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Study of Inorganic Pollutants Removal from Acid Mine Drainage by Hemp Hurds

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Abstract

Sulphates in wastewaters have an origin as the by-products of a variety of industrial operations. A specific and major producer of such effluents, which contained sulphates and heavy metals, is the mining industry. These contaminants should be removed from wastewater using an adequate process of treatment.

The paper deals with selected heavy metals (iron, cooper, and manganese) and sulphate removal from acid mine drainage outflowing from an abandoned mine in Smolnik (Slovakia) using the modified biosorbent - Holland hemp hurds. Pre-treatment of acid mine drainage was based on oxidation of ferrous cations from acid mine drainage by hydrogen peroxide and subsequent precipitation. The precipitate were analysed by infrared spectrometry which found the precipitate containing hydroxide and sulphate functional groups. During this process the concentration of sulphate decreased by 43.8 %. Hemp hurds modified by NaOH decreased concentration of Cu^{2+} in solution by about 70 %

Key words: sorption, precipitation, acid mine drainage, hemp hurds

1 Introduction

Acid mine drainage (AMD) causes environmental pollution that affects many countries with a historic tradition of mining, where AMD are formed after terminating mining activity, or in current mining industries [1]. It causes surface water pollution, which may impact aquatic life as well as the whole ecosystem [2]. Preventing the formation or the migration of AMD from its source is generally considered to be the preferable option but this solution is not feasible in many locations, and in such cases, it is necessary to collect, treat, and discharge mine water. There are various options available for remediating AMD, which may be divided into those that use either physic-chemical or biological mechanisms to neutralize water and remove inorganic pollutants from AMD [3].
The outflowing of mining water can contain high concentrations of sulphate. There are various methods of sulphate removal e.g. reverse osmosis, ion exchange, precipitation of

lime, cements, and salts of barium and the biological removal process [3]. The soluble salts of barium are most commonly used for precipitation of sulphate from aquatic acidic solutions to the insoluble product barium sulphate $BaSO_4$ [4].
AMD also contains various heavy metals. Use of natural organic sorbents material such as wood sawdust and hemp hurds can facilitate the removal of heavy metals and trace elements from wastewaters [5]. This is due to the presence of organic compounds bearing polar functional groups (e.g. alcohols, aldehydes, carboxylic acids, ketones, and phenolic hydroxides) which have the properties of natural organic sorbents with high sorption capacity [6]. 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. The use of waste products like wood sawdust and hemp hurds for adsorption experiments have been investigated as a replacement of current costly methods [7, 8]. Sawdust is mainly a 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 [6, 9].
The paper deals with the study of hemp hurds sorption properties for sulphate, copper and manganese removal from mine water in Smolnik. High concentrations of heavy metals, mainly iron in this mine water, have a negative impact on sorption process. This element was removed from AMD by oxidation with hydrogen peroxide. For the sorption experiment HOLLAND hemp hurds was used and its three modifications (EDTA, NaOH and $Ca(OH)_2$).

2 Material and Methods

2.1 Characterization of locality

Smolnik is historically one of the best-known and richest Cu – Fe ore deposits in Slovakia (Figure 1). Mining was primarily focused on the extraction of copper ore. Lack of interest in pyrite and copper ores led to the closure of the mine at Smolnik. The mine was flooded from 1990 until 1994, which caused a local environmental catastrophe in Smolnik Creek. The primary problem is the direct discharge of AMD into the Smolnik creek without pre-treatment [10, 11].

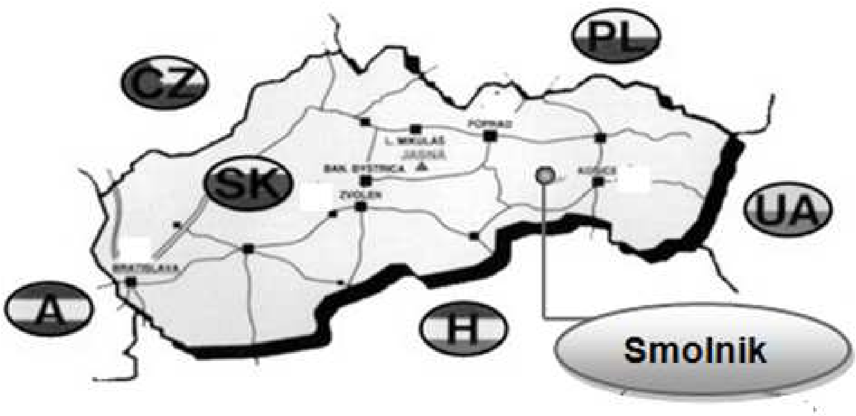

Figure 1: Location of interested area – Smolnik Creek [2]

2.2 Characterization and pre-treatment of AMD samples

The sample for the experiment was collected from an abandoned subsurface mine Smolnik (Slovakia), from the PECH shaft. The presence of iron, sulphates and other elements, mainly heavy metals, in AMD are changing in concentration over time. Samples from these waters are unstable, therefore a sample was frozen for the experiments. Input concentrations and value of pH are listed in Table 1.

Table 1: Properties of real sample of AMD

Concentrations of chosen parameters in AMD [mg.L^{-1}] (input pH = 4.0)						
Na	Ca	Mg	Cu	Mn	Fe	$(SO_4)^{2-}$
5.0	125.0	139.0	1.66	22.0	270.0	3 200

From the heavy metals, ferrous ions were dominant in the composition of AMD. For iron removal from AMD sample oxidation by H_2O_2 was used (Eq. 1). Iron was subsequently precipitated with a 0.1 M NaOH and approximate pH value of 4 [3]. Oxidation of ferrous ions to ferric ions is based on natural conditions (Eq. 2). It is due to the oxidation of ferrous ions to ferric ions.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- \tag{1}$$

$$Fe^{2+} + O_2 + 4H^+ \rightarrow Fe^{3+} + 2H_2O \tag{2}$$

Precipitate was filtered concentrations of Cu, Mn, Fe cations and sulphate anion were determined in the filtrate. Also the efficiency η was calculated using the following equation 3:

$$\eta = \frac{(c_0 - c_e)}{c_0} \times 100\%, \tag{3}$$

where c_0 is the initial concentration of appropriate ions (mg.L^{-1}), c_e is equilibrium concentration of ions (mg.L^{-1}). Precipitate was also tested by FTIR method.

2.3 Sorption experiment with Holland hemp hurds

For sorption experiments the pre-treated AMD were used. Holland hemp hurds from (the Netherlands Company Hempflax) [12] and its three modifications were used (Holland EDTA – modified by Ethylenediaminetetraacetic acid; Holland $Ca(OH)_2$ – modified by calcium hydroxide; Holland NaOH – modified by sodium hydroxide). Modified samples were prepared according to authors [13]. Original hemp hurds slices have a particle size distribution of 0.063 - 8 mm. For sorption, the particle size under the fraction 2 mm was used. For the purpose of sulphate, copper and manganese removal efficiencies, batch adsorption experiments were carried out. 1.0 g of each type of Holland hemp hurds was mixed with 100 mL of pre-treated solution [14]. After 24 hours reaction time, hemp hurds were removed by filtration through laboratory filter paper for qualitative analysis and residual concentrations of appropriate ions were determined by colorimetric method and pH change was also measured. Efficiency of hemp hurds sorption was also calculated.

2.4 Apparatus and instrumentation

For pH values determination pH meter inoLabph 730 (WTW, Germany) was used, colorimeter DR890 (HACH LANGE, Germany) with appropriate reagents was used to the determination of dissolved Cu, Mn, Fe and $(SO_4)^{2-}$ concentration.
IR spectrum was measured by Alpha FT-IR Spectrometer with ALPHA‘s Platinum ATR single reflection diamond ATR module (Bruker, Germany).

3 Results and discussion

Pre-treatment of AMD was based on research of water after its outflow from mine into oxidising conditions in the presence of air. It was determined that Fe^{3+} ions form iron (III) hydroxy sulphate in presence of sulphuric acid in water environment according to reaction (Eq’s. 1 and 2).
The infrared spectra of precipitates after oxidation by H_2O_2 shown in Figure 2 confirmed the presence of sulphate, but the bands of crystal-bound water and hydroxides is identified too. The IR spectrum includes a broad, water and OH-stretching band centred over an area of 3 300 – 3 200 cm^{-1}. Another prominent absorption feature is expressed at approx. 1 633 cm^{-1}, related to crystal-bound water in precipitate. Wavenumbers at 1 118 and 1 054 cm^{-1} reflect a strong splitting of the wavenumber ν3 (SO_4) fundamental due to the formation of a bidentate bridging complex between SO_4 and Fe [3]. This complex may result from the formation of compound containing crystal bound water, ferric ions, hydroxyl and sulphate anions. Related features due to the presence of structural SO_4 include a band at 595 cm^{-1} that can be assigned to ν4 (SO_4).

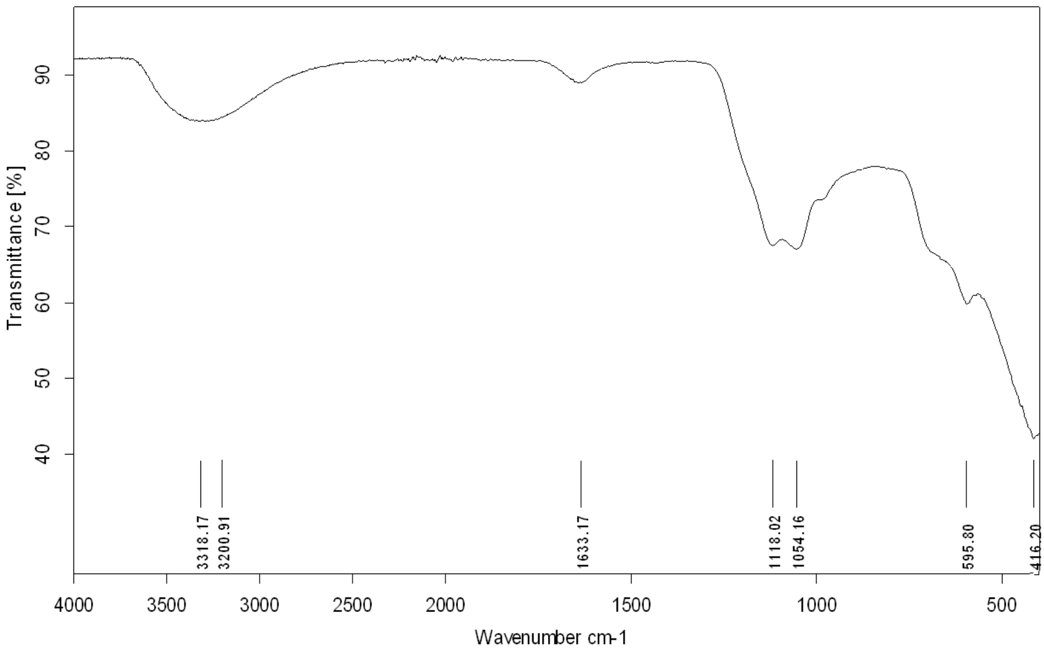

Figure 2: Infrared spectra of precipitate after iron oxidation

This natural process was simulated in laboratory conditions. The primary objective was the removing of iron cations from AMD due to their high concentration and possibility of further experiments disruption. However, as it was already mentioned, iron cations form insoluble precipitate consisting of ferric ions and sulphate anions. For this reason part of the sulphate equivalent was also removed from the amount of iron cations. The removal efficiency for iron was 99.99 %, sulphate 43.8 % and concentrations of Cu and Mn were not changed (Table 2.)

Table 2: Properties of real sample of AMD (input values and values after iron precipitation)

	Concentrations [mg.L^{-1}]			
	$(SO_4)^{2-}$	**Fe**	**Cu**	**Mn**
Input data (pH=4.0)	3,200	270	1.31	22.0
After iron oxidation and precipitation (pH=3.8)	1,800	0.03	1.31	22.0

Table 3 shows the decrease of concentrations in pre-treated AMD using hemp hurds. Sorption properties of hemp hurds and its three modifications were effective for removal of Cu cation. The sorbent Holland NaOH was the most efficient (approximately 70 %). The removal of manganese was less efficient than the removal of copper (c < 16 %) in case Holland EDTA modification and sulphate removal was about of 8.3 %. The pH values remained approximately the same.

Table 3: Concentrations of ions and pH change after sorption

Sorbents	**Cu**		**Mn**		**$(SO_4)^{2-}$**		**pH**
	c_e	**η**	**c_e**	**η**	**c_e**	**η**	
	[mg/l]	**[%]**	**[mg/l]**	**[%]**	**[mg/l]**	**[%]**	
Holland reference sample	0.6	54.2	19.2	12.7	1 650	8.3	4.3
Holland EDTA	1.1	16.0	19.2	12.7	1 775	1.4	4.1
Holland $Ca(OH)_2$	0.5	61.8	20.3	7.7	1 775	1.4	4.3
Holland NaOH	0.4	69.5	18.6	15.5	1 750	2.8	4.0

4 Conclusion

Removal of pollutants from AMD is an actual problem and the most used methods are economically and technologically difficult. Using the sorption potential of various materials is one of the modern, cheap and effective technologies. However, the sorption of contaminants from AMD depends on more factors such as the concentration of sulphate, heavy metals and the value of pH.

This study showed the sorption potential of hemp hurds and its three modifications for pollutant removal from AMD. The most effective sorbent was NaOH modified Holland hemp hurds with an efficiency of Cu^{2+} removal 69.5 %. The sorption is not a typical remediation method for sulphate removal and experiments with pre-treated AMD were not successful and the concentration remained on approximately the same as input values. Partially decreasing of the concentration of sulphate anions (45.45 %) was obtained together with iron precipitation via oxidation of Fe^{2+} to Fe^{3+} during the pre-treatment of AMD.

Acknowledgements

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