Sorption in Acidic Environment – Biosorbents in Comparison with Commercial Adsorbents

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The remains of human activities may be seen in several places of the landscape in positive or negative form. Probably the most common phenomenon that fundamentally impacts the country is mining activity. The problems connected with these activities especially arise at the end of the mining, closure and abandonment of the mining area. The most serious negative impact represents acid mine drainage.

Acid mine drainage is a worldwide problem, leading to ecological destruction in river basins and the contamination of water sources by sulphuric acid and heavy metals, including arsenic, copper, zinc or lead. Once acid-generating rock is crushed and exposed to oxidizing conditions of the surface environment, is very difficult to reduce or stop acid generation, and can continue for tens or hundreds of years until the available sulphide minerals are exhausted.

In order to minimize negative impacts of acid mine drainage appropriate treatment process has to be chosen. With respect to the amount of compound in acid mine drainage is difficult to find effective and inexpensive solution. One of the possible ways of treatment seems to be a sorption. In recent years research is increasingly focused on this effective and cheap method that provides the quantity of application possibilities for removal of compounds from aqueous environment.

Acid mine drainage especially with its low pH value and high amount of different inorganic compounds represents very difficult system for each treatment process. For this reason it is necessary to use partial steps in sorption research to reach valuable knowledge leading to set up final treatment process in real conditions.

This study is focused on the utilization of biosorbents and commercial adsorbents for copper removal from model sulphuric acid solutions (pH 4). Sorption of copper from single-component aqueous system and also from acid mine drainage was investigated. For this purpose four types of sorbents were used (hemp shives, peat, zeolite and synthetic sorbent Slovakite). The objective of this work was to evaluate the differences between sorption efficiencies of biosorbents and commercial adsorbents.

1. Introduction

The discharge of inorganic pollutants into the environment is a serious problem affecting water and soil quality, hence presenting a direct danger to biosphere, plants but also to man-made materials as concrete (Harbulakova et al., 2009). Numerous anthropogenic sources of pollutants can contaminate the soil and water environment, including inputs from waste waters flowing from mines and waste storage, runoff of pesticides from agricultural land or atmospheric deposition (Angelovicova and Fazekasova, 2014). Especially, opencast mining activities have a serious environmental impact, having generated millions of tons of sulphide-rich tailings (Andras et al., 2012). Another most serious negative impact represents acid mine drainage (AMD), whether in the form of direct discharges or as leachate from landfills. Ions of copper Cu(II), which are most frequently present in the mining wastewaters, can result in hemochromatosis and gastrointestinal catarrh diseases (Gündogan et al., 2004).

The commonly used procedures for removing metal ions from effluents are result of a need by industry to achieve acceptable effluent quality standards set by the local governments and include chemical

precipitation, ion exchange, lime coagulation, reverse osmosis, membrane separation, solvent extraction, etc (Holub and Balintova, 2013). These techniques, apart from being economically expensive, have several disadvantages like incomplete metal removal at low concentrations, high energy requirements and generation of toxic sludge or other waste by-products that require further disposal or deposition (Pejic et al., 2009). From this reason efficient and environment friendly methods are needed to be developed in order to reduce heavy metals. A search for a low-cost and easily available adsorbent has led to the investigation of materials of agricultural and biological origin, along with industrial by-products, as potential metal sorbents (Bailey et al., 1999). As low-cost adsorbents rice bran, soybean and cottonseed hulls, sunflower stalks, oat and wheat straws, wheat shell, grape stalk waste, cactus leaves, pine needles, almond shell, olive cake, canola meal, pine bark, moss etc, have been investigated. The main constituents of lignocellulosic materials are cellulose, hemicelluloses, lignin and extractive matters (Sciban et al., 2008). The usage of biosorbents is an alternative to conventional methods and includes usage of dead biomass as well as living plants and also bacteria as sorbents. The present paper is focused on utilisation of the low cost adsorbents based on dead biomass (peat and hemp shives) to remove copper ions from model acidic solutions. Achieved results from biosorption are compared to the adsorption using commercial adsorbents (inorganic composite sorbent "SLOVAKITE") and natural zeolite. Presented are also results of the experiments with the real sample of AMD.

The removal efficiencies and the sorption capacities were determined. The studied parameters were copper ions concentrations, changes of the solution pH during the experiment and the impact of the sorbent modification.

2. Material and methods

2.1 Adsorbents

In this study four types of adsorbents were used. Natural zeolite (clinoptilolite) samples with primary potassium cation, empirical formula of $Ca_{1.8}K_{1.8}Na_{0.2}Mg_{0.24}Al6Si_{30}O_{72}.24H_2O$ from Slovakia, provided by ZEOCEM, a.s., SK. The samples of zeolite were used in their natural state ("as received") with no chemical modifications.

Natural zeolite with granularity over 2 mm was grinded by planetary mill (Desk – top planetary ball Miller SFM-1) at 290 rpm (tray rotating) and 580 rpm (grinding jars rotating) for 6 min. The particle size distribution of the samples was determined using screens and a sieve shaker. For the experiments fraction between 0.25 mm and 0.125 mm was chosen.

The second commercial material used in experiments was inorganic composite sorbent "SLOVAKITE" (provided by IPRES engineering; Slovakia). This commercial material, registered under Slovak patent no. 283214, uses a synergic effect of combination of natural sorption abilities of different types of materials (e.g. dolomite, tuffs, claystone, kaolin, sandstone, gypsum etc.).

As a biosorption materials non-modified peat "PEATSORB" (provided by REO AMOS; Slovakia) and hemp shives (provided by Hempflax; Netherlands) were used. In experiments finer heterogeneous fraction of peat prepared by sieving through a 2 mm sieve was used.

The final fibre length of used technical hemp shives ranged between 4 mm and 0.063 mm. Hemp shives were used in their natural state and also modified. Hemp fibres were modified by chemical treatment in order to gradually remove either hemicelluloses or lignin. The progressive removal of the hemicelluloses and keeping the lignin content unchanged was brought by treating the fiber samples with 1.6 M NaOH solution, at room temperature, for 48 h, followed by neutralisation with 1 % acetic acid. Fibres were then washed with deionised water until the pH value was 7.

All the adsorbents were dried at 105 °C for 2 h and then allowed to cool in the desiccators before using in experimental set-up.

2.2 Adsorbates

Synthetic solution of Cu(II) was prepared from analytical grade $CuSO_4.5H_2O$. Working solutions were prepared by further dilution to the desired initial concentration. The initial pH of each solution was adjusted to the required value (pH≈4) using 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.

Samples of acid mine drainage from Smolnik mine were also used. The initial concentrations of dissolved heavy metals are presented in Table 1.

2.3 Apparatus and instrumentation

Concentrations of metal ions before and after the experiments were determined by colorimetric method using

Table 1: Chemical composition of AMD

Raw AMD	pH	Fe$_{total}$	Cu	Al	Mn	Zn
mg/L	3.99	260	1.7	50	23	7.9

Table 2: SSA of adsorbents

	Zeolite	Slovakite	Peat	Non – modified hemp	Treated hemp (NaOH)
SSA (m^2/g)	27.15	65.28	0.86	0.99	0.93

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).
Specific surface area was estimated by low temperature gas adsorption using nitrogen gas (Quantachrome NOVA 1000e, USA) and subsequent application of Brunauer – Emmett – Teller isotherm.

2.4 Removal efficiencies in single – component model solutions
For the purpose of removal efficiencies investigation, batch adsorption experiments were carried out. Each type of sorbent was mixed with 100 mL of single-component solutions containing 50 mg/L and 110 mg/L of copper cations. Batch experiments were carried out at room temperature (23±0.2°C) in beakers by adding of a constant mass of sorbent (1.0 g) in 100 mL of single – metal solution. After 24 hours reaction time, sorbents were removed by filtration through a laboratory filter paper for qualitative analysis, residual concentration of copper was determined by colorimetric method and pH change was also measured.

2.5 Treatment of AMD
The objective of this study was to treat AMD from Smolnik mine and investigate the differences in sorbents behaviour caused by real sample of AMD with comparison of synthetic samples. Thus real sample containing a mixture of heavy metals (concentrations listed upper in section 2.2.) was used to sorption experiments.
Before the sorption experiments AMD was pretreated due to high concentration of iron cations. Concentration of these cations is several times higher than the others and could distort the sorption. For this reason iron cations were removed by oxidation using 31% H_2O_2 and subsequent precipitation with 0.1 M NaOH.
100 mL of pretreated AMD was contacted with 1.0 g of each sorbent for 24 h. After the desired contact period the mixture was filtered and the filtrate was analysed using the colorimetric method. During the whole experiment pH was controlled to prevent the precipitation of others metals. The 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 and discussion

3.1 Specific surface area
One of the many properties used to characterize adsorbents is the specific surface area (SSA). SSA plays important role in adsorption process; however there are other mechanisms that can influence the progress of adsorption especially in the case of biosorption (e.g. ion-exchange abilities, complexation, chelation, ion entrapment in inter- and intrafibrillar capillaries and spaces of structural lignin and polysaccharide networks etc.). In order to evaluate the link between SSA and removal efficiencies estimation of SSA by physisorption of N_2 at 77 K according to the BET method was carried out. Degassing of all samples was carried out with respect of their thermal stability determined by thermal analyzer (Netzsch STA 449 F3, Germany). The results are presented in Table 2.

3.2 Single – component solution efficiencies
Results of sorption experiments in single – component solutions containing copper cations are presented in Tables 3 and 4. The best sorption properties shows Slovakite relative to its precipitation abilities due to the increasing pH values (see Tables 5 and 6). From biosorbents, the sodium hydroxide modified hemp demonstrated the best sorption properties.

Data obtained from experiments in this study indicated that modification with sodium hydroxide (i.e. removal of hemicelluloses) resulted in improvement of biosorption capacities compared to non-modified samples. This can be explained by the domination of sorption at outer surfaces of fibers and increased the roughness of hemp fiber surfaces and induced new capillary spaces in inter-surfacial layer between completely or partially separated fibers due to the removal of lignin and hemicelluloses (Pejic et. al, 2009). When the initial concentrations of aqueous $CuSO_4.5H_2O$ solution are changed from 50 mg/L to 110 mg/L (comparison between Table 3 and 4) the absolute amount of Cu(II) ions adsorbed per unit of adsorbent increases. For instance, changing the initial concentration from 50 to 110 mg/L, caused an increase of the amount of Cu(II) ions sorbed by treated hemp from 4.45 to 8.21 mg/g. However, the percent of adsorption decreases with increasing concentration (see Figure 1).

Comparison in removal efficiencies depending on the initial concentration are depicted in Figure 1.

3.3 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 containing solution was adjusted to the desired value using 0.001 M H_2SO_4. According to the literature (Balintova and Petrilakova, 2011), Cu is precipitated at pH 4.5 – 6.0 thus this fact must be included in the evaluation process. The final pH values after adsorption process are presented in Tables 5 and 6.

As can be seen, almost each adsorbent caused increasing in pH values. According to the manufacturer, the principal characteristic of Slovakite is its ability to act as buffer at the interface of the solid – liquid phase and increase pH value. In this case, the main mechanism of heavy metals removal is precipitation (due to increased pH) in the form of hydroxy-salts, hydrated oxides or hydroxides. The products of precipitation are subsequent fixed on the porous and extensive surface.

Natural zeolite preferentially adsorbs hydrogen cations from solution to heavy metal ions (Inglezakis et al., 2003), and thus in more acidic conditions more H^+ ions are adsorbed from solution. Natural zeolites are

Table 3: The final concentration of copper after 24 h of contact with sorbent; single-component solutions; initial concentration 50 mg/L, initial pH≈4; batching 1g/100 mL

Adsorbent	Final concentration (mg/L)	Adsorption capacity (mg/g)
Zeolite	11.28	3.87
Slovakite	0.15	4.99
Peat	13.75	3.63
Non – modified hemp	10.9	3.91
Treated hemp (NaOH)	5.55	4.45

Table 4: The final concentration of copper after 24 h of contact with sorbent; single-component solutions; initial concentration 110 mg/L, initial pH≈4; batching 1g/100 mL

Adsorbent	Final concentration (mg/L)	Adsorption capacity (mg/g)
Zeolite	53.8	5.62
Slovakite	13.4	9.66
Peat	47.8	6.22
Non – modified hemp	29.0	8.10
Treated hemp (NaOH)	27.9	8.21

Table 5: pH values at the end of 24 h exposures; single-component solutions, initial concentration 50 mg/L

	Zeolite	Slovakite	Peat	Non – modified hemp	Treated hemp (NaOH)
pH	5.47	7.1	3.32	5.99	5.47

Table 6: pH values at the end of 24 h exposures; single-component solutions, initial concentration 110 mg/L

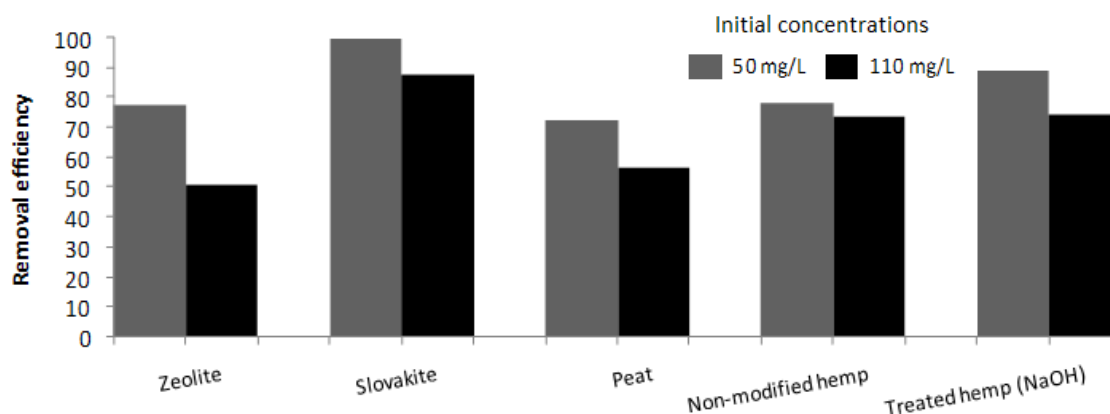|	Zeolite	Slovakite	Peat	Non – modified hemp	Treated hemp (NaOH)
pH	5.38	6.85	3.08	5.24	4.95

Figure 1: Removal efficiencies of the adsorbents; initial concentrations 50 and 110 mg/L; initial pH≈4; batching 1g/100 mL

generally weakly acidic in nature and sodium-form exchangers are selective for hydrogen (R–Na + H_2O ↔ RH + Na^+ + OH^-), which leads to high pH values when the exchanger is equilibrated with relatively dilute electrolyte solutions (Erdem et al., 2004) making metal hydroxide precipitation feasible. From this reason as reaction proceeds the solution pH increases. This pH increase can lead to precipitation, thus removal of heavy metal ions from solution not has to be only due to ion exchange.

On the contrary, peat caused decrease in pH value. This decreasing is due the mechanisms of sorption process, because it is commonly believed that ion-exchange is the most prevalent mechanism. 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 (Gossett et al., 1986). Studying nickel, Ho et al. (1995) noted that as the initial concentration increased, the equilibrium pH decreased. This is consistent with the principles of ion-exchange since as more nickel ions are adsorbed onto the peat, more hydrogen ions are released, thereby decreasing the pH. This theory was confirmed by comparison of results obtained from experiments with the different concentrations of Cu(II), where with increasing initial concentration (from 50 mg/L to 110 mg/L) decreases pH value.

3.4 Removal of copper from AMD

To investigate the differences in adsorbents behaviour in the real environment, real sample of AMD was contacted with each type of adsorbent for 24 h.

Table 7 summarizes the result of copper removal from real sample of AMD. Input data, results after iron oxidation and precipitation and results after sorption experiments using 1.0 g of adsorbent per 100 mL solution of AMD are presented.

As can be seen from the results in comparison with synthetic samples, there are little differences (e.g. for Zeolite sorption) that can be explained by total composition of AMD, where other metals affect the sorption (e.g. aluminium cations).

Slovakite shows the best sorption properties overall and from biosorbents, the sodium hydroxide modified hemp. Peat and non – modified hemp shives are on the same level with 64 % removal efficiency.

4. Conclusions

This study showed the differences in removal efficiencies of the selected commercial sorbents and biosorbents for copper removal from model acidic solutions and AMD. The best sorption properties shows commercial inorganic sorbent Slovakite – decrease of Cu concentration is up to 99.7 %. In the range of higher concentrations is efficiency a little bit lower, but also sufficient. Another positive fact is that the Slovakite during experiments is favourable to the pH of the solutions, and moves it towards the neutral value. It was confirmed the positive influence of NaOH modification of hemp shives on Cu removal efficiency. Presented results affirmed suitability of biosorbents using for copper removal from acidic environment.

Table 7: Results of sorption experiments on the real sample of AMD from Smolnik mine; batching 1g/100 mL

	Concentration of metal (mg/L)		pH
	Fe_{total}	Cu(II)	
Input data	260	1.7	3.99
After iron oxidation and precipitation	0.62	1.66	3.80
After zeolite sorption	-	1.44	4.10
After Slovakite sorption	-	0.07	6.74
After peat sorption	-	0.60	3.09
After non-modified hemp sorption	-	0.62	4.28
After treated hemp sorption	-	0.40	3.94

Acknowledgements

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