



Improvement of Sorption Capacity and Applicability of Biosorbent by Immobilization

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Abstract

The water contamination by toxic metal ions is a worldwide environmental problem. High concentrations are hazardous for all living organisms, causing many disorders and diseases and ecological damages to the surroundings. Biosorption is an innovative technology that employs inactive and dead biomass (bacteria, fungi, algae, biowaste) for the recovery of metals from aqueous solutions. Sulphate-reducing bacteria utilization is one of the options how to prepare applicable sorbent which removes metal ions from water. This material is created as a consequence of bacteria metabolism in anaerobic environment. The use of freely suspended biomass is often impractical and has some disadvantages. In contrast to this, application of immobilized biomass shows more benefits including increased mechanical strength, resistance to chemical environment, easy separation of cells and effluents, high biomass performance and repeated use in many adsorption/desorption cycles. Cell entrapment is the most widely used method for immobilization. In this technique, the cells are enclosed in a polymeric matrix which is porous enough to allow diffusion of substrate to the cells. The aim of this work was to examine and compare the sorption ability of biogenic iron sulphides created by sulphate-reducing bacteria in "free" and "entrapped" form. Precipitates were synthesized in reagent bottles with bacteria culture and growth media Postgate C, at 30 °C during 60 days, subsequently dried and analysed. Prepared samples were immobilized using sodium alginate. Sorption of cadmium from model solutions was realized in 100 ml Erlenmeyer flasks, with sorbent dose 1 g/l, during 24 hours. During experiments, the samples showed a satisfying stability and maximum adsorption capacity achieved 38 mg/g. The results refer to good sorption properties of immobilized samples and their potential for further practical use.

Keywords: Biosorbent, Immobilization, Toxic metals, Water contamination

Introduction

Biosorption, as a specific type of sorption, can be defined as the passive uptake, binding or concentration of selected metal ions on to certain biological material. Different types of non-living/inactive biomass or materials derived from biological sources are able to capture metals from solutions. The mechanism of biosorption is generally based on physicochemical interactions between the metal ions and the cellular parts of biological structures and functional groups present on the cell surface, such as electrostatic interactions, ion exchange and metal ion chelation, precipitation or complexation [1]. When studying different types of biomass, various sorbent pre/treatment techniques by chemicals or some physical methods are used in order to increase the sorption capacity and create the stable particles for practical use. Immobilization of microbial cells via entrapment in a polymer matrix is one of the methods. The polymers often used are polyacrylamide, collagen, chitosan, chitin, alginate or polysulfonate [2]. Immobilized sorbents are more stable at different pH, temperature, ionic composition of the solution and also facilitate the flow of liquid through the column. The decrease of sorption rate and the achievement of the equilibrium after a few hours can be disadvantages [3].

Several studies revealed that sulphate-reducing bacteria (SRB) synthesize adsorbents that can decrease various cations concentrations of common wastewater and acid mine drainage to low levels. The overall dissimilatory reduction is the most widely metabolic pathway of SRB and includes complete reduction of sulphate through a series of intermediate reactions [4]. The end product, hydrogen sulphide, can react with metal ions to form insoluble metal sulphides or reduce soluble toxic metals, often to less toxic or less soluble forms [5]. The significance of SRB activity in our study comes from the production of H₂S and its subsequent reaction with Fe²⁺ (the sulphide binding ion present in growth medium) to form ferrous sulphides. Bacteria are responsible for production of dissolved sulphide, but on the other side, they serve as surfaces for iron sulphide precipitation. Such sulphides commonly include mackinawite and greigite [6, 7] and serve as a sorbent material.

The main concern of this work was to prepare sorbent samples by sulphate-reducing bacteria cultivation and to study the adsorptive capacity of alginate beads containing created sulphides alongside the powder sulphides samples without immobilization in the process of metal ions removal from aqueous solutions.

Materials and Methods

Sorbent preparation

Bacteria were grown in selective nutrient Postgate's C medium [8] after obtaining from a mineral water collected at Gajdovka spring (Košice). The growth medium composition (per litre of distilled water) is following: 4,5 g Na₂SO₄, 0,5 g KH₂PO₄, 1 g NH₄Cl, 2 g MgSO₄·7H₂O, 0,1 g CaCl₂·H₂O, 0,2 g sodium acetate, 2 g sodium lactate, 1 g yeast extract, 0,1 g sodium thioglycollate, 0,1 g ascorbic acid, 0,5 g FeSO₄·7H₂O, 10 ml microelements solution and resazurin. Medium was boiled for 10 minutes, cooled down and bubbled with an inert gas (N₂). The pH was adjusted to 7,5. Cultures of SRB were maintained at 30 °C under anaerobic conditions in glass flasks during 60 days. Sufficient supply of nutrients was provided at regular intervals to the system for the optimal bacteria growth and the formation of required precipitates. At the end, solid particles were separated from the suspensions by centrifugation at 10000 rpm for 10 minutes, washed with degassed distilled water and centrifuged again. The samples were consequently freeze-dried for 48-72 hours and stored in a vacuum desiccator.

Sorbent immobilization

Dry powder sample of biogenic sorbent (after homogenization) was mixed with sodium alginate dissolved in distilled water in a ratio 1:9. After 20 minutes of components interaction, the mixture was dripped through a plastic pipette tip into a solution of 0.2 M calcium chloride and left to polymerize for 120 minutes. Creating gel beads were gently mixed by using a magnetic stirrer. Alginate is a natural polymer and could be converted into hydrogels via crosslinking with divalent calcium cations, based on the simple ion exchange principle, where water-soluble sodium alginate turns into insoluble and stable calcium alginate. Sample of pure calcium alginate without addition of biogenic sulphides (control sample) was prepared using the same procedure. After finishing, the samples were rinsed with distilled water, filtered, dried and stored for use.

Model solutions

Stock solution with concentration 1g/l of cadmium ions was prepared by dissolving 3CdSO₄·8H₂O (analytical grade) in distilled water. Model solutions for sorption experiments with initial concentration 10-200 mg/l Cd²⁺ were made by stock solution dilution.

Samples analysis

The structure and composition of immobilized and non-immobilized sorbent samples were analyzed using a scanning electron microscope equipped with energy dispersive X-ray microanalysis system (FE MIRA 3 TESCAN).

The concentration of metals in liquids was determined by atomic absorption spectrometry (AAS - VARIAN AA240FS).

Sorption studies

Batch studies were carried out in plastic Erlenmeyer flasks using mechanical laboratory shaker at 250 oscillations per minute at initial pH of 5,8. The sorbent dose 1 g/l was contacted with 100 ml model solution of a known concentration (10, 20, 50, 100 and 200 mg/l) of Cd²⁺. The pH of model solutions was adjusted with 0,01M NaOH and 0,01M HCl at the beginning. Sorption experiments were performed by using biogenic precipitates in the form of powder (sample A) and iron sulphides immobilized in alginate (sample B). The sampling was carried out after 24 hours and cadmium concentrations were measured by AAS.

The second study was concerned on the sorption progress during the experiments. 0,1 g of powdered sorbent (sample A), immobilized sorbent (sample B) or pure calcium alginate (control sample C) was added into 100 ml of metal solution with initial cadmium concentration 50 mg/l. pH adjusting and shaking conditions were identical to the first study. 2 ml of solution was withdrawn at known time (after 3, 5, 10, 15, 30, 60, 120, 240 minutes and 24 hours) and concentrations of metal ions were analysed (AAS). All experiments were realized in duplicates at laboratory temperature.

Adsorption isotherm models

The capacity of the adsorbent for the adsorbate is described by an adsorption isotherm, which is usually the ratio between the quantity adsorbed and that remaining in solution at fixed temperature at equilibrium. Equilibrium sorption isotherms can be used to compare different sorbents, as well as to compare the affinities of different substances for the same sorbents. Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species.

Langmuir isotherm relates metal uptake per unit weight of adsorbent (q_e) to the equilibrium adsorbate concentration in the bulk fluid phase (c_e). This model is based on the assumption that maximum adsorption (q_{max}) occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The Langmuir isotherm is given by equation:

$$q_e = \frac{q_{max} b c_e}{1 + b c_e} \quad (1).$$

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of metal adsorbed per unit mass of adsorbent (q_e) and the concentration of the metal at equilibrium (c_e). K and n are empirical constants and they characterize system and are indicators of the adsorption capacity and adsorption intensity. This model is given by equation:

$$q_e = K C_e^{1/n} \quad (2).$$

Results and Discussion

The process of biogenic sorbent preparation by SRB cultivation was successful, demonstrated by black iron precipitates formation, sensorial and visual detection of H₂S verified at regular intervals during 60 days. Dried solid particles separated from the suspensions (sample A) were mixed with sodium alginate in order to create immobilized sorbent (sample B) according to the

procedure mentioned above. The structure, shape and particle composition of all samples (including control sample C) were analyzed. SEM observations of biogenic precipitates, shown on Figure 1, revealed particle sizes from low micrometers to bigger aggregates. By immobilization in alginate, clusters of “FeS” were formed, incorporated into the interior of the matrix and adhered to the entire surface of the beads, which resulted in fragmented surface structure. The average particle size was about 1-1,5 mm as Figure 2 illustrates. The pure alginate sample contained spherical particles with relatively smooth surface, including some cracks and surface irregularities (Figure 3), which partially corresponds to the imprints of the pad where the soft gel beads were dried.

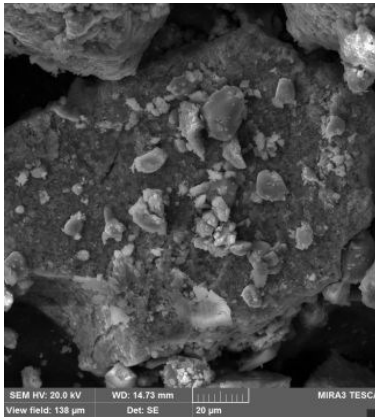


Fig. 1. Iron sulphides in powder (sample A)

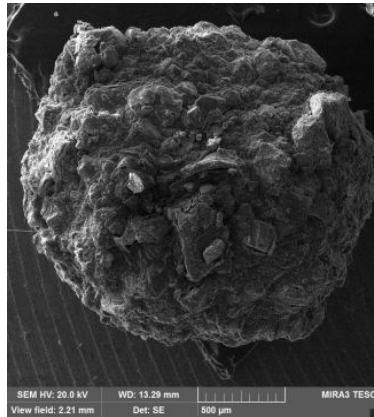


Fig. 2. Biogenic sorbent immobilized in alginate (sample B)

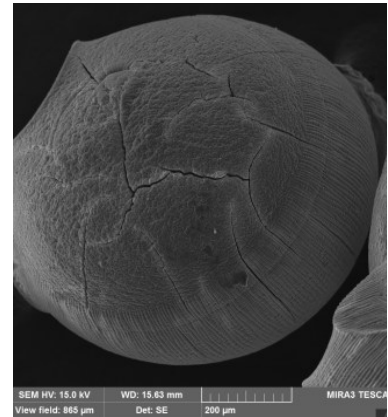


Fig. 3. Calcium alginate bead (sample C)

Table 1 includes the results of EDX analysis which confirmed predominant iron sulphides in sample A. Other components were sulphur, biomass and nutrient medium components. Sample C consists of calcium alginate, sample B composition points to the combination of both of them.

Tab. 1. EDX analyses of sorbent samples

Element [wt%]	Sample		
	A	B	C
Fe	39,1	27,1	-
S	32,7	10,4	-
C	11,6	22,3	30,6
N	0,6	-	-
O	12,7	26,2	47,7
Ca	0,2	7,7	13,6
Cl	0,4	6,3	8,1
K	0,8	-	-
Mg	0,5	-	-
Na	1,4	-	-

The results of sorption experiments carried out in this study were fitted with Langmuir and Freundlich adsorption models, based on the equilibrium value of sorbate uptake by the sorbents plotting against the equilibrium (final) sorbate concentration. Figure 4 shows fitting the experimental points obtained in cadmium sorption by biogenic iron sulphides in powder (sample A) and alginate-immobilized form (sample B). They indicate that Freundlich isotherm fits Cd^{2+} removal from model solutions by sample A better than Langmuir. Langmuir model fits best the cadmium sorption by immobilized sample B. The constants calculated from the corresponding isotherms with the correlation coefficients are presented in Table 2.

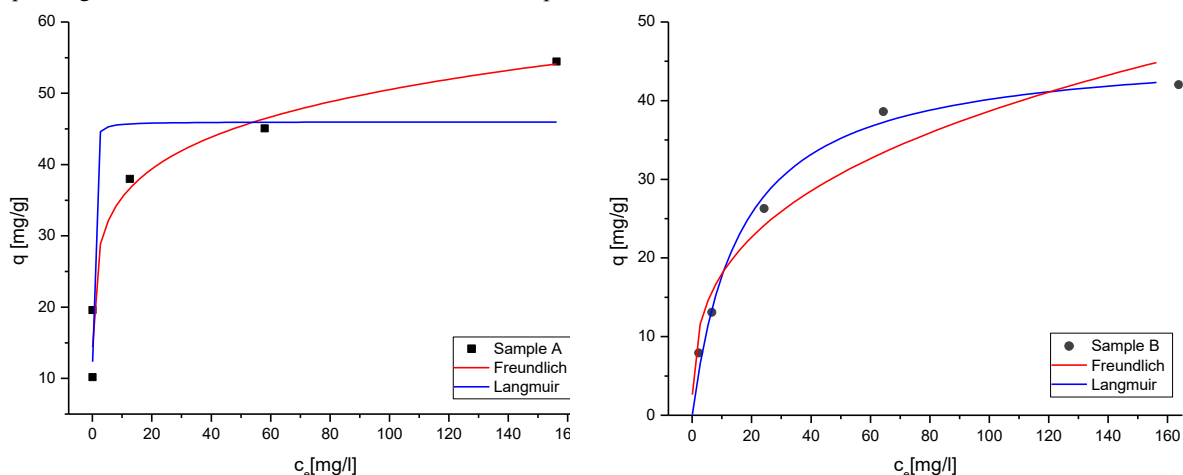


Fig. 4. Adsorption isotherms for cadmium sorption from model solutions

TABLE 2. The adsorption isotherms coefficients.

Isotherm	Langmuir			Freundlich		
	q_{max}	b	R^2	K	$1/n$	R^2
Sample A	46,02	12,21	0,89	24,79	0,15	0,97
Sample B	46,74	0,06	0,99	8,37	0,33	0,93

Values of regression coefficient R^2 indicate that the sorption process is satisfactorily described by the selected isotherm models except for limited application of Lagmuir model in the case of sorbent A, with R^2 0,89. The K constant (Freundlich model), related to the sorption capacity, confirmed higher value for sorbent A. The maximum sorption capacity was 46 mg/g for non-immobilized and 46,7 mg/g for immobilized sample.

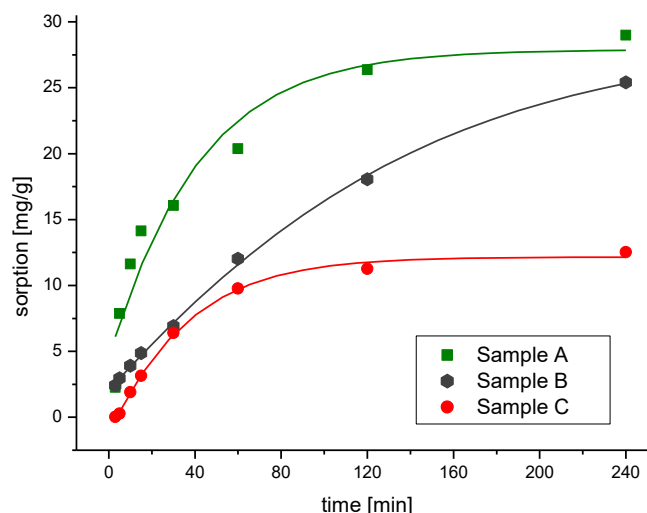
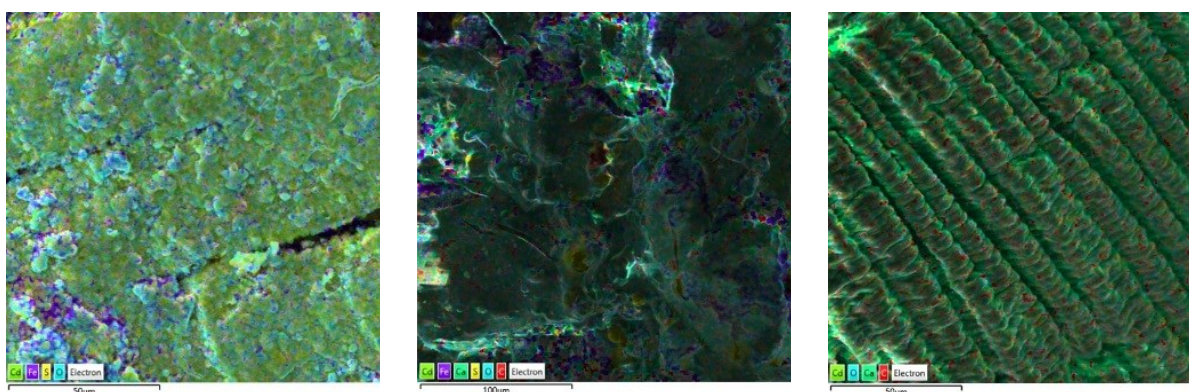


Fig. 5. Comparison of cadmium sorption from model solution by different sorbent samples

The process of sorption by non-immobilized and immobilized form of the biogenic sorbent compared to the pure calcium alginate during 240 minutes in a model solution with an initial amount of 50 mg Cd^{2+} is shown in Figure 5. The sorption capacity of the alginate sample reached equilibrium after approximately 2 hours, after 24 hours the value achieved 29,5 mg/g. The maximum sorption capacity reached 35,3 mg/g after 24 hours for sample A, 37,6 mg/g for sample B. At the end of experiments, the pH of model solution slightly increased to 6,9 and 7,1, respectively in the case of biosorbents, and 5,9 in the case of alginate. The obtained results also point to the fact that although polymers in the form of natural polysaccharides primarily serve as a material for encapsulation and immobilization, they are also characterized by a high ability to bind dissolved metal ions from solutions. The total contact area of the particles with the model solution is another factor which most likely influenced the results. The dosage weights were about 1 g/l for all samples, but the number of “particles” in one dosage (due to their different weight) varied. We can assume that larger active contact area of sample with the solution reflects in the achievement of the sorption capacity values. On the basis of these findings, it is necessary to examine and take into account these characteristics of the samples in further studies more detailed: the specific surface area, the size and number of particles.

Fig. 6. EDX mapping analysis of samples after cadmium sorption from solution
A - iron sulphides in powder; B - immobilized “FeS”; C - calcium alginate bead

Tab. 3. Composition of sorbent samples after cadmium sorption.

Element [wt%]	Sample		
	1	2	3
Fe	36,9	24,0	-
S	28,7	9,8	-
O	20,7	31,6	52,5
Cd	13,7	4,5	5,3
C	-	27,5	37,3
Ca	-	2,6	4,9

Figure 6 illustrates EDX mapping analysis of all samples after the sorption experiments, colored markers show the positions of the sorbents chemical elements and the places of cadmium adsorption onto the samples surfaces. The EDX analysis values are in Table 3, confirming cadmium binding in all cases, the most remarkable seems to be in sample A.

Conclusions

Biogenic precipitates created by SRB in powder form as well as entrapped into alginate beads were used for the removal of Cd^{2+} ions from aqueous solutions. The results show that both have potential and can be used as effective sorbents. The sorption capacity of immobilized sorbent was comparable to the powder sample, but the main advantage is better sample handling, what provides a prerequisite for further practical use. The distribution of cadmium ions between liquid and solid phase was analyzed by Freundlich and Langmuir isotherm models. The maximum sorption capacity according to models corresponds well to the values achieved in the experiments.

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