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The Elimination of Heavy Metal Ions from Waters by Biogenic Iron Sulphides

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Water pollution by heavy metals represent today important environmental problem because increased concentrations of them are dangerous for all living organisms. Biogenic iron sulphides produced by sulphate-reducing bacteria (SRB) represent material, which can be suitable for heavy metals sorption from waters. Hydrogen sulphide as a product of SRB metabolic processes creates with iron from nutrient medium biogenic sorbent in form of sulphides. The process of sorbent preparation was realized in the batch reactor during 21 days at 30 °C in anaerobic conditions. The culture of sulphate-reducing bacteria was isolated from the mineral spring Gajdovka (Košice, Slovakia) using Postgate C medium. The elimination of heavy metals from waters was examined using the prepared sorbent samples, model solutions with various zinc ions contents and mine drainage water samples from locality Banská Štiavnica (Slovakia).

1. Introduction

Although heavy metals are natural components of the environment but when their concentrations increase more than normal levels they become potentially hazardous. With the increasing concentrations they represent toxic substances that accumulate in food chains. They pose a threat to human health, animals and ecological systems. They include essential elements like iron as well as toxic metals like cadmium and mercury. Most of them show significant affinity to sulphur and disrupt enzyme function by forming bonds with sulphur groups in enzymes. Cadmium, copper, lead and mercury ions bind to the cell membranes hindering transport processes through the cell wall. Some of the metalloids, elements on the borderline between metals and non-metals are significant water pollutants (Manahan, 1999).

Mining influenced water is generated from chemical and biological processes in which sulphide minerals are oxidized to sulphates and metallic hydroxides. The amount and toxicity of the generated water depends on several factors such as mineralogy of the rock material, surface area, crystallography, temperature, oxygen concentration, and the amount of water contacting the material (Pinto et al., 2011). Mine drainages contain heavy metal contaminants, such as Cu^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}, which are not biodegradable and thus tend to accumulate in living organisms, causing various diseases and disorders (Motsi et al., 2009). These waters contain besides heavy metals increased concentrations of sulphates.

Treatment processes for metal contaminated waste streams include chemical precipitation, ion exchange, adsorption and ultra-filtration; the choice of method is based jointly on the concentration of heavy metals in the solution and the cost of treatment (Richardson and Harker, 2002). Popular method for the removal of heavy metals from the waste water is adsorption or biosorption.

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Biosorption is the process of removing compounds, metal ions or other materials using an inactive (non-living) sorbent of biological origin by means of attractive forces between the removed material and the biosorbent. Biosorption involves physical and chemical mechanisms such as: physical adsorption, ion exchange, complexation, precipitation, coprecipitation, and transport across a cell membrane (Volesky, 2004).

Sulphate-reducing bacteria (SRB) are important members of microbial communities with environmental and biotechnological interest. They can exist in a variety of environments such as soils, sediments, industrial and mining wastewaters. SRB are included in a group of chemoorganotrophic and strictly anaerobic bacteria, which contains representatives of the genera *Desulfovibrio*, *Desulfomicrobium*, *Desulfobacter* and *Desulfotomaculum*, among others (Luptáková and Kušnierová, 2005). They have the ability to reduce sulphate to sulphide and this sulphide reacts with certain metals dissolved (Cruz Viggi et al., 2011), such as copper, iron and zinc, forming insoluble precipitates (Martins et al., 2009; Mokone et al., 2012). In an iron rich environment the SRB form an iron sulphide (Fe_xS_y). The adsorption capacity of microbial produced iron sulphides has been researched as an alternative for heavy metal recovery and tested on common wastewater cations and acid mine drainages (Marius et al., 2005). It was found that iron sulphide material, produced by sulphate-reducing bacteria, is an excellent adsorbent for a wide range of heavy metals and had a very high specific uptake from solution for metal ions (Jong and Parry, 2004).

2. Materials and methods

2.1 Materials

In this study biogenic iron sulphides prepared by a mixed culture of sulphate-reducing bacteria were used. Bacterial culture was isolated from mineral water from spring Gajdovka (locality Kosice, Slovakia) using the nutrient medium Postgate C (Postgate, 1984). Chemical analysis to determine the chemical composition of the solution after SRB cultivation and to determine the created precipitates in nutrient medium was obtained by X-Ray Fluorescence.

2 different biogenic sorbent samples (named A and B) created by bacteria cultivation in modified medium Postgate C were used for sorption experiments. Stock solution containing 1 g/L of Zn (II) was prepared by dissolving $ZnSO_4.7H_2O$ of analytical grade in distilled water. Mine drainage water samples (Sample 1, Sample 2) with content of Zn (II) were collected at 2 places in Banská Štiavnica (Slovakia). They were the outflows from dump of “New Shaft”. Pb-Zn ores (such galenite, sphalerite) were mined in the past in Banská Štiavnica and therefore waters outflowing from dumps contain increased concentrations of these metals (Križáni and Andráš, 2008).

2.2 Sorbent preparation

Bacteria were cultivated in batch reactor (1000 mL) at 30 °C, under anaerobic conditions, using Postgate C medium in two modifications, for 21 days in order to create biogenic iron sulphides. A volume of growth medium was 900 mL with sodium lactate (2 g/L) as carbon and energy source and pH around 7. The modifications of the medium composition are described below in Table 1.

Table 1: The SRB cultivation conditions for sorbent preparation

Sorbent	Postgate C medium modification (per L)
A	1 g $FeSO_4.7H_2O$ addition
B	1 g $FeSO_4.7H_2O$ adittion 0.24 g $Fe_2(SO_4)_3.9H_2O$ adittion

2.3 Sorption experiments

Sorption experiments were conducted by mixing 0.1 g of biogenic sorbent samples (A, B) with 100 mL of model solution containing the desired concentration of heavy metal ions (10, 20, 50, 100, 150 and 200 mg/L). The mixture was stirred in 150 mL plastic Erlenmeyer flasks using mechanical laboratory shaker for 24 h. 2 mL of liquid phase were taken out in the following intervals: 3, 5, 10, 15, 30, 60, 120,

240, 300, 360 min., 24 h. and then they were filtered. The concentration of the zinc ions in the filtrates was determined by atomic absorption spectrometry (AAS).
The equilibrium of the sorption process was described by fitting the experimental points with Langmuir and Freundlich isotherm models. The Langmuir-type isotherm is characterized by a monotonic approach to a limited adsorption capacity that corresponds to the formation of a complete monolayer, where only a fixed number of active sites are available for adsorption. Sorbents that follow the Freundlich isotherm equation are assumed to have heterogeneous surfaces, consisting of sites with different adsorption potentials, and each type of site is assumed to adsorb solutes as in the Langmuir model (Mazlum et al., 2009).
The next step was focused on sorption of zinc from mine drainage water samples (Sample 1 and Sample 2). It was determined by contacting 100 mL of mine drainage water and 0.1 g of sorbent (A, B) for 24 h. The experiment conditions were identical to sorption of zinc from model solutions. The zinc ions concentrations were measured by AAS.

3. Results and discussion

3.1 SRB cultivation

The growth of SRB was detected by the formation of black precipitates at the bottom of the reactor and also appeared on the walls. In addition the smell provoked by the hydrogen sulphide was obvious.
X-Ray Fluorescence analysis of liquid and solid phase of nutrient medium after SRB cultivation showed that predominant elements in created precipitates are sulphur and iron (Table 2). These results confirm iron sulphides creation, which was expected. The presence of others elements is possible to explain as trace amounts of components from Postgate medium.

Table 2: Chemical composition of nutrient medium after SRB cultivation

Element	Element concentration in liquid phase (mg/kg)	Element concentration in created precipitates (mg/kg)
Ca	177.1	398.4
Cu	11.1	34.8
Fe	4.2	15,560
K	107.3	249.2
Na	150	290
Mg	20	98.1
P	81	65.4
S	845.8	14,500

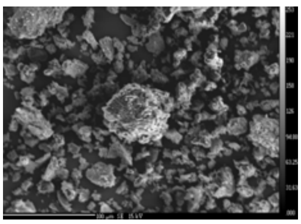

Figure 1: SEM micrograph of sorbent A

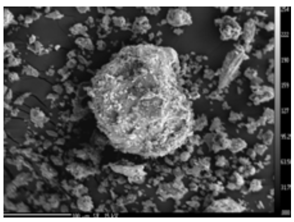

Figure 2: SEM micrograph of sorbent B

The sorbent samples were after cultivation filtrated, dried and analyzed by scanning electron microscopy (SEM), which illustrates Figure 1 and Figure 2. In order to verify the composition of dry precipitates from reactor were EDX analyses carried out. These results, which are depicted on Figure 3 and Figure 4, suggest that in both cases of SRB cultivation were biogenic iron sulphides prepared.

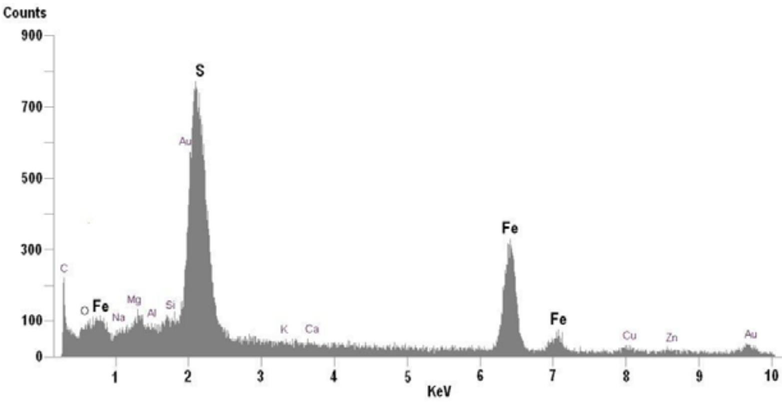

Figure 3: EDX spectra of biogenic iron sulphides – sorbent A

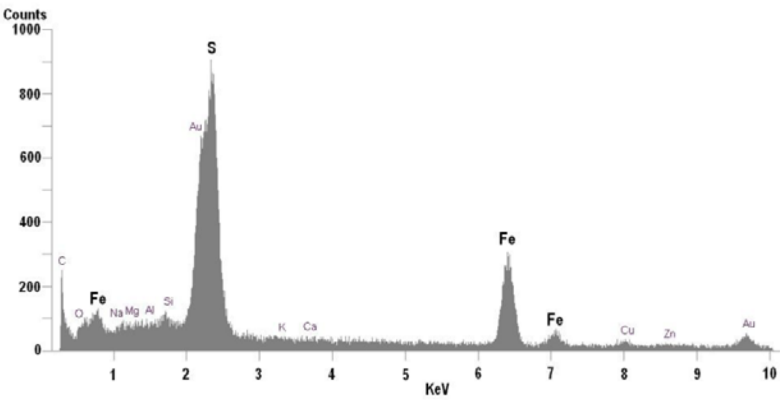

Figure 4: EDX spectra of biogenic iron sulphides – sorbent B

The adsorption of zinc ions from model solutions by biogenic iron sulphides was fitted to both the Langmuir and Freundlich adsorption isotherm models as shows Figure 5. Adsorption parameters are resumed in Table 3.

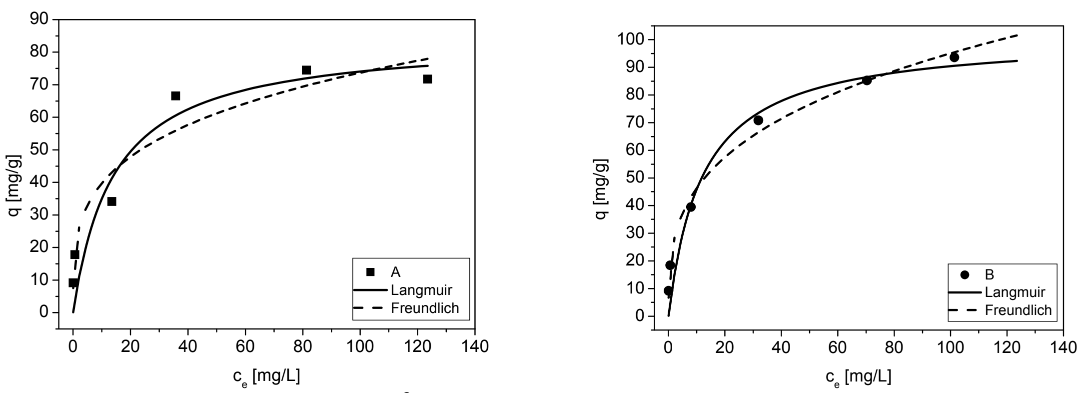

Figure 5: Adsorption isotherms for Zn^{2+} sorption by biogenic sorbent A and B

A better fit to the data gives Freundlich isotherm compared to Langmuir with a regression coefficient 0.94 (sorbent A) or 0.99 (sorbent B). Freundlich isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies.

Table 3: Langmuir and Freundlich adsorption isotherm model parameters

Isotherm model	Sorbent A	Sorbent B
Langmuir adsorption isotherm		
q_{max}	84.52	101.35
b	0.07	0.08
Freundlich adsorption isotherm		
k	21.45	22.56
n	3.7	3.2

The potential of biogenic iron sulphides to remove zinc ions from the mine drainage water samples (outflows from "New Shaft" dump, Banská Štiavnica, Slovakia) was determined by contacting 100 mL of mine drainage water and 0.1 g of sorbent for 24 h. The total metal concentrations found in the water before sorption experiments, concentrations of sulphates and pH values are reported in Table 4. Figure 6 shows the amount of zinc ions (q) adsorbed from solutions with time. The amounts of Zn^{2+} adsorbed by sorbent B from solutions were higher with time than values of sorbent A. The highest value of maximum sorption capacity was 5.62 mg/g (sorbent B).

Table 4: Analysis of mine drainage water samples

Sample	pH	Sulphates (mg/L)	Zinc (mg/L)	Copper (mg/L)	Manganese (mg/L)	Cadmium (μg/L)
1	6.1	930	5.6	0.14	2.81	26.3
2	6.5	880	5.5	0.11	2.29	22.6

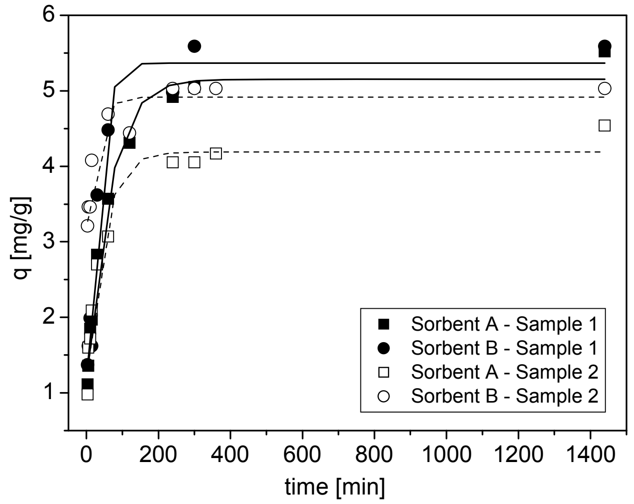

Figure 6: Zinc ions adsorption from mine drainage water samples by biogenic iron sulphides

4. Conclusion

The objective of this study was to evaluate the possibility of using a mixed sulphate-reducing bacteria culture for the treatment of heavy metal polluted waters. Two sorbent samples were prepared by cultivation of bacteria from Gajdovka spring (Kosice, Slovakia) in batch reactor using 2 modifications of Postgate C medium. The results of sorption experiments showed that the adsorption sites of prepared sorbents were available for zinc cations and that they represent a suitable material for removal of metal ions from model solutions. The experimental data from sorption studies gave a better fit for the Freundlich isotherm model. Desorption tests were not carried out. Sorption experiments with samples of mine drainage water showed that biogenic iron sulphides have the potential to remove zinc ions from real water too, not model solutions only. In the future the possibility of re-using the prepared biogenic iron sulphides samples and utilization of them for large scale operation will be examined.

Acknowledgements

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