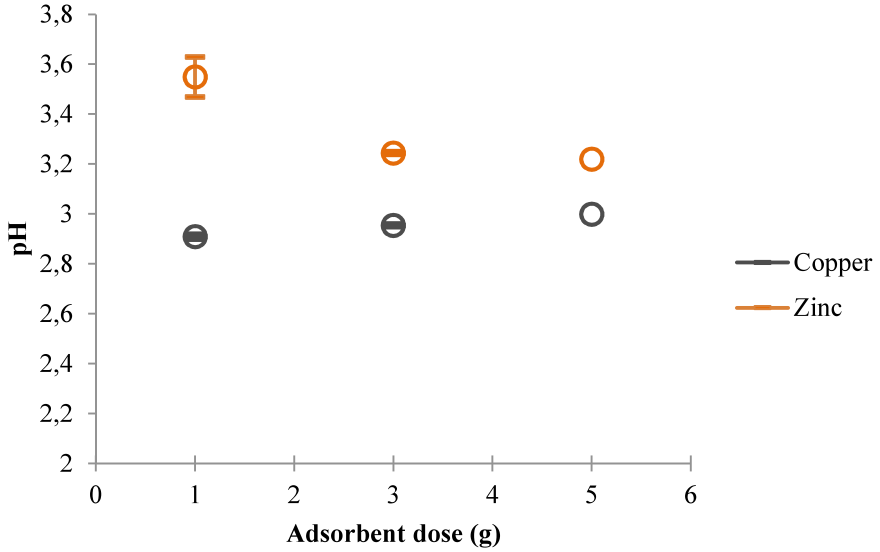


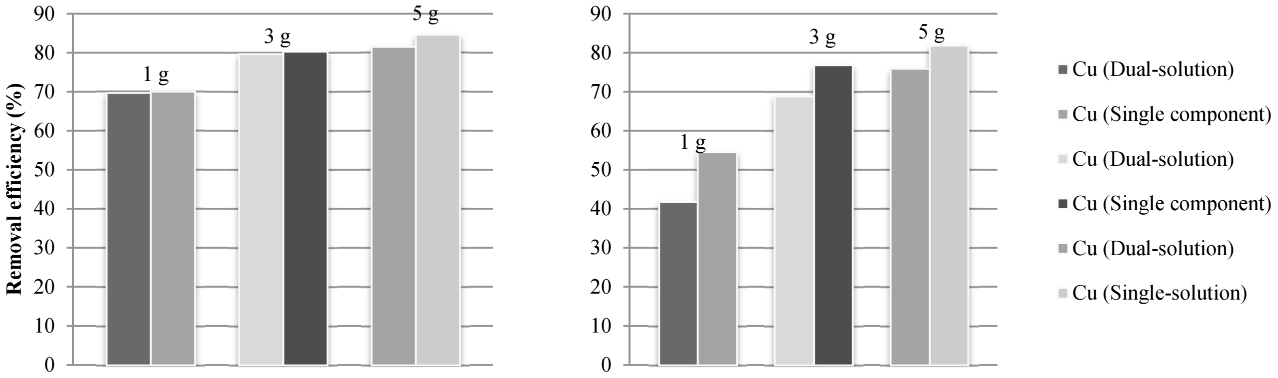
Fig. 2. pH values at the end of 24 h experiment at different adsorbent dose; single-component solutions, initial concentration 110 mg/L

3.3. Dual-component solutions efficiencies

However, in practice, AMD contains a mixture of different heavy metal ions and sulphates. Due to this fact experiments were also carried out with two sorts of cations in solutions, to investigate their influence on sorption. The results of the heavy metals adsorption from both single- and dual-component solutions are compared in Figs 3 and 4.

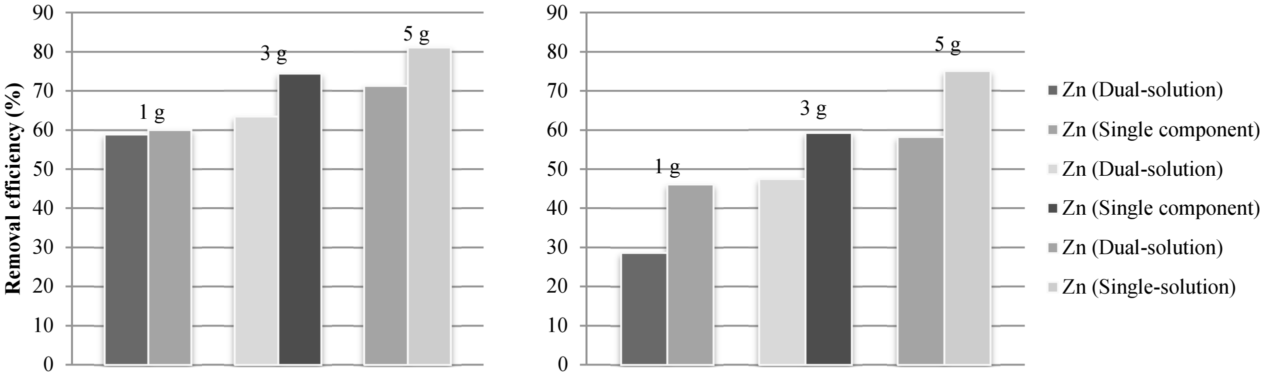
The differences between adsorption of single- and dual-component solutions with initial concentration of 50 mg/L are not significant. However, at solutions with initial concentration of 110 mg/L differences up to 18% were reached.

In all experiments the sorption efficiencies per unit mass of peat was higher for single-component solutions compared to dual-component solutions.



(a) (b)

Fig. 3. Comparison of the removal efficiencies of copper from single- and dual-component solutions / batching: 1.0 g, 3.0 g and 5.0 g peat/100 mL solution; pH 4.0; Initial concentration (a) 50 mg/L, (b) 110 mg/L /



(a) (b)

Fig. 4. Comparison of the removal efficiencies of zinc from single- and dual-component solutions / batching: 1.0 g, 3.0 g and 5.0 g peat/100 mL solution; pH 4.0; Initial concentration (a) 50 mg/L, (b) 110 mg/L /

4. Conclusions

The aim of this paper was investigate adsorption properties of peat for the purpose of copper and zinc removal from AMD.

In the first stage the experiments were focused on the study of adsorption efficiencies in single-component solutions. The metals removal from synthetic model solutions was about 85% and 81% of Cu^{2+} and Zn^{2+} respectively.

In dual-component solutions the sorption efficiencies are affected by mutual competition of adsorbed cations. The efficiencies of metals removal in dual-component solutions were decreased up to 20% and 14% for Zn(II) and Cu(II) respectively compared to their single component solutions. From the result is evident that copper cations are adsorbed better than zinc, which corresponds to all obtained results in this study.

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