Proposal and Testing of Multi-Step Process for Acid Mine Drainage Treatment

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Abstract

The mining represents one the most common human activities that fundamentally impact not only the country itself but also have adverse effects on the fauna, flora and human beings. The negative impacts also include acid mine drainage which is formed by the dissolution of products resulting from the oxidation (chemically and microbiologically mediated) of sulphide minerals, mainly pyrite or iron disulphide. According to stringent European Union effluent discharge regulations it is necessary to look into innovative technologies to remove considerable amount of effluent rather than discharging into surface water.

Resulting from previous partial achievements, the article is focused on the combination of chemical precipitation, ion exchange and biosorption techniques for the acid mine drainage treatment. Concentrations of four different metal cations (copper, iron, manganese, aluminium) and sulphates were observed. First stage of treatment included chemical precipitation by combination of oxidation using 31% hydrogen peroxide and subsequent precipitation with 0.1 M sodium hydroxide. After the first stage, the ion exchange using two different exchangers (PUROLITE MB400 resin and AMBERLITE MB20 resin) took place. The last stage of the experiments was focused of the biosorption study. Low – cost sorbents included in this case natural non – modified peat "PEAT-SORB" and hemp shives in modified state. Overall, the best results were observed after combination of MB20 resin in the second stage and subsequent using of modified hemp shives in the third stage of the treatment.

Keywords: sorption, precipitation, ion-exchange, heavy metals, sulphates, acid mine drainage

Introduction

Manufacturing processes, primarily mining activities, often result in the production of effluents containing high amounts of inorganic pollutants e.g. heavy metals or sulphates.

The problems connected with the extraction of sulphide ores are present throughout the whole process of mining, but arise especially during the last stage of mining, closure and abandonment of the extraction area, when the conditions for the generation of strong acid water are most likely to occur [1].

This generation consists from weathering of sulphide minerals under oxidation conditions (in contact with water, atmospheric oxygen, micro minerals and aerobic bacteria) and effluents are characterized with very low pH value of about 2 and limit concentrations of heavy metals (Cu, Zn, Cd, As, Mn, Al, Pb, Ni, Ag, Hg, Cr and Fe), toxic elements and sulphates [2–4]. Importantly, once acid mine drainage (AMD) has formed, it can remain for hundreds of years, and it is generally difficult and costly to control [5].

Currently used technologies for removal of inorganic compounds are result of a need by industry to achieve acceptable effluent quality standards set by the governments. These conventional and emerging treatment methods include precipitation, secondary co-precipitation, differential precipitation, ion exchange, membrane separation, evaporative recovery, reductive electrolysis, etc [6–9].

Precipitation has found its wide application for metals removal, particularly in industrial treatment technologies. 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 limitation can be found in treatment of wastewaters containing low concentrations of elements, what makes in this case applications of common methods for removing of heavy metals either technically complicated or economically unfavourable. Precisely such problems are creating a space for new and innovative methods for treatment of heavy metals and sulphates contaminated wastewater. It is also possible to combine different treatment techniques in order to apply the positive properties of each method.

Adsorption or ion-exchange onto low-cost particulate materials such as biosorbents now offers an attractive, inexpensive option for the removal of colloidal and dissolved metals [10].

Ion exchange represents a very powerful technology for removal of toxic elements from water and other solutions. Undesirable ions are replaced by others which do not contribute to contamination of the environment. The method is technologically simple and en-

Tab. 1. Properties of experimental AMD samples (input concentration)
Tab. 1. Właściwości badanych próbek kwaśnego drenażu kopalnianego

	pH	Fe$_{total}$	Cu	Al	Mn	SO$_4$
mg/L	3.52	305	0.86	44.8	24.4	2400

Tab. 2. Concentrations of heavy metals and sulphates after precipitation
Tab. 2. Zawartość metali ciężkich i siarczanów po strąceniu

	pH	Fe$_{total}$	Cu	Al	Mn	SO$_4$
mg/L	3.66	0.71	0.79	42.2	20.4	1820
Efficiency [%]	-	99.8	8.1	5.6	16.4	25.1

Tab. 3. Concentrations of heavy metals and sulphates after ion exchange by PUROLITE MB400
Tab. 3. Zawartość metali ciężkich i siarczanów po wymianie jonowej z użyciem PUROLITE MB400

	pH	Fe$_{total}$	Cu	Al	Mn	SO$_4$
mg/L	2.52	0.63	0.39	12.1	8.8	1200
Efficiency [%]	-	11.3	50.6	71.3	56.9	33.8

Tab. 4. Concentrations of heavy metals and sulphates after ion exchange by AMBERLITE MB20
Tab. 4. Zawartość metali ciężkich i siarczanów po wymianie jonowej z użyciem AMBELITE MB20

	pH	Fe$_{total}$	Cu	Al	Mn	SO$_4$
mg/L	2.60	0.69	0.39	11.3	8.2	1150
Efficiency [%]	-	2.8	50.6	73.2	59.8	36.6

ables efficient removal of even traces of pollutants from solutions [11].

The present paper is focused on the study of the chemical and physical methods combination for the heavy metals and sulphates removal from acid mine drainage out-flowing from the Pech shaft located on the deposit Smolník in the Slovak Republic. The treatment process includes oxidation and chemical precipitation in the first stage, followed by ion exchange using two different resins. Last stage is focused on the biosorption processes with the dead biomass (peat and modified hemp shives).

Material and methods

As mentioned above, the treatment process consists of three stages. Overall, concentrations of four different metal cations (copper, iron, manganese, aluminium) and sulphates were observed. 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. Concentrations of sulphates were analyzed by X-ray fluorescence analysis (XRF) using SPECTRO iQ II (Ametek, Germany) with silicon drift detector with resolution of 145 eV at 10 000 pulses.

pH values were determined by pH meter FiveGo FG2 (Mettler – Toledo AG, Switzerland) which was standardized using buffer solutions of different pH values (4.01, 7.00).

First stage is focused on the oxidation and chemical precipitation of iron cations due to their high concentration. Precipitation was followed by ion exchange and finally in the last stage AMD was contacted with two different biosorbents.

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

$$Efficiency = \frac{(C_0 - C_e)}{C_0} \, x \, 100\% \tag{1}$$

where c0 is the initial concentration of ions (mg.L-1), ce is equilibrium concentration of ions (mg.L-1).

Acid mine drainage samples

Real sample of AMD containing a high level of sulphates and heavy metals (concentrations of monitored metals are listed in Table 1). The experimental sample was collected from abandoned subsurface mine Smolník (Slovakia).

Oxidation and precipitation

Chemical precipitation (combination of oxidation using 31% hydrogen peroxide and subsequent precipitation with 0.1M sodium hydroxide) was used for the removal of iron cations due to their high concentration which is several times higher than concentration of the others monitored metals. The sample of 1 L of AMD was continually stirred after adding of 4 mL H$_2$O$_2$ and sequentially neutralised by NaOH under continuous

Tab. 5. Concentrations of heavy metals and sulphates after biosorption (Input: PUROLITE MB400 pre-treated AMD)
Tab. 5. Zawartość metali ciężkich i siarczanów po biosorpcji (wstępna obróbka PUROLITE MB400)

		pH	Fe$_{total}$	Cu	Al	Mn	SO$_4$
Peat	mg/L	2.61	0.53	0.08	9.7	7.6	1190
	Efficiency [%]	-	**15.9**	**79.5**	**19.8**	**13.6**	**0.8**
Hemp shives	mg/L	3.08	0.09	0.03	8.0	7.8	1060
	Efficiency [%]	-	**85.7**	**92.3**	**33.9**	**11.4**	**11.7**

Tab. 6. Concentrations of heavy metals and sulphates after biosorption (Input: AMBERLITE MB20 pre-treated AMD)
Tab. 6. Zawartość metali ciężkich i siarczanów po biosorpcji (wstępna obróbka AMBERLITE MB20)

		pH	Fe$_{total}$	Cu	Al	Mn	SO$_4$
Peat	mg/L	2.77	0.50	0.14	6.7	7.6	1120
	Efficiency [%]	-	**27.5**	**0.64**	**40.7**	**7.3**	**2.6**
Hemp shives	mg/L	3.39	0.00	0.06	5.3	7.1	905
	Efficiency [%]	-	**100**	**84.6**	**53.1**	**13.4**	**21.3**

stirring and pH measuring. The resulting precipitate was filtered through laboratory filter paper and concentration of monitored metals and sulphates in filtrate was determined.

Following reaction takes place during the experiment:

$$2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^- \qquad (2)$$
$$Fe^{3+} + OH^- + SO_4^{2-} \rightarrow Fe(OH)SO_4 \qquad (3)$$
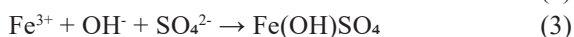
Ion exchange

For the removal of sulphates and metals by ion exchange process, two inorganic ion exchange resins PUROLITE MB400 and AMBERLITE MB20 were used.

PUROLITE MB400 is a high quality resin mixture for direct purification of water. It is suitable for use in regenerable or non–regenerable cartridges and in large ion exchange units. Passage of water at recommended flow rates through the resin as supplied can achieve almost complete reduction of total dissolved solids.

AMBERLITE MB20 resin is an ionically equilibrated mixed bed resin. It is a fully regenerated, ready-to-use mixture of a strong acid cation exchanger with a strong base type 1 anion exchanger. AMBERLITE MB20 resin has been developed for the production of high purity water. It can be used for all applications requiring totally demineralised water, free of silica and of carbon dioxide.

The cations removal efficiency by ion exchange process was tested at laboratory temperature (23±0.2°C) under static conditions. 1 g of each resin was mixed with 100 mL of AMD sample after precipitation. After 24 hours reaction time, resins were removed by filtration through a laboratory filter paper for qualitative analysis and equilibrium concentrations were determined.

Biosorption

In the biosorption study two types of adsorbents were chosen. 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. According the previous results, hemp shives were used only in the modified state. 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 1.6M 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.

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

For the purpose of removal efficiencies investigation, batch adsorption experiments were carried out. Each type of sorbent was mixed with AMD sample after precipitation and ion exchange. 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 AMD sample. After 24 hours reaction time, sorbents were removed by filtration through a laboratory filter paper for qualitative analysis, residual concentration metals and sulphates were determined by colorimetric method and pH change was also measured.

Results and discussion
Precipitation

The removal of sulphate ions from water environment is a complex problem due to the high solubility
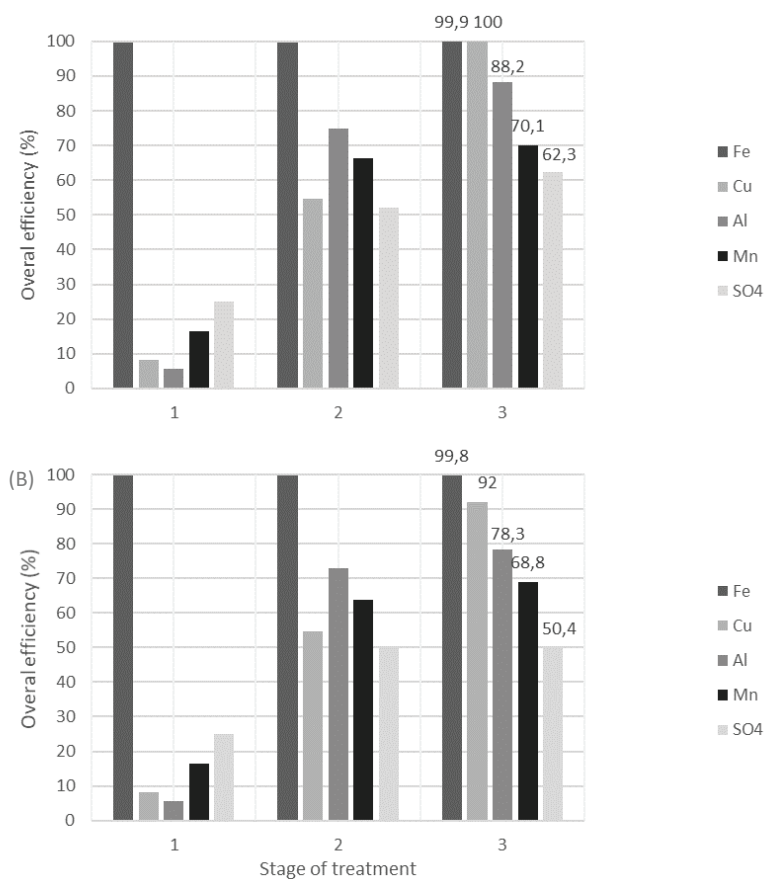
Fig. 1. Summarized results (A – best option: combination of MB20 resin and hemp shives sorption;
B – worst option: combination of MB400 resin and peat sorption) *1 – results after oxidation and precipitation; 2 – results after ion exchange; 3 – results after biosorption
Rys. 1. Podsumowane wyników (A - najlepsza opcja: połączenie sorpcji na żywicy MB20 i łuskach konopi;
B - najgorsza opcja: połączenie żywicy MB400 i sorpcji na torfie) * 1 - wyniki po utlenieniu i strącaniu; 2 - wyniki po wymianie jonowej; 3 - wyniki po biosorpcji

and stability of these anions in aqueous solutions [12]. The hydrogen peroxide, in acid solution, oxygenates from ferrous ions to ferric ions. During this oxidation is mainly formed the ferric hydroxy–sulphates that is insoluble precipitate. A substantial part of sulphates is remaining in the solution due to stability of sulphate anion [13].

The removal efficiency was 99.8% and 25.1% for iron and sulphates, respectively. Removal of the other monitored metals was insufficient what created the space for the application of ion exchange in the next step. Summary changes in concentrations and removal efficiencies are shown in Table 2.

Ion exchange

Samples of AMD after chemical oxidation were subsequently treated by ion exchange. The main goal was reduction of sulphates and metals that were not effectively removed in the first phase of treatment. From the results (listed in the Tables 3 and 4) it is evident that both MB400 and MB20 resins exhibit similar results. The most significant decreases in concentrations

are observed in the case of aluminum and manganese. pH values are stable at the level between 2.5 and 2.6. MB20 resin is partially more effective than MB400.

Biosorption

The last stage of experiments consists of biosorption. Four different combination of adsorbate/adsorbent system were evaluated:

- AMD after precipitation and ion exchange by PUROLITE MB400 vs. peat;
- AMD after precipitation and ion exchange by PUROLITE MB400 vs. hemp shives;
- AMD after precipitation and ion exchange by AMBERLITE MB20 vs. peat;
- AMD after precipitation and ion exchange by AMBERLITE MB20 vs. hemp shives.

The results are presented in the Tables 5 and 6.

Overall, biosorption was more efficient by using of modified version of hemp shives which exhibit better results for all monitored elements. The results showed that biosorption could be powerful method in the case

of trace concentration. Iron and copper cation were eliminated bellow 0.1 mg/L. On the other hand, decrease in manganese concentration was minimal (only bellow 15%).

Changes in pH values were also measured. Peat caused a small increase in pH value after sorption. Generally, peat as a product of humification causes increasing in pH values. 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 [14]. In this case only small concentration of metals is adsorbed and cannot significantly influence pH value in already acidic conditions. Increase in the pH values caused by hemp shives may be result of the OH functional groups release into the solution in both cases of adsorbates. This theory is also supported by the results obtained from the previous sorption experiments at higher concentration levels.

Overall results

For the clear representation of the results, the partial achievements were summarized into the graphical form (Fig. 1.).

Two of the combination were chosen (A – best option and B – worst option). As the most efficient option, combination of precipitation, ion exchange using MB20 and hemp shives sorption has proved. The efficiency in this case is around 100% for elimination of iron and copper cations. 88% of aluminum was also removed. The sulphate removal reached the level of 62%. The worst results were obtained using combination of precipitation, MB400 ion exchange and sorption by peat.

Conclusions

The experiments presented in this article were focused on the combination of chemical precipitation, ion exchange and biosorption techniques for the acid mine drainage treatment. Concentrations of four different metal cations (copper, iron, manganese, aluminium) and sulphates were observed.

Chemical precipitation (combination of oxidation using 31% hydrogen peroxide and subsequent precipitation with 0.1 M sodium hydroxide) was used for the removal of iron cations. Another positive fact in this first stage of treatment is partial removal (around 25%) of sulphates.

After the chemical precipitation, the ion exchange using two different exchangers (PUROLITE MB400 resin and AMBERLITE MB20 resin) took place. Decreasing in sulphates concentration was observed around 34% and 37% for MB400 and MB20 resins, respectively. The ion exchange also influenced the concentration of heavy metals; the most prominent was decreasing in manganese and aluminium concentration (around 60% and 70%, respectively).

AMD after precipitation and ion exchange was used as an input for the biosorption study. Low – cost sorbents included in this case natural non – modified peat "PEATSORB" (provided by REO AMOS; Slovakia) and hemp shives in modified state.

Generally, biosorption was more efficient by using of modified version of hemp shives. Hemp shives exhibit better results for all monitored elements. The results showed that biosorption could be powerful method in the case of trace concentration. Iron and copper cation were eliminated bellow 0.1 mg/L.

Overall, the best results were observed after combination of MB20 resin in the second stage and subsequent using of modified hemp shives in the third stage of the treatment.

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Wieloetapowy proces oczyszczania kwaśnych wód z drenażu kopalni – propozycja i weryfikacja

Górnictwo jest jedną z działalności człowieka, która ma zasadniczy wpływ na środowisko - faunę, florę i ludzi. Negatywne oddziaływania obejmują także kwaśne wody z drenażu kopalnianego, który powstaje w wyniku rozpuszczania produktów powstałych w wyniku utleniania (chemicznego i mikrobiologicznego) minerałów siarczkowych, głównie pirytu lub dwusiarczku żelaza. Zgodnie z rygorystycznymi przepisami Unii Europejskiej dotyczącymi zrzutu ścieków konieczne jest przyjrzenie się innowacyjnym technologiom, które pozwalają na usunięcie znacznych ilości ścieków, aby uniknąć odprowadzania ich do wód powierzchniowych. W artykule Autorzy skoncentrowali się na kombinacji technik wytrącania chemicznego, wymiany jonowej i biosorpcji. Badano stężenia czterech różnych kationów metali (miedzi, żelaza, manganu, glinu) i siarczanów. Pierwszy etap ługowania obejmował wytrącanie chemiczne przez połączenie utleniania przy użyciu 31% nadtlenku wodoru i następnie wytrącanie 0,1 M wodorotlenkiem sodu. Po pierwszym etapie prowadzono wymianę jonową za pomocą dwóch różnych wymienników (żywica PUROLITE MB400 i żywica AMBERLITE MB20). Ostatni etap eksperymentów skoncentrowano na badaniu biosorpcji. Niskokosztowe sorbenty obejmują w tym przypadku naturalne torfy niezmodyfikowane „PEATSORB" i zmodyfikowane łupiny konopi. Ogólnie najlepsze wyniki zaobserwowano po połączeniu żywicy MB20 w drugim etapie i zastosowaniu zmodyfikowanych łupin konopi w trzecim etapie.

Słowa kluczowe: sorpcja, strącanie, wymiana jonowa, metale ciężkie, siarczany, kwaśny drenaż kopalniany