The effect of preparation of biogenic sorbent on zinc sorption

Jana Jenčárová[1] and ***Alena Luptáková***[1]

The aim of this study is to prepare biogenic sulphides by using bacteria for the removal of zinc cations from their solutions. The production was realized in a bioreactor under anaerobic conditions at 30 °C. Sorbents were prepared by sulphate-reducing bacteria in different nutrient medium modifications, under two modes of bacteria cultivation. Created precipitates of iron sulphides were removed from the liquid phase of the cultivation medium by filtration, dried and used for the sorption experiments.

Keywords: *sorption, biogenic sorbent, zinc*

Introduction

Water pollution by metals, originated especially in various industry sectors as of final component industrial effluents, represent an important environmental problem because of their toxicity and insusceptibility. Heavy metals are used in several industries, including mining, metallurgy, electroplating and metal finishing (Pagnanelli et al., 2010). Conventional methods for removing metal ions from the aqueous solution, such as chemical precipitation, filtration, ion exchange, electrochemical treatment, membrane technologies, can be replaced by sorption which utilizes various natural materials with a biological origin. Biosorbents possess metal-sequestering properties and can be used to decrease the concentration of metal ions in solutions to low levels (Wang and Chen, 2009). The current spectrum of effective adsorbents includes various algae, bacteria, yeasts, fungi but also agricultural waste materials and other biomass (Chen et al., 2000; Lesmana et al., 2009, Volesky, 2004).

A specific type of sorbent with biological origin is represented by biogenic iron sulphides produced by sulphate-reducing bacteria (SRB). Sulphate-reducing bacteria are either heterotrophic or autotrophic anaerobes capable of reducing sulphates to sulphides by dissimilatory bioenergetic metabolism (Gibert et al., 2005). They use sulphates as a terminal electron acceptor for the metabolism of organic substrates (Postgate, 1984). The reduction of sulphate ions to hydrogen sulphide gas (Eq. (1)) generates alkalinity and promotes metal precipitation (Eq. (2)).

$$2\ CH_2O + SO_4^{2-} \rightarrow 2\ H_2CO_3 + H_2S \quad (1)$$
$$H_2S + Me^{2+} \rightarrow MeS\downarrow + 2H^+ \quad (2)$$

The produced hydrogen sulphide forms with metal cations insoluble precipitates of metal sulphides (Odom et al., 1993, Zagury et al., 2006). Iron sulphides are produced by bacteria in liquid medium with added Fe ions. Biogenic iron sulphide is a well-known absorbent for heavy metals and has a specific uptake capacity for different metal ions from solutions (Neal et al., 2001).

Materials and methods

SRB isolation and cultivation

For bacteria isolation Postgate's medium C and mineral water collected from Gajdovka spring (Košice) were used. It is water with pH 7.5, H_2S odour and with natural content of SRB. The predominant genus in mixed cultures of SRB is usually *Desulfovibrio*. Bacteria were cultivated under anaerobic conditions at 30 °C in glass reaction flasks (500 ml).

Nutrient medium had the following composition (gram per liter of distilled water): 0.5 g KH_2PO_4, 1 g NH_4Cl, 4.5 g Na_2SO_4, 2 g $MgSO_4.7H_2O$, 0.1 g $CaCl_2.H_2O$, 4 g sodium lactate, 1 g yeast extract, 0.1 g sodium thioglycollate, 0.1 g ascorbic acid and 1 g $FeSO_4.7H_2O$. The initial pH of the nutrient medium was adjusted to 7.1-7.3 using 5 M NaOH or 1 M HCl.

The process of nutrient medium preparation is on Fig. 1. Fig. 2 shows the reaction flasks after 7 days of SRB cultivation. The positive progress of the iron sulphides production by the biologically produced hydrogen sulphide is indicated by the presence of black precipitates.

[1] *Ing. Jana Jenčárová, PhD., Ing. Alena Luptáková, PhD.,* Institute of Geotechnics of the Slovak Academy of Sciences, Watsonova 45, 043 53 Košice, Slovakia, jencarova@saske.sk

Biogenic sorbent preparation

The Fe-sulphide precipitates production was realized in bioreactor under anaerobic conditions at 30 °C in modified Postgate's medium C. In two cases of sorbents preparation was used the nutrient medium with addition of 0,24 g $Fe_2(SO_4)_3.9H_2O$ and in two cases was without it.

The bioreactor was on the beginning filled with 450 ml of medium and 50 ml of bacteria inoculum obtained from reaction flasks, where the SRB isolation was successful. The 21 days-cultivation was realized under 2 different modes. Batch mode worked 3 weeks without addition of fresh nutrient medium. During the "semicontinuous" mode was fresh medium supplied into the reactor every 7 days, as shows Fig. 3. Detailed conditions of 4 sorbent type preparations are resumed in Tab. 1.

Fig. 1. Nutrient medium preparation.

Fig. 2. Reaction flask during SRB cultivation; flask 1- with black precipitates of iron sulphides; flask 2 - without visible iron sulphide precipitates.

Fig. 3. Bioreactor during nutrient medium exchange.

Tab. 1. The conditions of biogenic sulphides preparation.

Sorbent	Nutrient medium - Postgate's medium C	Bacteria cultivation mode
A	Without $Fe_2(SO_4)_3.9H_2O$ addition	"Batch"
B	With $Fe_2(SO_4)_3.9H_2O$ addition	"Batch"
C	Without $Fe_2(SO_4)_3.9H_2O$ addition	"Semicontinuous"
D	With $Fe_2(SO_4)_3.9H_2O$ addition	"Semicontinuous"

After 21 days of cultivation the generated precipitates were filtered through 0.45 µm membrane filter, dried and stored in anaerobic conditions. Dry samples were used for sorption experiments.

Sorption experiments

Sorption experiments were realized at room temperature in plastic Erlenmeyer flasks. During the experiments the biogenic iron sulphides (named A, B, C, D) produced by SRB and model solutions with various concentrations of Zn^{2+} ions (10-200 $mg.l^{-1}$) were used. Stock solution containing 1 $g.l^{-1}$ of Zn (II) was prepared by dissolving $ZnSO_4.7H_2O$ of analytical grade in distilled water.

Experiments were performed using 100 ml of model solution. The sorbent dose was $1g.l^{-1}$. The pH of solutions before sorption experiments was adjusted to 5.8 ± 0.1 with 0,01 M NaOH and 0,01 M HCl.

Samples during experiments were continuously stirred by mechanical laboratory shaker at 250 oscillations per minute for 4 hours. The concentrations of zinc ions were determined by atomic absorption spectrometry (AAS).

Results and discussion

Iron sulphides were successfully produced in the bioreactor in both medium modifications, as well as in batch and in semicontinuous conditions. So this way, we prepared 4 different biogenic sorbent types – named A, B, C and D. The visual control indicated sulphide precipitates creation in all nutrient mediums. In all cases the SRB presence was confirmed by light microscope. The SRB presence evidence, especially genera *Desulfovibrio* is shown on Fig. 4.

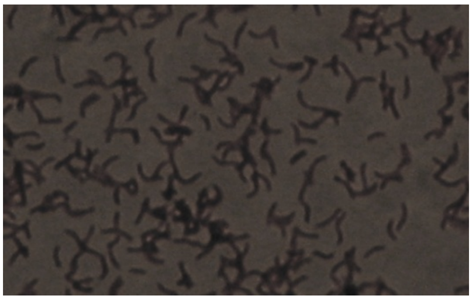

Fig. 4. Sulphate-reducing bacteria, genera Desulfovibrio.

Figures 5 and 6 compare sorption of Zn^{2+} ions from model solutions by "semicontinuously" prepared sorbent in two different Postgate's medium C modifications (sorbent types C and D). The concentrations of metal ions in model solutions were 10, 20, 50, 100, 150 and 200 $mg.l^{-1}$. We can see that sorption process in initial 20 minutes was very similar in case of both sorbents. It is visible, that after this time the process of zinc ions sorption by sorbent C went more slowly, while sorption by sorbent D was continuing in some cases till 240 minutes. Sorbent D seems to be more suitable for solutions with higher metal pollution. Sorption results for solutions with lower metal concentration were not very different at the end of the experiment.

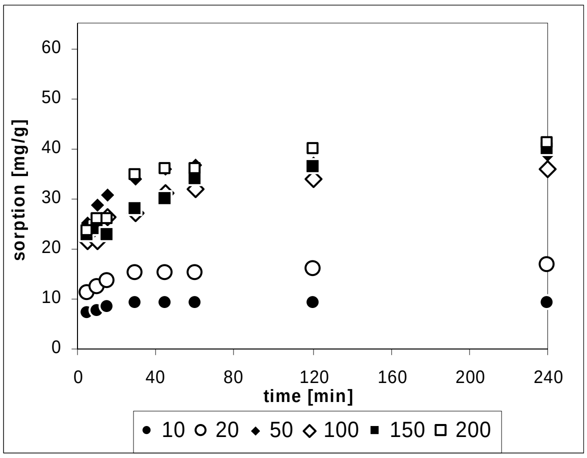

Fig. 5. Sorption of Zn^{2+} by semicontinuous sorbent prepared in modified Postgate's medium C without $Fe_2(SO_4)_3.9H_2O$ addition (Sorbent C).

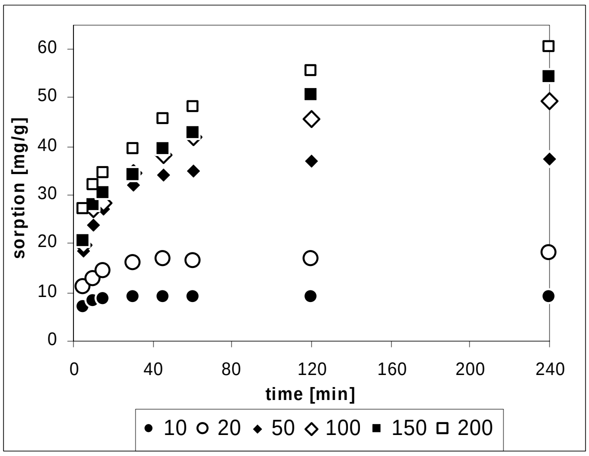

Fig. 6. Sorption of Zn^{2+} by semicontinuous sorbent prepared in modified Postgate's medium C with $Fe_2(SO_4)_3.9H_2O$ addition (Sorbent D).

Figures 7 and 8 show sorption of Zn^{2+} during 240 minutes by sorbents A, B, C and D, while the initial concentration of metal ions in model solutions was 10, 20 and 50 $mg.l^{-1}$.

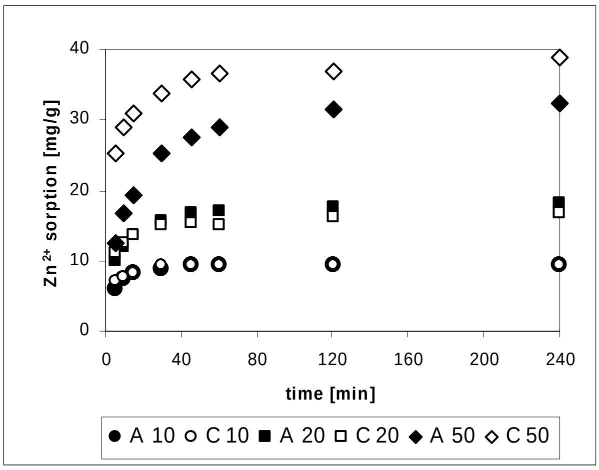

Fig. 7. Sorption of zinc ions from model solutions using sorbent A and C.

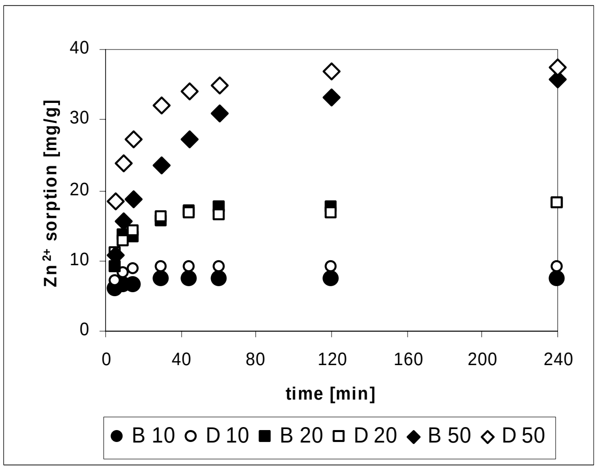

Fig. 8. Sorption of zinc ions from model solutions using sorbent B and D.

Figures compare zinc ions removal from model solution by biogenic sulphides created in the same type of nutrient medium, but with the difference in the cultivation mode. After 240 minutes of experiments the measured values were very similar and there was not recorded very significant impact of the sorbent preparation mode on the sorption results. Only from solutions with Zn^{2+} - 50 mg.l^{-1} were "semicontinuously" prepared sorbents (C, D) removing more zinc ions than "batch" prepared (A, B) in the same times.

On Figure 9 are depicted the values of zinc ions removal from model solutions in percentage. It is visible, that they are very similar in cases when initial concentration of metal ions in solution was lower (10 and 20 mg.l^{-1}). Almost all values achieved more than 99 %. When the initial zinc ions concentration in model solutions was 50 mg.l^{-1}, there were only 70-80 % of them were removed by sorbents. It could be probably interpreted by "exhausted" sorbent capacity, or short sorption experiment duration.

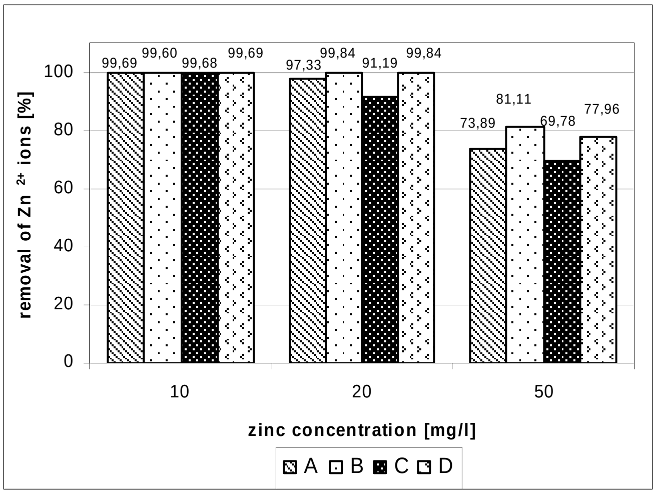

Fig. 9. Removal of zinc ions from model solution by different sorbents.

Conclusion

Our experimental studies confirm that using biogenic iron sulphides prepared by sulphate-reducing bacteria isolated from mineral spring Gajdovka and by suitable nutrient medium, could be an alternative technology for wastewater treatment to remove metal ions from industrial wastewaters**.**

Sorption experiments showed, that sorption of zinc ions from model solutions is possible. For solutions with higher concentrations using the sorbent prepared in modified Postgate's medium C with $Fe_2(SO_4)_3.9H_2O$ addition was the best alternative. Between sorbents prepared in the same cultivation mode, when the initial metal concentration in model solutions was lower than 50 mg.l^{-1}, only little differences in sorption results were obtained.

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