

BIOSORPTION/DESORPTION OF CADMIUM(II) AND ZINC (II) FROM AQUEOUS SOLUTIONS BY ACTIVATED SLUDGE IMMOBILIZED ONTO CHITOSAN BEADS

Małgorzata Kuczajowska-Zadrożna^{1*},
Urszula Filipkowska², Tomasz Józwiak², Paula Szymczyk²

¹*Department of Department of Biotechnology in Environmental Protection,
University of Warmia and Mazury in Olsztyn
ul. Słoneczna 45g, 10-702 Olsztyn, Poland
e-mail: mkuczajowska@uwm.edu.pl*

²*Department of Environmental Engineering,
University of Warmia and Mazury in Olsztyn
ul. Warszawska 117, 10-720 Olsztyn, Poland*

Abstract

In this study, we evaluated the effectiveness of cadmium and zinc adsorption and desorption from solutions containing single metals and a mixture of metals in the ratio of 1:2 by activated sludge immobilized onto chitosan (ASC). The optimal pH value determined for metals adsorption ranged from pH 5 to pH 6, whereas that established for desorption reached pH 2. In the case of individual metals, the state of adsorption equilibrium in the solution was achieved after 180 min, whereas in the case of a metal mixture – after 270 min. In the case of desorption, the state of equilibrium was achieved after 45 min. It was stated that both adsorption and desorption proceeded according to the pseudo-second order reaction. The study enabled determining the maximum adsorption capacity based on Langmuir, Freundlich and Sips models. The Sips model was found suitable for the description of adsorption of single metals onto ASC, whereas both Sips and Freundlich models – for description of the adsorption of a metal mixture, which was indicated by the determined values of R² coefficient. The adsorption capacity of ASC determined from Sips model for individual solutions of cadmium and zinc reached 216 and 188.3 mg/g d.m., respectively, whereas that determined for their mixture reached 106 mg/g d.m. for both metals.

Key words: *adsorption, desorption, heavy metal, chitosan beads*

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1. Introduction

The contamination of waters with metals has for years been posing a severe environmental problem owing to their toxicity and capability to accumulate in aquatic organisms. The protection of water bodies necessitates the application of effective treatment technologies that are aimed at reducing the loads of metals discharged with industrial wastewater.

Today, the following methods are recommended for metals removal: chemical precipitation, coagulation, oxidation/precipitation, reduction/precipitation, membrane processes, and ionic exchange [1]. These methods differ in the effectiveness and complexity of technological solutions. Equally effective methods for the removal of heavy metal ions from aqueous solutions include adsorption and chemisorption. According to literature data, the most popular adsorbents include zeolites [2,3], silica gels [4,5], and activated carbons [6,7]. But still, new materials of biological origin are sought after to be used for metal ions removal from solutions as economic, effective and easily available sorbents.

Biosorbents may include materials commonly occurring in natural environment, bacteria [8], algae [9], fungi [10,11], as well as those of plant and animal origin (modified plant products [12], peat [13], alginate gels [14], chitin [15], and chitosan [16]).

Chitosan is a cheap biosorbent produced on the industrial scale through deacetylation of alkaline chitin – one of the most abundant biopolymers in nature. It occurs in exoskeletons of crustaceans: crabs, shrimps, krill as well as in cell walls of selected bacteria and fungi [17].

An important trait of chitosan is the degree of acetylation: the higher the degree, the higher the effectiveness of sorption [18]. The process of chitin deacetylation consists in the exchange of acetamide groups (integrating chitin's structure) into amine groups, which affects its chemical and physical properties. A higher number of amine groups makes chitosan a polymer with better solubility, which allows for its extended use in, among other things, adsorption process.

The biomass of microorganisms being the by-product of wastewater treatment with activated sludge is an equally effective biosorbent [19]. Bacteria, fungi, protozoa, and rotifers constitute the biological component or biological mass of activated sludge. Activated sludge produced in the biological treatment facilities of the treatment plant is considered a good bioadsorbent for the removal of heavy metal ions from aqueous solution [20].

A drawback of biosorbents in the form of free biomass is their low mechanical resistance and difficulties in their separation from the solution. The use of immobilized particles of biomass ensures its greater applicability as well as enables easy recovery of the biomass from wastewater, possibility of its regeneration and high effectiveness of metal elimination [21].

An overview of literature demonstrates that chitosan is not only a good carrier applied in biomass immobilization but also an effective adsorbent of metals [22-24]. For this reason, in this work, biomass being a by-product in the

form of excessive activated sludge after methane fermentation from a municipal wastewater treatment plant in Olsztyn was immobilized with chitosan in order to produce a stable, inexpensive and effective biosorbent for the removal of cadmium and zinc and their mixtures from aqueous solutions.

The use of a biosorbent requires the knowledge of the parameters which affect the course of adsorption process, like pH and contact time. Adsorption constants determined from models, especially the maximum adsorption capacity, enable the classification of biosorbents usability for industrial purposes and for design of technological solutions of wastewater treatment. In this study, the adsorption of single metals and their mixtures was analyzed based on the course of adsorption isotherms and maximum adsorption capacity determined from Freundlich, Langmuir and Sips equations.

2. 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 [25]. 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.m.) 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 deionized water till neutral pH value has been reached.

2.2. Determination of pH value of adsorption and desorption

Analyses of the pH value of adsorption were carried out in the range from pH 3 to pH 10. In brief, 4g ASC were added to 50 cm³ of a solution with the concentration of 200 mg/dm³ and with the specified pH value adjusted using 0.1 and 1M NaOH or 1M H₂SO₄. The samples were shaken on a shaker for 120 min at 170 rpm. Afterwards, the biosorbent saturated with metal was transferred into a reaction vessel, to which H₂SO₄ was added. The range of pH values for sulfuric acid was from pH 2 to pH10.

2.3. Determination of the effect of time on adsorption and desorption

Studies on metals adsorption by ASC included determination of the time needed to reach reaction equilibrium. To this end, 80 g of biosorbent were weighed into a reaction vessel, then 1 dm³ of cadmium or zinc solutions with the concentration of 200 mg/dm³ or 1 dm³ of a Cd:Zn mixture in the ratio of 200:400 mg/dm³ was added to the reaction vessel. The vessel was placed on a magnetic stirrer. Next, samples were collected in a time range of 0 to 360 min and analyses were carried out to determine the concentration of metals left in the solution. After adsorption, the biosorbent (10 g) saturated with metal was filtered, rinsed and transferred into a reaction vessel to which there were added 500 cm³ of 0.1M H₂SO₄. The reaction vessel was placed on a magnetic stirrer. Samples were collected after 0, 5, 10, 15, 30, 60, 90, and 120 minutes and analyses were carried out to determine the concentration of metals released from biosorbent to the solution.

2.4. Determination of the maximum adsorption capacity

Analyses were conducted for individual metals and for their mixture (1:2) at the optimal, earlier established pH = 6.0. Ranges of the concentrations of metals in the solution and the value of the maximum concentration were adjusted so as to achieve the course of adsorption isotherm until complete saturation of active sites of the biosorbent with metals.

The biosorbent (8 g and 100 cm³) was introduced to reaction flasks with the volume of 200 cm³. The samples were shaken on a shaker for 6 hours and the concentration of metals left in the solution after sorption was determined.

2.5. Determination of heavy metals

Adsorption analyses were conducted with the use of hydrated sulfate salts of cadmium and zinc. Stock solutions of metals were prepared in a concentration of 20g/dm³ using the following salts: Cd(SO₄)₂ · 8H₂O and ZnSO₄ · 7H₂O (Sigma-Aldrich). The concentration of metals left in the aqueous solution of each of the analyzed samples was controlled with the flame method using an AA 280FS atomic adsorption spectrometer by 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, (mg/g d.m.); Q_1 - weight of metal desorbed from biosorbent, (mg/g d.m.); C_0 - initial concentration of metal in the solution, (mg/dm³); C_s - metal concentration in the solution after adsorption, (mg/dm³); C_d - metal concentration in the solution after desorption, (mg/dm³); m - biosorbent concentration, (g d.m./dm³).

3.1. Kinetic model

The rate of cadmium, zinc and copper adsorption from the solution by the biosorbent was determined based on experimental results demonstrating changes in the concentration of adsorbed metals (Q) depending on time (t). Results were interpreted with a pseudo-second order model:

$$\frac{dQ}{dt} = k_s (Q_s - Q)^2 \quad (3)$$

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

$$\frac{dQ_1}{dt} = k_d (Q_d - Q_1)^2 \quad (4)$$

where: Q_s - weight of metal adsorbed in the state of equilibrium, (mg/g d.m.); Q - weight of metal adsorbed by the biosorbent in a time unit, (mg/g d.m.); Q_d - weight of metal desorbed in the state of equilibrium, (mg/g d.m.); Q_1 - weight of metal desorbed from the biosorbent in a time unit, (mg/g d.m.); k_s - adsorption rate constant; (g d.m./mg·min); k_d - desorption rate constant, (g d.m./mg·min); t - time, (min).

3.2. Equilibrium isotherm models

Langmuir, Freundlich and Sips models (Eqs. 5-7, respectively) were applied to analyze the equilibrium sorption data:

$$q_s = \frac{q_{\max} \cdot b \cdot C_s}{1 + b \cdot C_s} \quad (5)$$

$$q_s = K_F C_s^{1/n} \quad (6)$$

$$q_s = \frac{q_{\max} \cdot b \cdot C_s^{1/n}}{1 + b \cdot C_s^{1/n}} \quad (7)$$

where: q_{\max} , b , K_F , n are constants of isotherms; C_s is metal concentration in the solution after adsorption; q_s is the weight metal adsorbed by the biosorbent.

Program STATISTICA 10.0 was applied for statistical determination of the degree of curves fit (with the determined constant) to the experimental data with

the use of non-linear estimation by the method of least squares, at a significance level of $p < 0.05$.

4. Results and discussion

The pH value is an important parameter which affects both adsorption and desorption of metals. The optimal pH value is usually established experimentally for each metal. Fig. 1 presents the effectiveness of single metals (Cd and Zn) adsorption from an aqueous solution and the effectiveness of metals desorption from ASC.

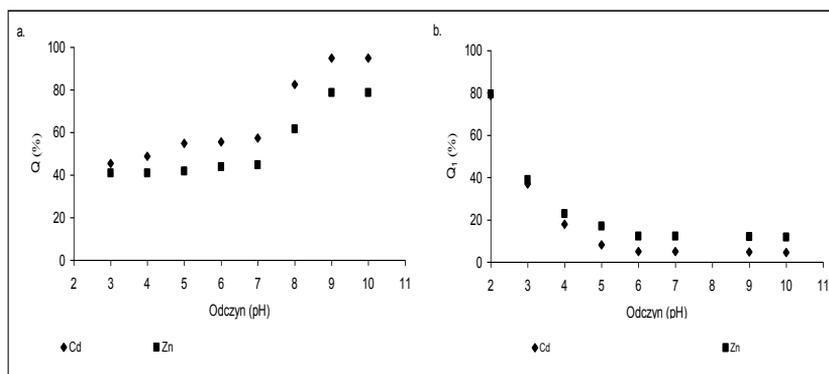


Figure 1. Effectiveness of adsorption (a) and desorption (b) of cadmium and zinc at various pH values

Results obtained in the study demonstrate that the effectiveness of cadmium and zinc removal from the solution increased slightly in the pH range of 3 to 7. In the pH range of 8 to 10, a tangible increase was noted in removal effectiveness from 57% to 95% for cadmium and from 45% to 79% for zinc (Fig. 1a).

The increased effectiveness of both metals adsorption onto ASC at higher pH values may be explained by the fact that at lower pH the ions of metals compete with protons for the active sites on biosorbent surface. In addition, enhanced protonation of the amine groups of chitosan at lower pH values induced electrostatic repulsion of metal ions, which facilitated the adsorption of metal ions at high pH values.

In the case of desorption, the highest effectiveness (79%) of metals release to the solution was determined at pH 2. Increasing the pH value from 3 to 10 caused a significant decrease in process effectiveness in the case of both cadmium (37%–5%) and zinc (39%–12%) (Fig. 1b).

ASC possesses various functional groups, mainly carboxyl, hydroxyl and amine ones. In the medium with acidic pH, the concentration of H_3O^+ considerably exceeds the concentration of metal ions. Active sites occurring on

adsorbent's surface are protonated, which makes that metal ions remain unbound, i.e. desorption of metals increases.

Determination of technological parameters needed in the design of systems for metals removal from wastewater with the adsorption method requires the knowledge of process rate. The knowledge of adsorption and desorption kinetics is especially significant in the case of planning a cyclic process.

Results of analyses of the correlation between the weight of adsorbed individual metals and their mixture in biosorbent and adsorption time were presented in Fig. 2.

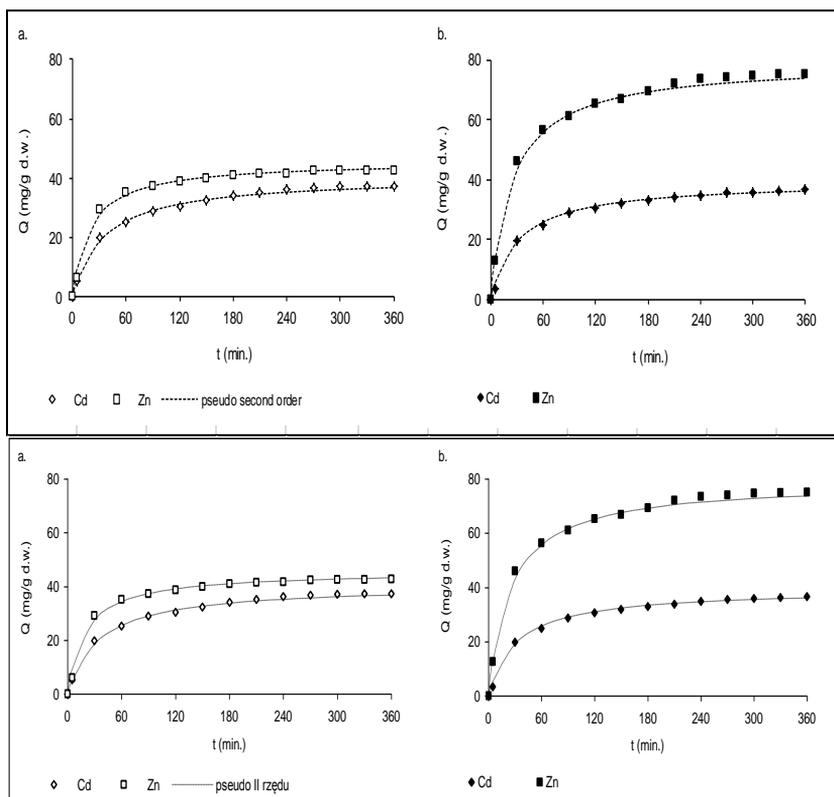


Figure 2. Correlation between the weight of adsorbed individual metals (a) and their mixtures (b) and adsorption time

The analysis of experimental results demonstrated that the time after equilibrium concentration has been reached differed depending on whether the metal occurred in the solution individually or in a mixture of both metals. For cadmium and zinc occurring individually in the solution, this time reached 180

min, whereas for the mixture of both metals – it increased to 270 minutes. In the equilibrium state, the load of cadmium removed from solutions of single metals and from a mixture of cadmium and zinc was comparable and reached 34.0 mg/g d.m. and 35.6 mg/g d.m., respectively. In contrast, significant differences in the Q value were observed in the case of zinc. The load of zinc removed from solutions of single metals reached 42.0 mg/g d.m., whereas from a mixture with cadmium – it was significantly higher and reached 74.0 mg/g d.m.

The analysis of experimental data showed that the time needed to reach the equilibrium concentration of metals desorption from biosorbent was significantly shorter compared to adsorption, irrespective whether determined for single metals or their mixtures, and reached 45 min. However, the load released to the solution of metals varied (Fig.3.). For single metals it accounted for 37.0 mg/g d.m., whereas for a mixture of metals – the weight of cadmium eluted from the biosorbent reached 34.4 mg/g d.m. and that of zinc reached 43.0 mg/g d.m.

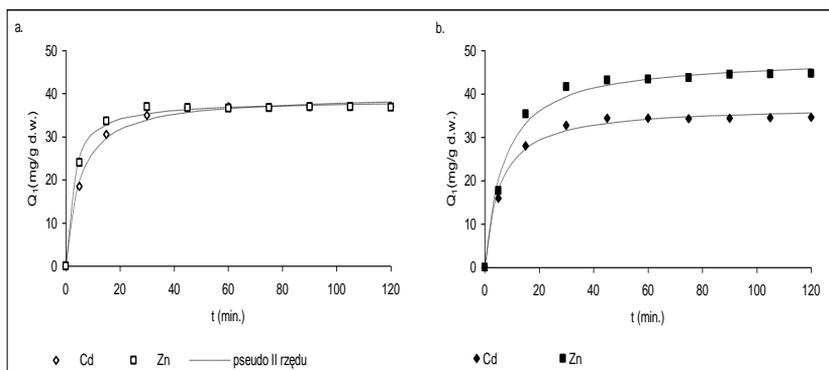


Figure 3. Correlation between the weight of desorbed single metals (a) and their mixtures (b) and desorption time

Due to a high number and diversity of chemical groups of ASC, the mechanisms of adsorption and desorption processes were investigated using the pseudo-II order kinetic model which covers both mass transfer and chemical reactions rate [26]. The obtained values of kinetic constants were summarized in Tab. 1.

The determined values of constants (Tab. 1) enable concluding that processes of adsorption and desorption followed the pseudo-second-order kinetic model that was well correlated with experimental data, which was indicated by R^2 values (0.9950 – 0.9989). It suggests that the process of adsorption and desorption proceeded as a result of chemisorption with the share of valent forces through the binding or exchange of electrons between adsorbent and adsorbate.

Other investigations with the use of metal biosorbents, e.g., humic acid [27], activated sludge [28], citrus peels [29], or dehydrated powders of aquatic

plants [30], also demonstrated that the kinetics of sorption and desorption was consistent with the pseudo-second-order kinetic model.

Table 1. Values of kinetic constants of adsorption and desorption of single metals and their mixtures

	Metal	$Q_{s,d}$ (mg/g)	$k_{s,d}$ (g/mg·min)	R^2
adsorption	Cd	40.4	0.0007	0.9988
	Cd:Zn (1:2)	39.3	0.0008	0.9984
	Zn	45.6	0.0010	0.9965
	Zn:Cd (2:1)	78.9	0.0005	0.9989
desorption	Cd	39.6	0.0050	0.9974
	Cd:Zn (1:2)	37.2	0.0050	0.9962
	Zn	38.4	0.1000	0.9974
	Zn:Cd (2:1)	48.4	0.0030	0.9950

The adsorption of metals under equilibrium conditions was evaluated based on the course of adsorption isotherms, and maximum adsorption capacity determined from Freundlich, Langmuir and Sips equations for individual metals and for a Cd:Zn mixture (1:2).

Experimental results of analyses of the quantity of adsorbed metal depending on the concentration of metal left in the solution and determined on their basis isotherms of Freundlich, Langmuir and Sips were presented in Fig. 4. Constants determined from Equations 5, 6 and 7 for single metals and their mixture were summarized in Tab. 2. The coefficient of determination R^2 was adopted as a measure of curve fit (at the established parameters) to experimental data.

Results obtained in the study enable concluding that the Sips model is suitable for the description of adsorption of single metals onto ASC, and that adsorption of a mixture of metal may be well described by both Sips and Freundlich models, which was indicated by the determined values of R^2 coefficient (Tab.2).

The course of isotherms consistent with Freundlich equation indicates that the biosorbent possesses active sites with a different force of binding, and that the adsorption process is complex. The tested biosorbent possessed functional groups with diversified chemical structure, as a result of which adsorption of metals could proceed via both ionic exchange and electrostatic attraction or formation of hydrogen bonds.

In turn, the effectiveness and universal character of Sips model were confirmed by Perez-Martin et al. [31], who investigated adsorption of cadmium ions from an aqueous solution onto orange waste. Experimental data were analyzed with the use of the following models: Langmuir, Freundlich, Redlich-Peterson and Sips, at pH 4–6. The maximum adsorption capacity determined from the Sips model ranged respectively from 45 to 48 mg/g d.m.

Investigations of lead, cadmium and zinc adsorption onto sintered cattle bone powder also demonstrated the universal character of the Sips model and the obtained values of the maximum adsorption capacity reached 158, 31 and 72 mg/g d.m., respectively [32].

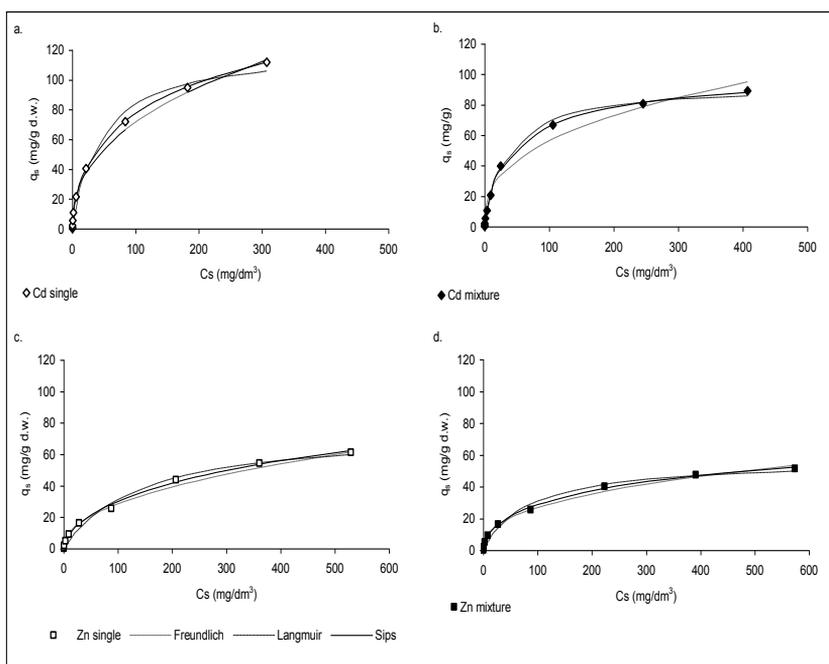


Figure 4. Experimental results of adsorption onto ASC for: a. Cd single, b. Cd mixture, c. Zn single, d. Zn mixture, and adsorption isotherms determined from Freundlich, Langmuir and Sips equations.

Table 2. Adsorption constants determined from Langmuir, Freundlich and Sips equations for the tested biosorbent as well as cadmium and zinc from aqueous solutions containing single metals and their mixture

Model	Metal			
	Cd single	Cd mixture	Zn single	Zn mixture
Langmuir				
q_{\max} (mg/g)	121.7	93.2	76.3	57.1
b (dm ³ /mg)	0.022	0.029	0.007	0.012
R^2	0.990	0.998	0.993	0.992
Freundlich				
K_F (dm ³ /mg)	10.9	10.3	3.4	4.5
n	0.41	0.37	0.46	0.39
R^2	0.998	0.989	0.998	0.997
Sips				
q_{\max} (mg/g)	216.0	106.0	188.3	106.0
b (dm ³ /mg)	0.039	0.046	0.014	0.030
n	0.58	0.78	0.57	0.55
R^2	0.999	0.999	0.999	0.999

5. Conclusion

Activated sludge immobilized onto chitosan (ASC) displayed high effectiveness of cadmium and zinc ions removal from aqueous solutions of single metals and their mixture. The quantity of adsorbed ions of metals depended on the pH value and contact time. The process of adsorption and desorption proceeded accordingly to the pseudo-second-order kinetic model that well correlated with experimental data, which was indicated by the determined R^2 values. It suggests that the process of adsorption and desorption proceeded as a result of chemisorption.

The adsorption of metals under equilibrium conditions was evaluated based on adsorption capacity determined from Freundlich, Langmuir and Sips equations. It was concluded that the adsorption of single metals onto ASC was best described by the Sips model and that the adsorption of a metal mixture was well described by both Sips and Freundlich models. The adsorption capacity of ASC determined from the Sips model for individual solutions of cadmium and zinc reached 216 and 188.3 mg/g d.m., respectively, whereas that determined for their mixture reached 106 mg/g d.m. for both metals. The preliminary results point to the feasibility of applying ASC for the removal of cadmium and zinc from aqueous solutions and for effective recovery of these metals with the use of sulfuric acid.

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