Cyclical Cadmium Adsorption and Desorption by Activated Sludge Immobilized on Alginate Carriers

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Abstract

This paper concerns cadmium desorption in subsequent cycles of adsorption/desorption by chemical sorbents such as 2% sodium alginate, sodium alginate with the addition of poly(vinyl) alcohol (PVA) in the following proportions: 1.5% alginate and 0.5% PVA, 2% alginate and 2% PVA, 2% alginate and 5% PVA, and two kinds of activated sludge immobilized on alginate sorbents. It was proved that adsorption by alginate and alginate with PVA obeys a second-order rate law. The higher the PVA amount in alginate, the lower the reaction rate.

Mineral acids such as hydrochloric and sulphuric acids were used as desorption agents. It was observed that all sorbents tested remove cadmium with high and almost constant efficiency from the solution containing 50 mgCd/dm³, whereas desorption effectiveness depended on the kind of sorbents and desorbing agents.

Keywords: adsorption, desorption, cadmium, kinetic, alginate, poly(vinyl) alcohol, immobilized activated sludge, adsorption-desorption cycles

Introduction

The contamination of wastewater by heavy metals is a recognized world-wide environmental problem. Conventional treatment methods such a chemical precipitation, chemical oxidation or reduction, ion exchange and filtration used to reduce metal concentrations to environmentally acceptable levels tend to be too costly or ineffective when metal concentrations are low (i.e. 100 mg/dm³) [1]. For this reason the removal of metals by adsorption, especially with the use of biosorbents, has recently become a subject of interest. This has included cost of these biosorbents, which is significantly less than that of commercial ion exchange resin [2]. The adsorption of metals onto various types of biomass has been studied in detail [3, 4].

The use of native biomass in its freely suspended state is limited owing to inherent disadvantages such as small particle size and low mechanical strength of the biomass. In addition, a density similar to the suspending medium may complicate biomass separation.

The above-mentioned disadvantages may be overcome using microorganism immobilization. Immobilization causes an increase of biomass durability. In some cases it improves the sorption properties of biomass [5]. The authors proved the higher effectiveness of mercury adsorption by *Chlorella emersonii* immobilized on alginate in comparison to the cells freely suspended in a solution. According to the authors it resulted from the decrease of toxic mercury interaction to *Chlorella emersonii*. For this reason mercury removal by immobilized algae could be the result of both biosorption and bioaccumulation. Mercury concentration removed only by alginate was very low and amounted to merely 7% of its initial concentration.

According to Garnham et al. [6], cobalt, zinc and manganese adsorption by alginate and immobilized biomass of *Chlorella salina* was almost identical. Similarly,

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Table 1. Operating conditions of activated sludge.

Activated	Duration of phases [h]				
sludge	filling	mixing	aeration	sedimentation	decantation
1	once	-	21.5	2.0	0.5
2	0.5	2.5	2.8	2.0	0.2

Wojnowska-Baryła et al. [7] on the basis of constants determined from Freundlich and Langmuir equations proved that both alginate and immobilized *Klebsiella pneumoniae* were effective cadmium sorbents.

Kuczajowska-Zadrożna [8] examined that activated sludge characterizes itself by a low adsorption capacity, but high adsorption affinity to cadmium, whereas alginate has high adsorption capacity, but low affinity to the metal. According to the authors, activated sludge immobilization on alginate turned out to be advantageous. As a result of activated sludge immobilization obtained biosorbent showed higher adsorption capacity in comparison to activated sludge, and comparable sorption capacity and higher affinity in comparison to only alginate.

Owing to immobilization cost, using the immobilized activated sludge as a biosorbent is profitable, when it characterizes itself the high adsorption effectiveness. Using the immobilized activated sludge allows to metal recovery from biosorbent effectively as a result of desorption and to use it repeatedly in the subsequent adsorption/desorption cycles [9]. There is little literature data about metal desorption from alginate carriers and immobilized biomass in subsequent cycles of adsorption/desorption.

The research objective was to evaluate the efficiency of cadmium adsorption/desorption by alginate with the addition of PVA and by activated sludge immobilized on these carriers. The experiment range included the determination of the influence of the PVA addition on adsorption and desorption rate for alginate and of the efficiency of cyclical cadmium adsorption/desorption for alginate with PVA, and immobilized activated sludge treating urban and synthetic sewage. Hydrochloric and sulphuric acids were used as desorbing agents. Research range established should allow choosing the most effective cadmium sorbent and to determine cadmium desorption capacity depending on desorbing solutions tested.

The efficiency of metals desorption from loaded biosorbents, and the reusability of the biosorbent in repeated adsorption-desorption operations, were determined to evaluate the feasibility of applying this biosorbents in the heavy metals removal processes.

Materials and Methods
Preparation of Alginate Carriers

The following kinds of carriers were prepared: 2% alginate, 1.5% alginate with 0.5% PVA, 2% alginate with 2% PVA, and 2% alginate with 5% PVA. Sodium alginate, and sodium alginate with PVA were mixed

and dissolved in 98, 98, 96 and 93 g of distilled water, respectively. A homogenous alginate and PVA solution was dropped into the saturated boric acid with the addition of 0.05 M $CaCl_2$. Obtained granules at a diameter of 2.8 mm were left in the solution for 24 h, and then the chlorides were removed by washing with deionized water.

Preparation of Activated Sludge

Two kinds of activated sludge were used in the experiment. They were derived from laboratory cultures in SBR reactors, differed in operating parameters (Tab. 1) and wastewater composition.

Culture 1. Activated sludge (1) was grown under aerobic conditions in a reactor of 5 dm^3 volume, with synthetic wastewater of a composition given by Macaskie et al. [10]: TRIS buffer - 120 mg, $(NH_4)_2SO_4$ - 0.96 mg, disodium β-glycerol phosphate - 0.675 mg, KCl - 0.62 mg, $MgSO_4·7H_2O$ - 0.063 mg, $FeSO_4·H_2O$ - 0.00032 mg, glycerol - 0.6 mg, tap water - to 1 dm^3. Sewage was dosed to the reactor once in 24 hours, after sludge sedimentation and decantation of supernatant. Cycle length was 24 h.

Culture 2. Activated sludge (2) was grown under anaerobic-aerobic conditions in the SBR reactor at the volume of 0.32 m^3, where municipal sewage from Kortowo was supplied. Basic pollution indicators were the following: COD - 250 mg O_2/dm^3, BOD_5 - 150 mg O_2/dm^3, total Kjeldahl nitrogen - 34 mg N/dm^3, ammonium nitrogen - 22 mg N_{NH4}/dm^3, total phosphorus 7.5 mg P/dm^3. Sewage was supplied to the reactor 3 times in 24 hours. The cycle lasted 8 h.

Preparation of Activated Sludge Immobilized on Alginate

Activated sludge taken from the culture was initially thickened by sedimentation. After decantation of supernatant activated sludge was filtrated by medium filter paper. 25 g of activated sludge was supplied to the solution of sodium alginate with PVA and distilled water. It was replenished with distilled water to 100 g and then the proceedings were as in pt. 2.1.

Research on the Arrangement of Sorption and Desorption Time
Time Course of Biosorption

The biosorbent with final concentration of 40 g/dm^3 was suspended in 500 cm^3 of heavy metal solution in a

glass container and the suspension was gently agitated at room temperature. The initial cadmium concentration amounted to 50 mg Cd/dm³. Samples were taken from the solution at desired time intervals (0, 2, 4, 6, 8, 10, 15, 30, 45, 60, 90, 120 min) and they were subsequently centrifuged at 15,000 rpm for 10 min. The heavy metal concentration in the resulting supernatant was determined.

Determination of Optimal pH of Desorption

The desorption efficiency was analyzed in dependence on pH respectively with 1 M H₂SO₄ and 1 M HCl as eluants. The analysis of the pH effect: 500 cm³ of the 50 mg Cd/dm³ aqueous solution was introduced into the 1 dm³ test tubes with 40 g of sorbent and stirred on a magnetic stirrer. The pH was adjusted to 5.0, 4.0, 3.0, 2.5, 2.2 by adding respective amounts of 1 M mineral acid.

Time Course of Desorption

After biosorption experiments, the metal-loaded biosorbents were harvested from the biosorbent/metal solutions containing initially 50 mg Cd/dm³. The biosorbents concentration was 40 g/dm³. The biosorbents were then rinsed and resuspended with deionized water.

Proper amounts of 1 M H₂SO₄ were added into solutions of metal-loaded biomass to adjust the pH value to nearly 2.2. Desorption time amounted to 60 min. After gentle agitation (0, 2, 4, 6, 8, 10, 15, 30, 45, 60, 90, 120 min), samples were taken from the suspensions at designated time spans. The samples were centrifuged immediately, and the metal concentration in the supernatant was determined as described in pt. 2.3.

The constants of adsorption and desorption were determined based on the experimental data $(Q_i, t_i)_{i = 1... n}$ by the method of non-linear regression with the use of APNIELIN software (author: S. Grabowski, University of Warmia and Mazury in Olsztyn). An iteration method was used. Corrections to the determined parameters are calculated by replacing the increment of the function with its total differential, which allows a linear problem to be solved in each iteration. In order to evaluate the goodness of fit the coefficient φ^2 was used [11]. This coefficient is a quotient of the sum of squares of deviations between two experimental data (Q_i) and values $(Q(t_i))$ to the sum of squares of deviations between the experimental data (Q_i) and their average value:

$$\varphi^2 = \frac{\sum_{i=1}^{n}(Q_i - Q(t_i))^2}{\sum_{i=1}^{n}(Q_i - Q)^2} \tag{1}$$

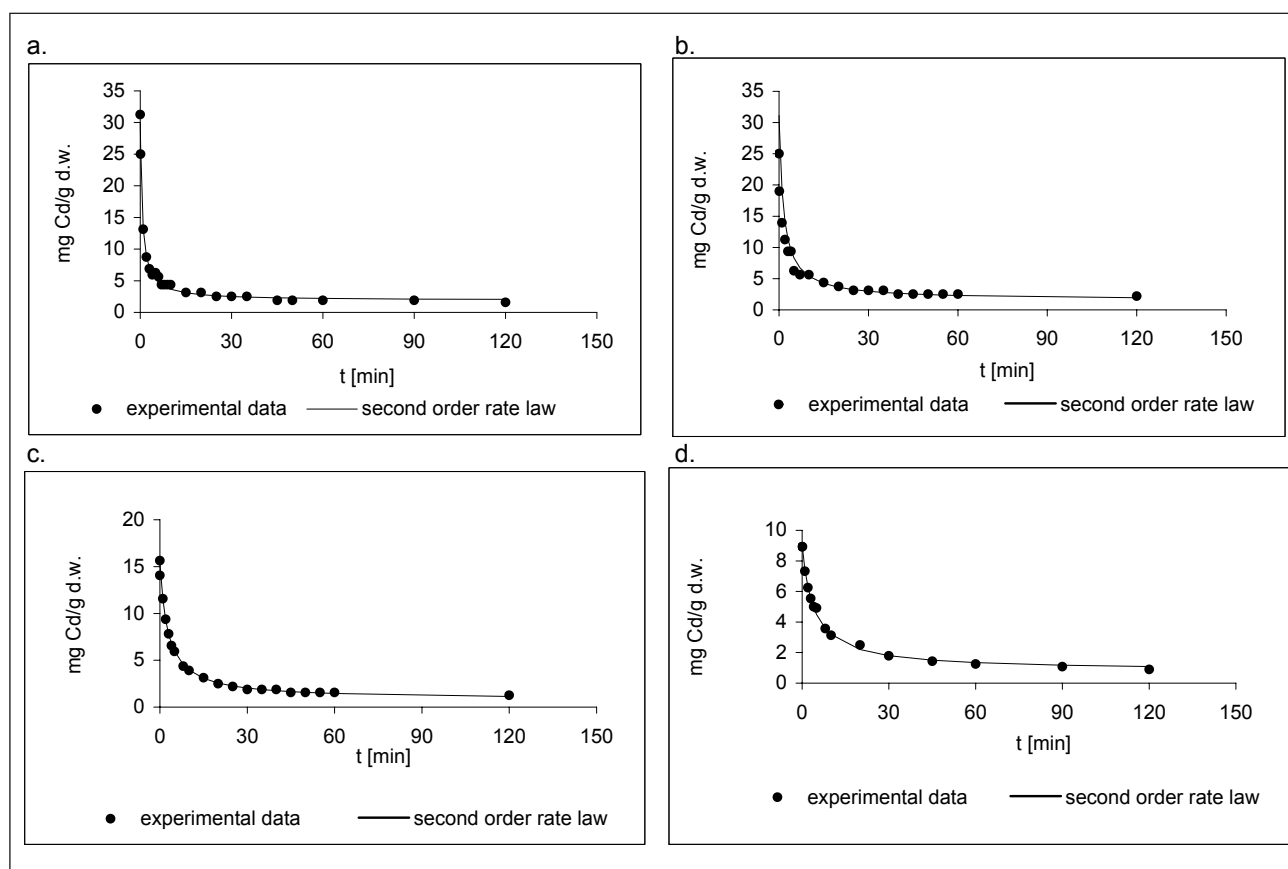If the coefficient φ^2 is closer to zero the fit is better.

Fig. 1. Kinetics of cadmium adsorption on alginate sorbents. a. alginate 2%; b. alginate 1.5% and PVA 0.5%; c. alginate 2% and PVA 2%; d. alginate 2% and PVA 5%.

Table 2. Constants of reaction rates of cadmium sorption by alginate sorbents.

Sorbent type	Rate constants of second order rate law k_s (g d.w./mg·min.)	Amount of cadmium adsorption at equilibrium $Q_{e,s}$ (mg Cd/g d.w.)	φ^2 (–)
Alginate 2%	0.053	28.0	0.0059
Alginate 1.5% + PVA 0.5%	0.023	29.5	0.0128
Alginate 2% + PVA 2%	0.025	14.6	0.0039
Alginate 2% + PVA 5%	0.030	8.2	0.0033

Research on Cadmium Desorption in Adsorption/Desorption Cycles
Adsorption-Desorption Cycle

Biosorbents: two kinds of activated sludge immobilized on alginate, alginate with PVA, and alginate carriers, i.e. sodium alginate and PVA mixture (control samples) were mixed with deionized water with the addition of 50 mg Cd/dm^3. After 45 min, the metal-loaded biosorbents were harvested, rinsed with deionized water and resuspended in deionized water. The pH of the suspensions were adjusted to around 2.2 by 1 M HCl or H$_2$SO$_4$, respectively, in order to recover metal ions. After being gently agitated for 15 min., the biosorbent suspensions were separated, and the metal concentration in the supernatant was measured. The regenerated biosorbents were again suspended in metal-containing solutions for the next adsorption run keeping neutral pH by 1 M NH$_4$OH. The adsorption/desorption steps described above were repeated several times.

Analytical Methods

Cadmium adsorption and desorption were analyzed by measuring the amount of cadmium residue in the aqueous solution using the atomic absorption method SpectrAA, Varian. The 10 cm^3 samples were centrifuged for 15 min at 12,000 rpm and the cadmium concentrations were read out from the standard curve.

Results
Adsorption and Desorption Kinetic

Time course profiles for the adsorption of Cd^{2+} by alginate 2% sorbent and alginate with the addition of PVA in the following proportions: 1.5% with 0.5%, 2% with 2% and 2% with 5% are shown in Figs. 1 a-d. In all cases, metal concentration decreased rapidly during the first 10 min., and then remained nearly constant, suggesting that the biosorption on alginate and alginate with PVA is fast. The second-order rate law based on adsorption equilibrium capacity [12] was used to estimate the rates of cadmium adsorption onto alginate sorbent:

$$\frac{dQ_{t,s}}{dt} = k_s \, (Q_{e,s} - Q_{t,s})^2 \qquad (2)$$

where:

k_s - rate constant of second order equation (g d.w. /mg Cd ·min),

$Q_{t,s}$ - amount of cadmium adsorption at time t (mg Cd/g d.w.),

$Q_{e,s}$ - amount of cadmium adsorption at equilibrium (mg Cd/g d.w.).

The constants of adsorption rate are shown in Tab. 2. From the presented data it results that adsorption constants for alginate with the addition of PVA were about 2-fold lower in comparison to alginate 2%.

Based on the research it was claimed that after 45 min. cadmium removal effectiveness was high - 94% for alginate, and alginate with PVA mixture - 92% (1.5% with 0.5%), 90% (2% with 2%) and 84%
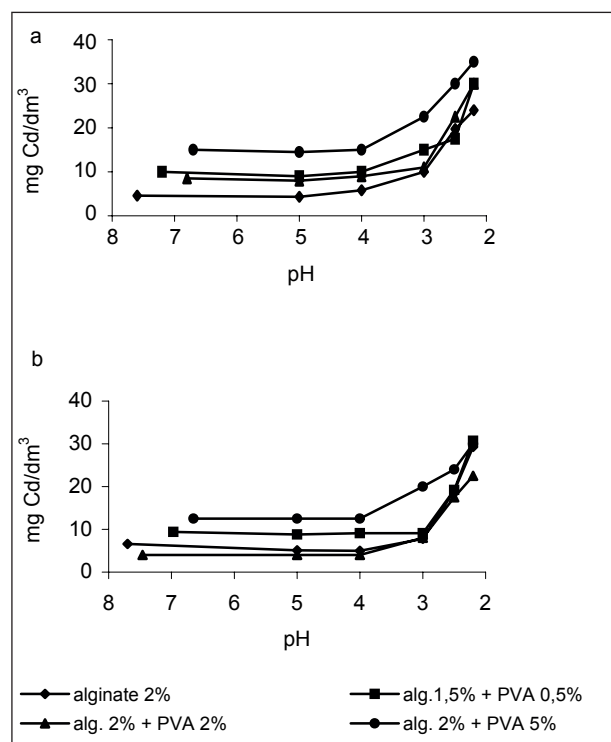

Fig.2. Effect of pH on cadmium desorption. a. 1M H$_2$SO$_4$; b. 1M HCl.

(2% with 5%), respectively. For this reason adsorption time of 45 min was admitted as sufficient for further research.

To determine what pH is required to achieve maximal desorption capacity, solutions containing metal-loaded sorbents were treated with 1 M HCl or H_2SO_4, respectively, to adjust pH to designated values. The amount of metal re1eased from the acid-treated biosorbents with different pH was then determined. Basically, metal recovery was invisible for pH over 4.0, whereas as the pH decreased the desorption efficiency increased rapidly, until it reached a value from 22.5 to 37.5 mg Cd/dm³, when pH was about 2.2 (Fig. 2 a,b). Therefore, it was concluded that in this case the optimal procedure for metal recovery is to adjust pH to approximately 2.2.

The kinetics of cadmium desorption from the heavy metal-loaded biosorbents is demonstrated in Fig. 3 a-d. It was proved that the desorption had a two-stage nature. After supplying the metal-loaded biosorbent to deionized water and adjustment pH to 2.2 (stage 1) metal was immediately released in the amount from 12.1 mg Cd/g d.w for 2% alginate to 4.0 mg Cd/g d.w. for 2% alginate with 5% PVA. After obtaining pH 2.2, further cadmium release to the solution (stage 2) occurred according to the first reaction order:

$$\frac{dQ_{t,d}}{dt} = k_d(Q_{max,d} - Q_{t,d}) \qquad (3)$$

where:

k_d - constant of cadmium desorption (min⁻¹),
$Q_{e,s}$ - amount of in the solution at time t (mg Cd/g d.w.),
$Q_{max,d}$ - maximum cadmium amount after desorption (mg Cd/g d.w.).

Experimental data and isotherms determined for stage 2 are shown in Figs. 3 a-d. It can clearly be seen that metals were desorbed very rapidly (Tab.3), and the desorption reached equilibrium within 5-15 min.

The proportions between cadmium amount released in stage 1 and 2 are shown in Fig. 4, and initial reaction rate in Fig. 5. From the obtained data it results that after pH adjustment to 2.2 the most cadmium (78.8%) was released from 2% alginate.

The conducted tests were the basis of determination of desorption time in further research of cyclical adsorption/desorption. It was assumed that desorption time would amount to 15 min. After this time an equilibrium desorption state was obtained for all tested sorbents. Equilibrium desorption efficiency was lower in comparison to adsorption efficiency and amounted to 55.7% for alginate and 73.9% (1.5% with 0.5%), 76.2% (2% with 2%) and
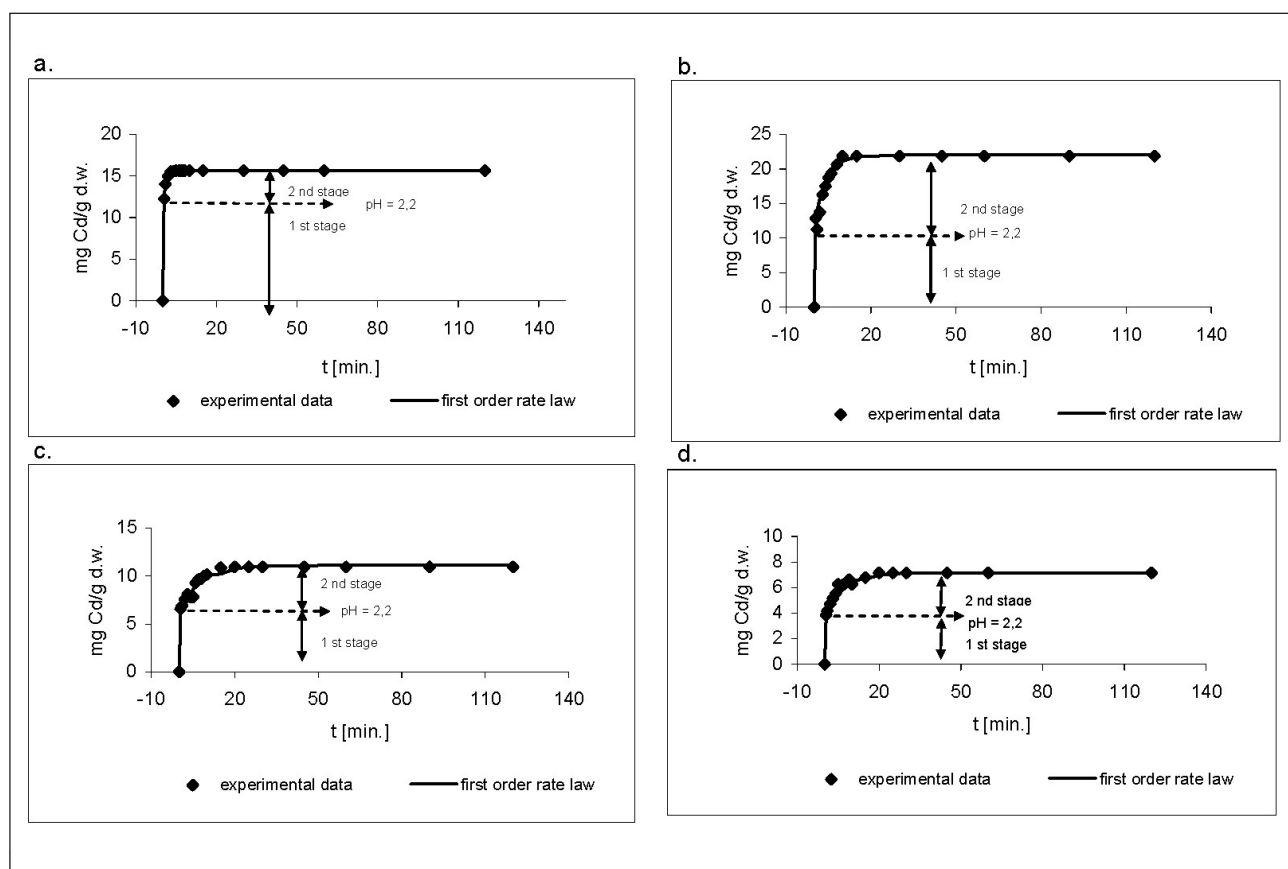

Fig. 3. Kinetics of cadmium desorption from alginate sorbents. a. alginate 2%; b. alginate 1.5% and PVA 0.5%; c. alginate 2% and PVA 2%; d. alginate 2% and PVA 5%.

Table 3. Constants of reaction rates of cadmium desorption by alginate sorbents.

Sorbent type	Amount of cadmium released from sorbent during first desorption stage $Q_{0,d}$ (mg Cd/g d.w.)	Constant of desorption rate during second stage k_d (1/min.)	Amount of cadmium released from sorbent during second desorption stage $Q_{max,d} - Q_{0,d}$ (mg Cd/g d.w.)	φ^2 (–)
Alginate 2%	12.30	1.30	3.30	0.0029
Alginate 1.5% + PVA 0.5%	12.40	0.23	9.40	0.0438
Alginate 2% + PVA 2%	6.56	0.17	4.56	0.0540
Alginate 2% + PVA 5%	3.86	0.20	3.29	0.0271

87.3% (2% with 5%) for alginate with PVA mixture, respectively.

Adsorption/Desorption Cycles

Repeated adsorption/desorption (A/D) operations were performed to examine the reusability and efficiency of metal recovery from the biosorbents. As opposed from the adsorption, which occurred with high and almost constant efficiency in the subsequent cycles, cadmium desorption was diverse. For some sorbents (Fig. 6), the amount of desorbed cadmium in the cycle was higher than adsorbed. This was possible because part of cadmium was not desorbed in the initial cycles and remained accumulated in the sorbent.

Determination of the adsorption and desorption efficiency in the subsequent cycles allowed to divide tested sorbents and biosorbents for 3 groups.

For sorbents in group 1, cadmium desorption in the initial cycles was clearly lower than adsorption, and increased from third or fourth cycle. It was found that the efficiency of cadmium desorption was lower than desorption efficiency after four A/D cycles. The cadmium desorption was found to increase as the number of A/D cycles increased. Cadmium amount accumulated in sorbent increased initially, and next decreased (Fig. 6). Such behaviour was observed for 2% alginate, 1.5% alginate with 0.5% PVA, and activated sludge immobilized on these carriers (Tab. 4).
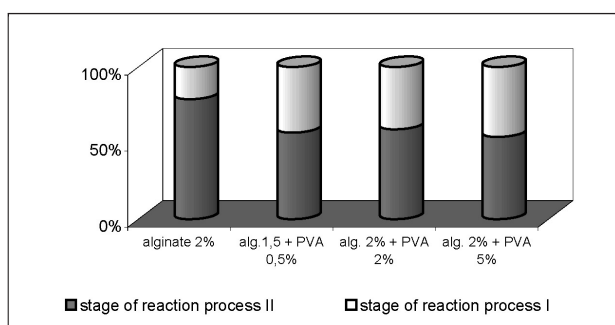
For sorbents in group 2, cadmium desorption in the initial cycles was lower than sorption, and next established on the constant level. The amount of cadmium accumulated in the initial cycles increased, and in the following ones it remained at a constant (or almost constant) level (Fig. 7). Such behaviour predominated in the case of 2% alginate with 2% PVA, and activated sludge (1) and (2) immobilized on this carrier, and activated sludge (1) immobilized on 2% alginate with 5% PVA.

For sorbents in group 3, cadmium desorption was less effective than adsorption in all cycles; metal was accumulated successively in the sorbent (Fig. 8). Such behaviour occurred in the case of 2% alginate with 5% PVA, and activated sludge (2) immobilized on 2% alginate with 5% PVA.

In order to compare sorbents and biosorbents tested, the total amount of cadmium adsorbed and desorbed in all cycles was calculated. Obtained values are shown in Table 4. The experiment proved that in the case of adsorption the amount of cadmium adsorbed was almost identical, independently if sulphuric or hydrochloric acids were used as desorption agents. For this reason the mean values of the percentage of cadmium remained in the sorbent after last cycles of sorption/desorption for both acids are presented in Table 4. It was claimed that the amount of cadmium remained after last adsorption/desorption cycle was dependent on desorbing agent. However, a clear dependence between sorbent kind and desorption efficiency for a given acid was not obtained. Only in the case of 2% alginate with

Fig.4 Amount of cadmium released to the solution in I and II desorption stage of reaction process (%).
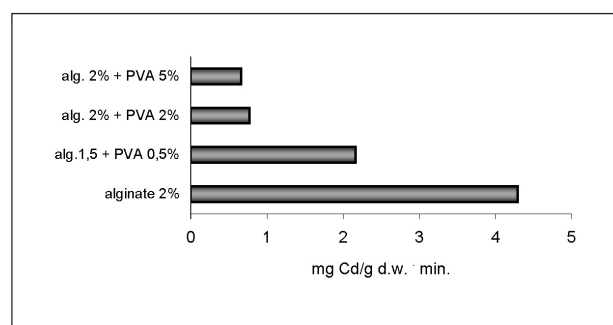

Fig.5 Initial desorption rate determined from the first-order rate law in reaction process II.
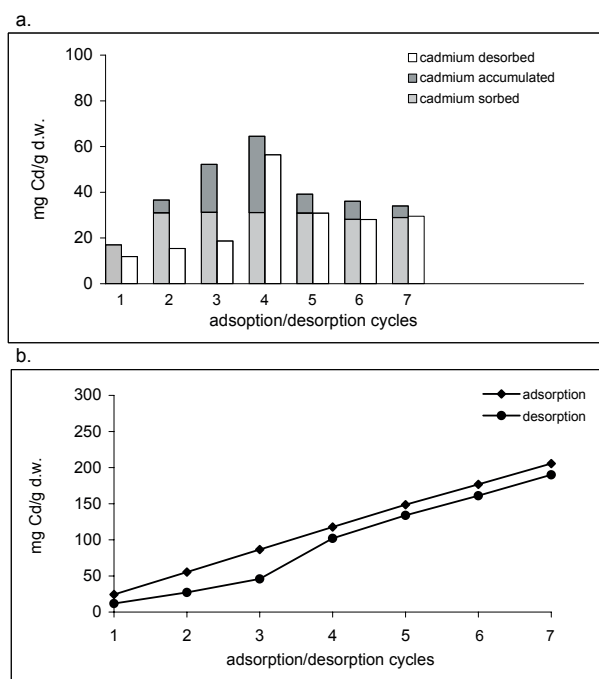
Fig.6. Cyclical cadmium adsorption/desorption from activated sludge (1) immobilized on alginate 1.5% and PVA 0.5% by H_2SO_4 calculated as: a. amount of cadmium sorbed, desorbed and accumulated in the cycle; b. sum of the amount of cadmium sorbed and desorbed in subsequent cycles.
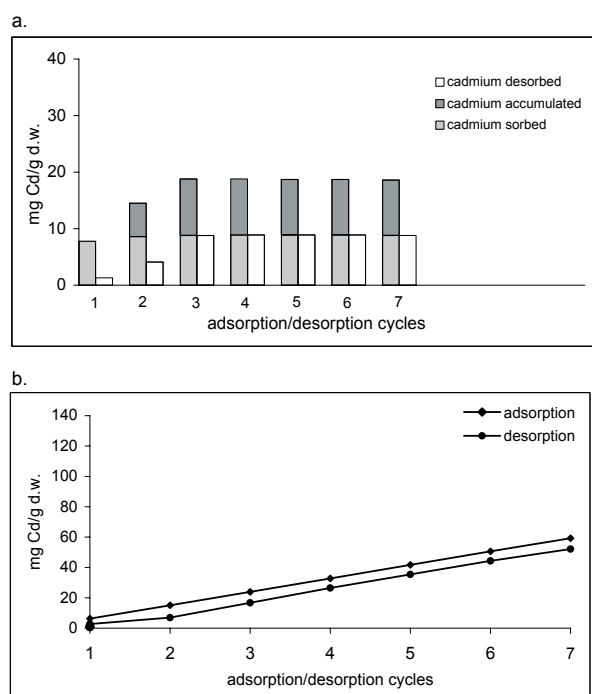
5% PVA and activated sludge immobilized in this carrier desorption with sulphuric acid was more effective.

During the cyclical adsorption/desorption most of the cadmium was sorbed by 2% alginate with 5% PVA and activated sludge (2) immobilized on this carrier - about 260-270 mg/g d.w. Although in these carriers a relatively large amount of cadmium remained in the last cycle. Residual sorbents cumulated from 169 to 220 mg of cadmium.

Cadmium was desorbed most effectively from the biosorbent containing activated sludge (1) immobilized on alginate and PVA in the following proportions: 1.5% with 0.5% and 2% with 2%, when HCl was used as desorbing agent.

Discussion

Research showed that cadmium adsorption on alginate sorbents obeys a second- order rate law, whereas desorption was more complex and proceeded in two stages. Cadmium sorption rate for alginate sorbents, similar to desorption, decreased by the increasing amount of poly(vinyl) alcohol.

Based on the results of cadmium cyclical adsorption/desorption by mineral acids for alginate sorbents and immobilized activated sludge it can be concluded that the effectiveness depended on activated sludge and carrier kind, and on desorption agents.

Fig.7. Cyclical cadmium adsorption and desorption from activated sludge (1) immobilized on alginate 2% and PVA 5% by H_2SO_4 calculated as: a. amount of cadmium sorbed, desorbed and accumulated in the cycle; b. sum of the amount of cadmium sorbed and desorbed in subsequent cycles.
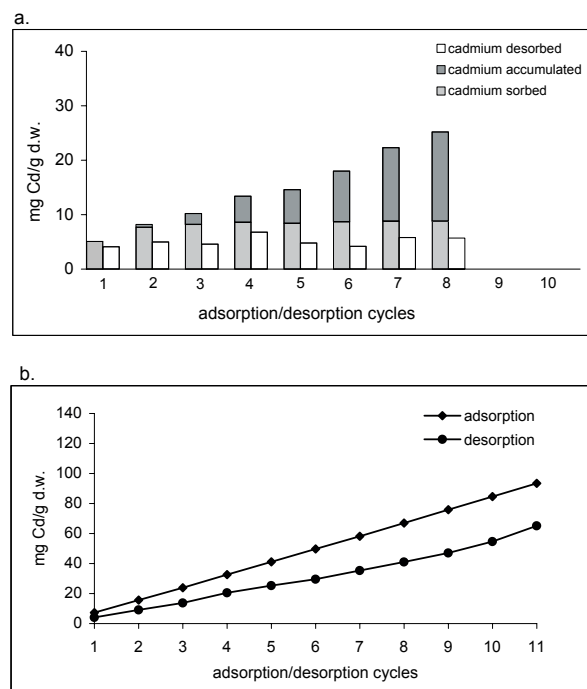

Fig.8. Cyclical cadmium adsorption and desorption from activated sludge (2) immobilized on alginate 2% and PVA 5% by HCl calculated as: a. amount of cadmium sorbed, desorbed and accumulated in the cycle; b. sum of the amount of cadmium sorbed and desorbed in subsequent cycles.

Table 4. Characteristics of cyclical sorption and desorption of tested sorption agents.

Sorbents		Number of cycles	Sorption [mg Cd]	% of cadmium remained in the sorbent after last cycles of sorption/desorption	
				H_2SO_4	HCl
Group 1	alginate 2%	7	171.1	12.3	28.0
	alginate 2% + activated sludge (1)	9	219.7	23.9	7.1
	alginate 1,5% + PVA 0,5%	8	189.0	7.0	8.8
	alginate 1,5% + PVA 0,5% + activated sludge (1)	7	166.7	11.2	1.2
	alginate 1,5% + PVA 0,5% + activated sludge (2)	9	212.4	7.2	7.8
Group 2	alginate 2% + PVA 2%	7	170.8	7.2	15.9
	alginate 2% + PVA 2% + activated sludge (1)	8	169.4	2.3	1.7
	alginate 2% + PVA 2% + activated sludge (2)	7	192.6	9.8	13.0
	alginate 2% + PVA 5% + activated sludge (1)	7	166.5	6.6	11.7
Group 3	alginate 2% + PVA 5%	11	267.2	18.4	30.3
	alginate 2% + PVA 5% + activated sludge (2)	11	259.8	13.0	22.5

Research proved that in the subsequent adsorption/desorption cycles cadmium biosorption was the lowest in the first cycle, and next occurred with high and almost constant effectiveness. Similar observation was reported as regards the improvement of metal adsorption capacity through regeneration of the biomass. Using *Pseudomonas putida* II-11 as the biosorbent, Wong et al. [13] found that the adsorption capacity of Cu was enhanced after being treated with HCl. They attributed the behaviour to HCl induced structural changes which increased surface binding of the metal. Similarly Huang and Huang [14] proved that acid-washed *Aspergillus oryzae* mycelia shows much higher metal removal capacity than untreated mycelia. From the X-ray EDA spectra *A. oryzae* mycelium after being acid-washed contains a higher percentage of surface nitrogen. This indicates that acid treatment may dissolve polysaccharide compounds in the outer layer of the fungal wall and therefore produce additional binding sites (amino group). The capacity of metal adsorption increased by increasing the concentration of acid solution. This implies that the acid treatment on the fungal mycelia results in not only a physical cleaning or washing-out, but also in some chemical transformation.

During the experiment it was stated that desorption efficiency depended on the desorbing agent. The amount of cadmium remained changed in a relatively wide range from 1.2 to 30.3%.

Oliver, Carey after Wong et al., [13] collected samples of digested sludge from eight wastewater treatment plants in southern Ontario. Acid leaching experiments were carried out with either sulphuric or hydrochloric acid until pH of 1.5 was reached. It was proved that for the cadmium concentration about 57 mg Cd/kg, desorption effectiveness was comparable and amounted to 52 and 55%, respectively.

The cadmium recovery from metal-loaded biosorbents was approached by utilizing various desorption agents, including HCl, H_2SO_4, $NaHCO_3$ [15, 16], EDTA and Na_2SO4 [17]. Zhang et al. [18] claimed that from among eight eluanting agents containing competing counter-ions, proton exchangers and complexing agents were used for desorption of metal ion-loaded *R. nigricans*. HCl had the best desorption efficiency among the chemical reagents tested.

The amount of cadmium desorbed in the subsequent adsorption/desorption cycles was diverse. The research of cadmium adsorption and desorption conducted for pure cultures *Pseudomonas aeruginosa* PU21 by Chang et al. [19] proved that in the case of cadmium the adsorption capacity increased in the next cycles, whereas the desorption capacity remained on the almost constant level. In this case the enhancement in Cd adsorption may be related to the observation that, after each A/D cycle associated with Cd, the cell particles became finer. Thus, the increase in surface area of the biomass may be a cause of the increase in Cd adsorption capacity.

The amount of adsorption and desorption cycles changed depending on carrier and activated sludge kind, and counted from 7 to 11. The most cycles were obtained for 2% alginate with 5% PVA and activated sludge (2) immobilized on this carrier. Obtained diversity in adsorption capacities can be explained by the difference in the chemical/physical structures between the alginate and alginate with PVA. The alginate sorbents were formed by cross linking between the alginate and calcium ions. The gel formation of PVA solution was mainly attributed to

the hydrogen bonds between PVA skeletons and the water molecules [20].

On the ground of the experiment it can be affirmed that during the cyclical adsorption and desorption from among the sorbents the highest amount of cadmium was sorbed by 2% alginate with 5% PVA, and from among the biosorbents 2% alginate with 5% PVA with activated sludge (2), which was connected with their big durability. Among alginate sorbents with PVA cadmium was desorbed the most effectively by hydrochloric acid from 2% alginate with 2% PVA, and among biosorbents from activated sludge (1) immobilized on 1.5% alginate with 0.5% PVA.

Conclusions

1. Cadmium adsorption on alginate sorbents obeys a second-order rate law. The constants of reaction rate decreased by increase of PVA amount in alginate from 0.036 dm^3/mg·min^{-1} (2% alginate) to 0.005 dm^3/mg·min^{-1} (2% alginate with 5% PVA).
2. Cadmium desorption was two-stage. In the first stage most cadmium released from 2% alginate. In the second stage cadmium desorption obeys a first-order rate law.
3. During the cyclical adsorption/desorption the sorption efficiency in the subsequent cycles stayed on the constant level, whereas the desorption efficiency was diverse. 2% alginate with 5% PVA and 2% alginate with 5% PVA with activated sludge (2) had the highest capacity of cadmium cumulation.
4. In the cyclical sorption/desorption alginate sorbents could be used from 7 to 11 cycles, and then the structure loosing and disintegration were observed. 2% alginate with 5% PVA and 2% alginate with 5% PVA with activated sludge (2) had the highest durability.

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