

CYCLICAL METAL ADSORPTION AND DESORPTION THROUGH SLUDGE IMMOBILIZED IN CHITOSAN MEDIA

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Abstract

In this research, a cyclical adsorption/desorption of cadmium and zinc from solutions containing a single metal or its mixture in ratio of 1:1 and 1:2 using immobilized activated sludge in the chitosan (ASC) was examined. In the adsorption studies, the optimal dose of ASC was 4 g/L. The highest desorption efficiency was achieved for 1M HNO₃. Both adsorption and desorption occurred in accordance with a pseudo-second order reactions which is confirmed by R² values. Mass of zinc adsorbed and desorbed in one cycle from a solution containing a single metal was 0.78 and 0.40 mmol/g d.w. when cadmium was lower (respectively 0.41 and 0.21 mmol/g d.w.). In subsequent cycles, both metals were adsorbed and desorbed at a lower efficiency. The highest efficiency of desorption was observed for a mixture of Cd:Zn in the ratio of 1:1 and 1:2, respectively 86% and 89% of cycle 1, whereas for the zinc it was 70% and 53%. Desorption efficiency of both metals and its mixtures, in subsequent cycles gradually decreased.

Key words: immobilization, chitosan, adsorption, desorption, heavy metal

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1. Introduction

Progressive urbanization and industrialization resulted in generation of large quantities of wastewater that contain significant concentrations of toxic pollutants including heavy metals. In practice, physical, chemical and biological processes are used for the removal of pollutants from industrial wastes before being discharged into the environment. These processes are in many cases ineffective and expensive, when impurities are present in low concentrations [1]. Among the methods used for removing metals from wastewater and contaminated waters, sorption processes are particularly interesting, mainly due to the possibility of using a wide variety of chemical sorbents and biosorbents for this purpose.

Biosorbents, which can be used on an industrial scale should be easily accessible and cost-effective, e.g. industrial waste, which can be obtained free of charge or for a low fee; organisms readily available in large quantities in nature; and organisms which can be easily grown for biosorption purposes [2].

Algae [3, 4], plant materials (shells, bark, sawdust) [5-7] and the animal materials, such as chitin and chitosan [8-10], as well as the sludge from wastewater treatment [11] were tested as biosorbents.

Activated sludge is a biosorbent, consisting of different types of microorganisms, mainly bacteria, fungi, yeasts, algae and protozoa. It is easily accessible in the sewage treatment plant and has a high adsorption potential [12, 13]. Removal of metal ions involving such diverse biomass composition is made possible by two types of processes: biosorption independent of cell metabolism and metals actively transported into cells. In the first case, appropriate functional groups are responsible for the metal ions binding (carboxyl, hydroxyl, amino, phosphate, sulfhydryl, thioether, carbonyl, imidazole, sulfate, sulfonate), occurring on the surface of the cell wall, cell membrane or within exopolymers produced by cells [14], and the process itself of binding metal ions occurs due to the phenomena of ion exchange, complexing, chelating and electrostatic interactions [15].

Biomass used in biosorption may be alive or dead. The use of dead biomass is a preferred alternative for biosorption metal due to the lack of limitations related to their toxicity, no requirements for the delivery of nutrients for the biomass cell growth, easy recovery and reuse of the biomass, the ability to easily immobilize dead cells and easier mathematical modeling of the metal removing process [16].

The use of biosorption properties of biomass in the freely suspended form is limited due to the low mechanical strength and dispersion occurring during the sorption. Immobilizing biomass eliminates these problems and enhances the application capabilities. In practice, immobilized biosorbents should be characterized by high metals adsorption efficiency from solutions and the easy desorption using inexpensive desorbents.

A review of the literature suggests that the chitosan is not only a good carrier used for biomass immobilization, but also an effective metal adsorbent [17-19].

For this reason, in the work on the biomass immobilization, a waste product which was excess activated sludge after methane fermentation from sewage treatment plant in Olsztyn, chitosan was used to obtain a durable, inexpensive and efficient biosorbent for the removal of cadmium and zinc and its mixtures from aqueous solutions. Previous studies have demonstrated the high effectiveness of this biosorbent in removing cadmium and zinc from aqueous solutions, confirmed by the high adsorption capacity determined from the Sips model- 216 and 188.3 mg/g d.w. respectively [20]. This prompted the authors to use this biosorbent in cyclic adsorption/desorption of cadmium and zinc, and to determine the operating conditions of both processes. The conducted experiments allowed the determination of constants in the kinetic equations of adsorption and desorption, which is an important element in the design of metal recovery processes using biotechnological methods.

2. Materials and Methods

2.1 Preparation of immobilized biomass (ASC)

The experiment was conducted with excess activated sludge after methane fermentation obtained from a wastewater treatment plant in Olsztyn. The collected sludge was dehydrated by double rinsing with acetone and centrifugation for 10 min at 4500 rpm, and dried in a water bath at a temperature of 50°C for 48 h. The dried sludge was ground in a porcelain mortar and sieved through a screen with a mesh diameter of 0.01 mm.

Experiments were conducted with chitin of krill, obtained from the Marine Fish Institute in Gdynia, with a dry matter content of 95.64% and ash content of 0.32%. Chitin was modified according to the methodology described in [21]. Its modification included rinsing with distilled water and hydrochloric acid, followed by cooking with a potassium base in order to loosen its structure, elute calcium and magnesium ions and residues of lipids as well as to increase the degree of deacetylation.

A weighted portion of chitin (3.3 d.w.) was dissolved in 100 g of 5% CH₃COOH for 24h, then 3.3g of activated sludge were added, and homogenous suspension was prepared that was next instilled into 10% NaOH. The formed beads (3.5 mm in diameter) were left for 24h in a solution for complete gelling. Afterwards, they were rinsed with deionizer water till neutral pH value has been reached.

2.2 Dose of ASC

In order to determine the optimal biosorbent dose used for testing, patterns of cadmium and zinc in the water (pH = 9.0) at a concentration of 0.09 and 1.53 mmol/L were prepared in a flask with a capacity of 100 mL. The test dose range was between 1 to 8 g d.w./L. The samples were shaken on a shaker for 2 hours and the concentration of metals left in the solution after adsorption was determined.

2.3 Desorbent dose

Examination of the influence of nitric acid concentration on the release of cadmium and zinc from the biosorbent was preceded by adsorption of metals in a concentration of 0.09 and 1.53 mmol/L on a magnetic stirrer while maintaining pH = 9.0 using NaOH and HNO₃ for 12 hours. After the adsorption, biosorbent was rinsed with distilled water several times, dried and poured HNO₃ solution at the appropriate concentration. The samples were shaken on a shaker for 2 hours and the concentration of metals released to the solution after desorption was determined.

All the necessary chemicals used in the experiments were of analytical grade and obtained from Sigma-Aldrich Poland.

2.4. Examination of metal adsorption/desorption kinetics in cycles

Biosorbent at 0.4 g dw / L was introduced into the reaction vessel with a capacity of 100 mL, followed by addition of solutions of the single metals: Cd (0.18 mmol/L), Zn (3.06 mmol/L) or a mixture of metals in a ratio of Cd:Zn 1:1 and 1:2. The reaction vessel was placed on a magnetic stirrer. Then, in the interval from 1 to 360 min. samples were taken and the concentration of metals remaining in the solution was determined. Biosorbent saturated with metal, after filtration and washing with distilled water was placed in the reaction vessel, which was introduced to 100 ml mol/L HNO₃ solution. Then, in the interval from 1 to 120 min. samples were collected and the concentration of metals remaining in the solution was determined.

After one cycle biosorbent grains were filtered, washed with deionized water and then poured over with 100 mL of the single metal solutions or its mixtures. Subsequent cycles of

adsorption maintained at pH = 9.0 and pH = 2 for desorption with mol/L NaOH and mol/L HNO₃.

2.5. Metal solution preparation

Analytical grade standard solutions of Cd and Zn for AAS (1,000 g/dm³) obtained from Sigma-Aldrich Poland were used as stock solutions. All working solutions were prepared by diluting the stock solutions with deionizer water. The concentrations of metal ions were determined by atomic adsorption spectrometer (AAS) AA280FS (Varian).

3. Theory

The quantity of metal adsorbed from the solution was determined based on a change in the concentration of metal left in the solution and calculated from the following equation:

$$Q = \frac{C_0 - C_s}{m} \quad (1)$$

The quantity of desorbed metal was calculated from the following equation:

$$Q_1 = \frac{C_d}{m} \quad (2)$$

where:

Q	– weight of metal adsorbed in biosorbent	(mmol/g d.w.)
Q_1	– weight of metal desorbed from biosorbent	(mmol/g d.w.)
C_0	– initial concentration of metal in the solution	(mmol/L)
C_s	– metal concentration in the solution after adsorption	(mmol/L)
C_d	– metal concentration in the solution after desorption	(mmol/L)
m	– biosorbent concentration	(g d.w./L)

3.1. Kinetic model

Reaction rate constants were calculated with Lagergren's equation, which consists of correlations between the mass of metal desorbed from 1 g of adsorbent and time, and is defined as the pseudo-n-order reaction. The order of reaction was determined by adopting determination coefficients (R^2) as selection criteria.

Model of pseudo-first-order reaction:

$$\frac{dQ_t}{dt} = k_{1s} (Q_s - Q_t) \quad (3)$$

Model of pseudo-second-order reaction:

$$\frac{dQ_t}{dt} = k_{2s} (Q_s - Q_t)^2 \quad (4)$$

Desorption rate constants of single metals were calculated in an analogous way, also based on the pseudo-first-order and pseudo-second-order equation:

$$\frac{dQ_t}{dt} = k_{1d} (Q_d - Q_t) \quad (5)$$

$$\frac{dQ_t}{dt} = k_{2d}(Q_d - Q_t)^2 \quad (6)$$

where:

- Q_t – weight of metal adsorbed by the biosorbent in a time unit (mmol/g d.w.)
- Q_s – weight of metal adsorbed in the state of equilibrium (mmol/g d.w.)
- Q_d – weight of metal desorbed in the state of equilibrium (mmol/g d.w.)
- k_{1s} – rate constant of pseudo-first-order adsorption (1/m)
- k_{2s} – rate constant of pseudo-second-order sorption (g d.w./mmol·min)
- k_{1d} – rate constant of pseudo-first-order desorption (1/m)
- k_{2d} – rate constant of pseudo-second-order desorption (g d.w./mmol·min)
- t – time (min)

4. Results and discussion

4.1. ASC dose

The results of studies on identifying the optimum dose of the sorbent to remove metals from an aqueous solution are shown in Figure 1.

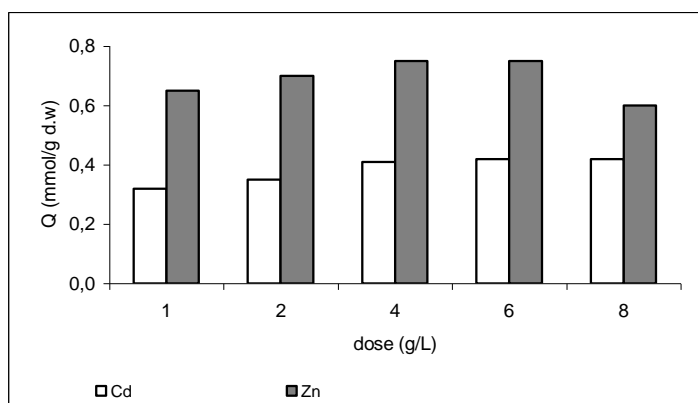


Figure 1. The mass of metal adsorbed at various doses of biosorbent

Studies have shown that the increase in biosorbent dose from 1 to 4 g/L led to increased removal of cadmium from 0.32 to 0.41 mmol/g d.w. An increase in the dose to 8 g/L did not improve the adsorption efficiency. In the case of zinc, increase of metal adsorption in the range of 1 to 6 g/L has also been observed and was respectively 0.65 and 0.75 mmol/g d.w. However increasing the biosorbent dose up to 8 g/L resulted in a reduction in weight of the zinc removed to 0,6 mmol/g d.w.

Dose of biosorbent is a parameter strongly influencing the efficiency of biosorption. The increase in biomass concentration generally increases the amount of adsorbed metal because of the greater surface of biosorbent, which increases the number of binding sites [22]. On the other hand, the amount of the adsorbate in solution per biosorbent weight unit decreases with increasing biosorbent dose, which can cause complex interactions. An important factor in high doses of adsorbent is a shortage of the metal in the solution to provide complete coverage of active sites available in biosorbent, which usually results in low efficiency [23].

4.2. Desorbent dose

The influence of the dose of desorbing agent on the amount of cadmium and zinc released from biosorbent was examined. Fig. 2 shows the relationship between the amount of released metals according to the dose of nitric acid.

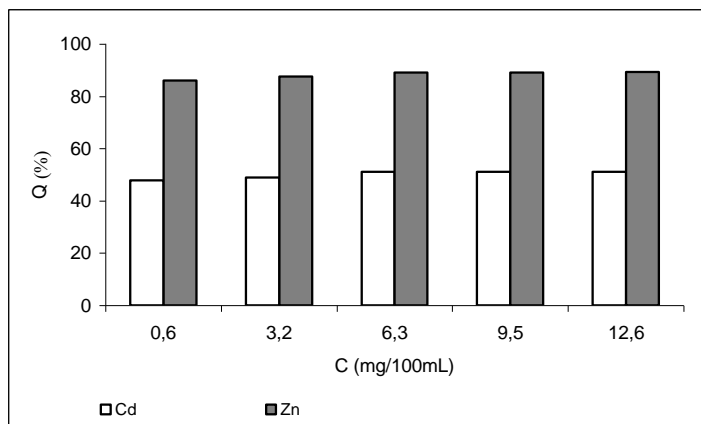


Figure 2. Effectiveness of metals leaching from biosorbent depending on the concentration of nitric acid

Experimental data suggests that the tested concentration range allowed to determine the optimal dose of nitric acid i.e. the dose above which the efficiency of the process did not increase. Taking into account the degree of metals removal with the ASC: 51% for cadmium and 89% for zinc, the dose of 6.3 g per 100 mL (mol/L solution) was considered optimum.

Kuczajowska-Zadrożna and Filipkowska [24] achieved similar results in studies on desorption of cadmium, zinc and copper from immobilized activated sludge in a mixture of alginate and poly(vinyl alcohol). At the same concentration of nitric acid designated as the optimum dose efficiency of leaching cadmium and zinc was respectively 64 and 67%. However, in the study on desorption of cadmium from citrus peels [25] obtained higher efficiency of leaching metal from biosorbent after 120 min. of desorption for 0.1 mol/L HNO_3 (98%) than 1.0 mol/L HNO_3 (80%).

4.3. Adsorption/desorption kinetics of metals in cycles

In order to determine the technological parameters required for designing systems for the removal of metals from wastewater by adsorption it is necessary to know the speed of the process.

Experimental data showing the mass (Q_s) of the single metals and its mixtures adsorbed on the ASC according to the time is shown in Fig. 3. Analysis of the experimental data showed that the shortest time to reach equilibrium concentration (120 min.) for adsorption of cadmium in the ASC was obtained in the case of a single metal and its mixtures with zinc in a ratio of 1: 1 in cycle 1 and the load removed was respectively 0.40 and 0.32 mmol/g d.w. In cycles 2 and 3, doubling of the time for achieving equilibrium concentration was observed (Figure 3 a, b). After the same time, i.e. 240 min. adsorption equilibrium was observed for a mixture of Cd:Zn ratio of 1:2 in all the cycles (Fig. 3c). Time to reach equilibrium for zinc and its mixtures with cadmium was significantly longer in cycle 1 (270 min.), whereas in cycles 2 and 3 was shorter for 90 minutes and the removed load was in a range from 0.07 to 0.15 mmol/g d.w. (Fig. 3 d, e, f).

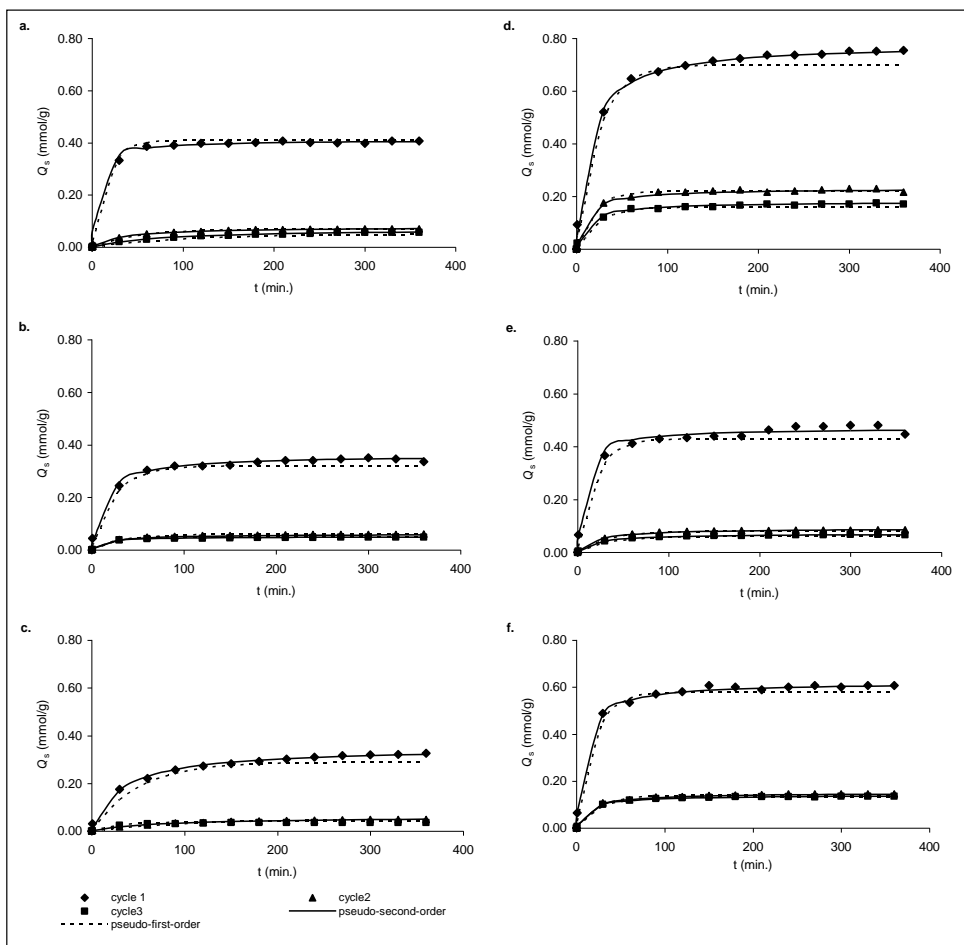


Figure 3. Relationships between the mass of adsorbed metals and time of adsorption: a. Cd, b. Cd:Zn (1:1), c. Cd:Zn (1:2), d. Zn, e. Zn:Cd (1:1), f. Zn:Cd (2:1).

Deng et al. [26] in the study of adsorption of cadmium and zinc on the aquatic plant powder achieved equilibrium concentration in a much shorter period of time (15 min.) but the (load of cadmium and zinc removed) was significantly lower. It was amounted 0.014 mmol/g d.w. (Cd) and 0.030 mmol/g d.w. (Zn) for *Ruppia maritima* and 0.017 mmol/g d.w. (Cd) and 0.020 mmol/g d.w. (Zn) for *Echinodorus amazonite*.

Evaluation of the effectiveness of cyclical adsorption and desorption was to determine the kinetics of the process, i.e. the order of reaction and rate constants. The obtained values of kinetic constants, i.e. the rate constants of pseudo-first (k_{1s}) and pseudo-second-order (k_{2s}) and the mass of metal adsorbed at equilibrium (Q_s) for the individual metals, as well as its mixtures are shown in Table 1.

Table 1. Values of kinetic constants of adsorption from solutions of single metals and from their mixture

Metal ions	Pseudo-first-order								
	k_{1s} (1/min)			Q_s (mmol/g d.w.)			R^2		
	Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2	Cycle 3
Cd	0.06	0.02	0.01	0.41	0.07	0.05	0.9994	0.9974	0.9964
Cd 1:1	0.04	0.03	0.05	0.32	0.06	0.05	0.9959	0.9966	0.9969
Cd 1:2	0.02	0.01	0.03	0.29	0.05	0.04	0.9931	0.9979	0.9963
Zn	0.04	0.05	0.04	0.70	0.22	0.16	0.9961	0.9974	0.9948
Zn 1:1	0.05	0.03	0.03	0.43	0.08	0.06	0.9916	0.9984	0.9965
Zn 2:1	0.05	0.04	0.04	0.58	0.14	0.13	0.9969	0.9954	0.9984
	Pseudo-second-order								
	k_{2s} (mg/g·min)			Q_s (mmol/g d.w.)			R^2		
	Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2	Cycle 3
Cd	0.49	0.40	0.19	0.41	0.07	0.07	0.9961	0.9995	0.9988
Cd 1:1	0.23	0.88	1.89	0.36	0.06	0.05	0.9979	0.9997	0.9989
Cd 1:2	0.09	0.23	1.58	0.35	0.05	0.04	0.9979	0.9983	0.9986
Zn	0.09	0.40	0.44	0.78	0.08	0.12	0.9987	0.9987	0.9975
Zn 1:1	0.33	0.56	0.75	0.47	0.15	0.07	0.9997	0.9991	0.9996
Zn 2:1	0.19	0.46	0.58	0.62	0.15	0.14	0.9994	0.9989	0.9992

Based on the determined constants (Tab. 1) it can be concluded that in the case of a single metal or a mixture thereof for the ASC adsorption occurred according to the pseudo-second-order reaction which is confirmed by the calculated R^2 value (0.9961- 0.9996) and the calculated values Q_s are very close to the experimental data (Fig. 4).

Similarly, [27] in the kinetic studies of adsorption of Co (II) on the magnetic chitosan and [28] adsorbing Cu (II) on a porous modified chitosan it was shown that the equation of pseudo-second-order best describes the experimental data.

Greater adsorption of individual metals and its mixtures was observed in all cycles for zinc as compared to cadmium. The effect of addition of the second metal caused a decrease in adsorption, which has been observed particularly in the cycle 1 of zinc, where Q_s of zinc amounted to 0.78 mmol/g d.w. and the for the mixture of Zn 1:1 and 2:1, 0.47 and 0.62 mmol/g d.w, respectively. However the reaction rate constants (k_{2s}) for the mixture of metal were particularly better in cycle 3.

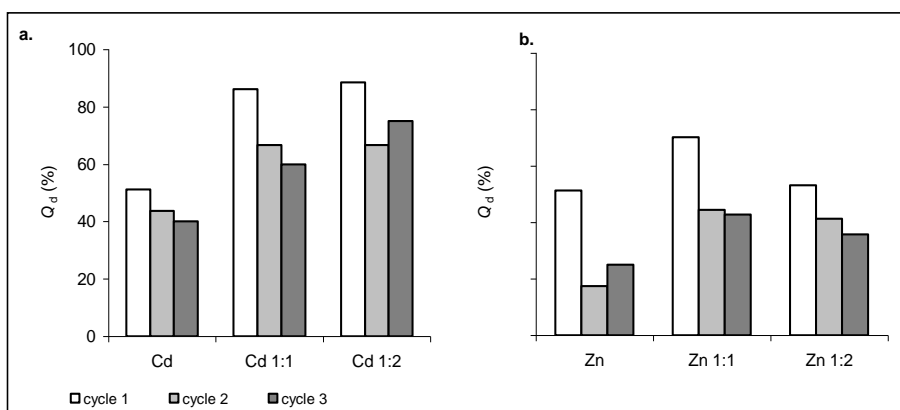
The obtained values of kinetic constants for the desorption of individual metals and its mixtures are shown in Table 2. On the basis of the values of R^2 (0.9895 - 0.9991), it was found that the process of desorption of metal with ASC occurred according to the kinetics equation of the pseudo-second-order. This was also confirmed by the research on desorption of Cu with selected calcareous soils as well as Pb and Cd with zeolite [29-30].

The results showed that, as in the adsorption, the mass of zinc released from the ACS from a single solution and its mixture is equal to, or greater than cadmium for all cycles. The desorption process occurred much faster than adsorption as evidenced by the high values of the constants (k_{2d}) within the range of 2.54 to 51.1 mmol/g·min for Cd, and from 1.45 to 17.04 mmol /g ·min for zinc.

Table 2. Values of kinetic constants of single and mixture metals desorption from solutions

Metal ions	Pseudo-second-order								
	k_{2d} (mmol/g·min)			Q_d (mmol/g d.w.)			R^2		
	Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2	Cycle 3
Cd	20.66	10.05	7.10	0.21	0.03	0.03	0.9894	0.9985	0.9975
Cd 1:1	5.83	34.9	51.10	0.31	0.04	0.03	0.9875	0.9986	0.9917
Cd 1:2	2.54	24.47	29.20	0.31	0.04	0.03	0.9915	0.9997	0.9995
Zn	1.45	7.08	15.77	0.40	0.04	0.03	0.9986	0.9976	0.9983
Zn 1:1	14.40	17.40	16.35	0.33	0.04	0.03	0.9982	0.9894	0.9969
Zn 2:1	12.84	13.56	13.58	0.33	0.06	0.05	0.9992	0.9991	0.9987

Studies on cyclical adsorption/desorption showed that cadmium demonstrated higher desorption efficiency with ASC, except for cycle 1 and single metals desorbed (Fig. 4).

**Figure 4.** The efficiency of desorption of individual metals and its mixtures in cycles: a. Cd, b. Zn

The highest elution efficiency was observed for mixture of Cd:Zn in the ratio 1:1 and 1:2, respectively 86% and 89% in cycle 1. In addition, reduction of desorption efficiency was observed for cadmium and its mixtures with zinc in the subsequent cycles. In analogy to the higher cadmium desorption single zinc was observed in cycle 1. The highest efficiency of desorption was found for the Zn:Cd 1:1 mixture (70%). The lower efficiency of the zinc desorption compared to cadmium was probably dictated by the high accumulation of metal in biosorbent.

5. Conclusion

Studies of cyclical adsorption/desorption have shown high efficiency in the removal of cadmium and zinc from aqueous solutions and desorption from immobilized activated sludge in the chitosan (ASC) of the single metals and mixtures thereof. The process of adsorption and desorption occurred in accordance with the model of the pseudo-second-order kinetic, which correlated well with the experimental data, as evidenced by the determined R^2 value.

Biosorbent cyclically adsorbed and desorbed zinc more effectively in comparison with cadmium, either from solutions containing a single metal or a mixture of Zn:Cd 1:1 and 2:1. Mass of zinc adsorbed and desorbed in cycle 1 from a solution containing a single metal was

0.78 and 0.40 mmol/g d.w. when cadmium was two times lower. In subsequent cycles, both metals were adsorbed and desorbed with less effectiveness.

The constants of ASC adsorption rate were the highest in cycle 3. In subsequent cycles, their values change over a fairly wide range. The values for cadmium varied from 0.09 to 1.89 mmol/min·mg depending on the cycle and the ratio of the metals in solution and for zinc from 0.09 to 0.75 mmol/min·mg. The desorption process occurred much faster than adsorption as evidenced by the high values of the constants (k_{2a}) within the range of from 2.54 to 51.1 mmol/g·min for Cd, and from 1.45 to 17.04 mmol/g·min for zinc.

It has been found that the desorption process of cadmium and zinc mixed in different proportions occurred with greater efficiency compared to the desorption efficiency of cadmium and zinc from solutions containing individual metals. The highest elution efficiency was observed in a mixture of Cd:Zn a ratio of 1:1 and 1:2, respectively 86% and 89%. The lower desorption efficiency of zinc compared to cadmium was probably dictated by the high accumulation of metal in biosorbent.

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8. References

- [1] Vijayaraghavan K, Yun Y; (2008) Bacterial biosorbents and biosorption. *Biotechnol Adv* 26, 266–291. DOI: 10.1016/j.biotechadv.2008.02.002
- [2] Park D, Yun YS, Park JM; (2010) The past, present, and future trends of biosorption. *Biotechnol Bioproc E* 15, 86–102. DOI: 10.1007/s12257-009-0199-4
- [3] Plaza Cazón J, Viera M, Donati E, Guibal E; (2013) Zinc and cadmium removal by biosorption on *Undaria pinnatifida* in batch and continuous processes. *J Environ Manage* 129, 423–434. DOI:10.1016/j.jenvman.2013.07.011
- [4] Abdel-Aty AM, Nabila S, Ammar NS, Ghafar HHA, Ali RK; (2013) Biosorption of cadmium and lead from aqueous solution by fresh water alga *Anabaena sphaerica* biomass. *J Adv Res* 4, 367–374. DOI: 10.1016/j.jare.2012.07.004
- [5] El-Shafey EI; (2010) Removal of Zn(II) and Hg(II) from aqueous solution on a carbonaceous sorbent chemically prepared from rice husk. *J Hazard Mat* 175, 319 – 327. DOI: 10.1016/j.hazmat.2009.10.006
- [6] Palma G, Freer J, Baeza J; (2003) Removal of metal ions by modified *Pinus radiata* bark and tannins from water solution. *Wat Res* 37, 4974–4980. DOI: 10.1016/j.watres.2003.08.008
- [7] Šćiban M, Radetić B, Kevrešan Ž, Klačnja M; (2007) Adsorption of heavy metals from electroplating wastewater by wood sawdust. *Bioresour Technol* 98, 402 – 409. DOI: 10.1016/j.biortech.2005.12.014
- [8] Xiong C; (2010) Adsorption of cadmium(II) by chitin. *J Chem Soc Pak* 32, 429–435.
- [9] Shaheen SM, Eissa FI, Ghanem KM, Gamal El-Din HM, Al Anany FS; (2013) Heavy metals removal from aqueous solutions and wastewaters by using various byproducts. *J Environ Manage* 128, 514–521. DOI: 10.1016/j.jenvman.2013.05.061.
- [10] Sargin I, Kaya M, Arslan G, Baran T, Ceter T; (2015) Preparation and characterisation of biodegradable pollen–chitosan microcapsules and its application in heavy metal removal. *Biores Technol* 177,1–7. DOI: 10.1016/j.biortech.2014.11.067.
- [11] Khosravan A, Lashkari B; (2011) Adsorption of Cd(II) by Dried Activated Sludge. *Iranian J Chem Eng* 8(2), 41–56.

- [12] Kumar PS, Gayathri R; (2009) Adsorption of Pb²⁺ ions from aqueous solutions onto bael tree leaf powder: isotherms kinetics and thermodynamics study. *Journal of Eng. Sci Technol* 4(4), 381 – 399.
- [13] Ong S, Toorisaka E, Hirata M, Hano T; (2010) Adsorption and toxicity of heavy metals on activated sludge. *ScienceAsia* 36, 204– 209.
- [14] Gadd GM; (2009) Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment. *J Chem Technol Biotechnol* 84, 13–28. **DOI:** 10.1002/jctb.1999
- [15] Mack C, Wilhelmi B, Duncan JR, Burgess JE; (2007) Biosorption of precious metals. *Biotechnol Adv* 25, 264–271. **DOI:** 10.1016/j.biotechadv.2007.01.003
- [16] Dhankhar R, Hooda A; (2011) Fungal biosorption – an alternative to meet the challenges of heavy metal pollution in aqueous solutions. *Environ Technol* 32, 467–491. **DOI:**10.1080/09593330.2011.572922
- [17] Liu Y, Liao T, He Z, Li T, Wang H, Hu X, Guo Y, He Y; (2013) Biosorption of copper(II) from aqueous solution by *Bacillus subtilis* cells immobilized into chitosan beads. *Trans Nonferrous Met Soc China* 23, 1804–1814. **DOI:**10.1016/S1003-6326(13)62664-3
- [18] Wan M, Wang C, Chen C; (2013) The Adsorption Study of Copper Removal by Chitosan-Coated Sludge Derived from Water Treatment Plant. *Int J Environ Sci Dev* 4(5)
- [19] Rangel-Mendez JR, Monroy-Zepedab R, Leyva-Ramosb E, Diaz-Flores PE, Shirai K; (2009) Chitosan selectivity for removing cadmium (II), copper (II), and lead (II) from aqueous phase: pH and organic matter effect. *J Hazard Mater* 162, 503–511. **DOI:** 10.1016/j.jhazmat.2008.05.073
- [20] Kuczajowska-Zadrożna M, Filipkowska U, Józwiak T, Szymczyk P; (2015) Biosorption/desorption of cadmium(II) and zinc (II) from aqueous solutions by activated sludge immobilized onto chitosan beads. *P C A C D XX*, 142–155. **DOI:** 10.15259/PCACD.20.13
- [21] Stanley WI, Watters GG, Chan B; (1975) Lactase and other enzymes Bound to chitin with glutaraldehyde. *Biotechnol Bioeng* XVII, 315–325. **DOI:** 10.1002/bit.260170303
- [22] Esposito A, Paganelli F, Lodi A, Solisio C, Veglio F; (2001) Biosorption of heavy metals by *Sphaerotilus natans*: an equilibrium study at different pH and biomass concentrations. *Hydrometallurgy* 60, 129–41. **DOI:**10.1016/S0304-386X(00)00195-X
- [23] Fomina M, Gadd GM; (2014) Biosorption: current perspectives on concept, definition and application. *Bioresour Technol* 160, 3–14. **DOI:** 10.1016/j.biortech.2013.12.102
- [24] Kuczajowska-Zadrożna M, Filipkowska U; (2015) Kinetics of desorption of heavy metals and their mixtures from immobilized activated sludge. *Desalin Water Treat* **DOI:**10.1080/19443994.2015.1031708
- [25] Njikam E, Schiewer S; (2012) Optimization and kinetic modeling of cadmium desorption from citrus peels: A process for biosorbent regeneration. *J Hazard Mater* 213–214, 242– 248. **DOI:** 10.1016/j.jhazmat.2012.01.084
- [26] Deng PY, Liu W, Zeng BQ, Qiu YK, Li LS; (2013) Sorption of heavy metals from aqueous solution by dehydrated powders of aquatic plants. *Int J Environ Sci Technol* 10, 559–566. **DOI:** 10.1007/s13762-013-0186-3
- [27] Chen YW, Wang JL; (2012). The characteristics and mechanism of Co(II) removal from aqueous solution by a novel xanthate-modified magnetic chitosan. *Nucl Eng Des* 242, 452–457. **DOI:**10.1016/j.nucengdes.2011.11.004
- [28] Wu SJ, Liou TH, Yeh CH, Mi FL, Lin TK; (2013) Preparation and characterization of porous chitosan-tripolyphosphate beads for copper(II) ion adsorption. *J Appl Polym Sci* 127, 4573–4580. **DOI:** 10.1002/app.38073

- [29] Reyhanitabar N, Karimian; (2008) Kinetics of copper desorption of selected calcareous soils from Iran, *American-Eurasian J Agric Environ Sci* 4 (3), 287–293.
- [30] Jho EH, Lee SB, Kim YJ, Nam K; (2011) Facilitated desorption and stabilization of sediment-bound Pb and Cd in the presence of birnessite and apatite. *J Hazard Mat* 188, 206–211.