Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1031708

57 (2016) 9396–9408
April

Taylor & Francis
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Kinetics of desorption of heavy metals and their mixtures from immobilized activated sludge

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Received 5 October 2014; Accepted 6 March 2015

ABSTRACT

In order to use biosurfactants to desorb metals from biosorbents without changing their adsorption capacity, there is a need to determine conditions of process. In this study, we examined the kinetics of desorption of cadmium, zinc, and copper and their mixtures from activated sludge immobilized in 1.5% sodium alginate with 0.5% polyvinyl alcohol. Metals leaching from immobilized biomass were analyzed with the use of three biosurfactants—saponin, JBR 515, JBR 425, and nitric acid. Desorption effectiveness of single metals and their mixtures was also investigated as influenced by different desorption parameters such as pH, contact time, and dose of desorbents. The obtained values of kinetic constants of pseudo-first-order (k_1) and pseudo-second-order (k_2) showed that in case of all analyzed desorbents, the process of metals leaching from immobilized activated sludge proceeded according to the pseudo-second-order reaction as indicated by the R^2 values. Out of the analyzed desorbents, saponin and nitric acid proved to be the most effective in leaching both individual metals and their mixtures from the biosorbent. Saponin showed high leaching effectiveness in a pH range of 1–5, whereas the optimal conditions for nitric acid were at pH 1–2. The effectiveness of metals desorption from biosorbent using saponin reached 94.8% (Zn), 86.6% (Cu), and 51.2% (Cd) (a solution of single metal) and 92.7, 73.6, and 43.1%, respectively, for a solution of metal mixture. These results show that saponin is an attractive and environmentally friendly desorbent for the removal of metals and their mixtures from biosorbent.

Keywords: Biosorption; Desorption; Heavy metals; Biosurfactants

1. Introduction

Heavy metals pose a severe environmental problem due to their abundance, stability, tendency for accumulation, and toxicity [1–4]. According to the American Agency for Toxic Substances and Disease Registry, lead, mercury, and cadmium were ranked second, third, and seventh, respectively, amongst 275 listed hazardous substances. Other elements classified on this list included cobalt, nickel, zinc, chromium, manganese, and copper. Moreover cadmium, copper, lead, mercury, nickel, and zinc are considered the most hazardous and are included on the US Environmental Protection Agency's list of priority pollutants [5].

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Among well-known sources of heavy metals pollution, particularly cumbersome is industrial wastewater. These wastewaters originate mainly from the chemical, automotive, and paper industries as well as from petroleum refineries, metallurgic and mining plants, galvanizing plants, dye and tanning companies [6–8]. In industrial wastewater, heavy metals hardly ever occur as single components; they usually appear in mixtures with various concentrations of their components [9–11]. For instance, wastewater discharged from cellulose-paper plants have been reported to contain cadmium, chromium, copper, mercury, nickel, lead, iron, manganese, and zinc [12].

Conventional methods of heavy metals removal from water solutions together with chemical precipitation, ion exchange, reversed osmosis, or adsorption may be ineffective or expensive, especially at low concentrations of metals [13]. In addition, their use results in generation of high quantities of toxic sludges whose removal or treatment is expensive and environmentally unfriendly [14].

An alternative to the conventional methods of heavy metals removal from water solutions is biosorption. For this reason, recent investigations have been focusing on the search for new, inexpensive, easily available, and environmentally friendly biosorbents capable of removing considerable quantities of heavy metal ions [15–18].

Biosorbents may include common natural materials, bacteria [19,20], algae [21,22], fungi [23–25] as well as biomass of micro-organisms being a waste product of the fermentation industry or of wastewater treatment with activated sludge [26–28].

Small sizes of particles, density similar to that of a solution, and low mechanical resistance of biomass may contribute to significant expenditures linked with biosorbent separation from wastewaters. Higher stability of biomass, its easier separation from a solution, and improved sorption effectiveness may be achieved through immobilization.

In practice, immobilized biosorbents should be characterized by high effectiveness of metals sorption from solutions and easiness of desorption with the use of cheap desorbents such as weak solutions of mineral and organic acids and complexing agents.

Desorption is often induced by reduction of pH value using mineral acids (hydrochloric, nitric, and sulfuric). The application of acids enables to achieve high process yield in recovery of such metals as: copper, zinc, cadmium, and lead [29,30] but, simultaneously, causes damage to the structure of biosorbents. Many authors have been using complexing agents like EDTA and NTA for desorption process [31–33]; however, their use ought to be restricted due to low susceptibility of EDTA to biodegradation and to carcinogenic properties of NTA [34]. For this reason, increasing attention has been paid recently to the search for novel metal-extracting substances like surfactants and biosurfactants.

Biosurfactants are surface-active compounds of natural origin, produced via microbiological synthesis or from plants. Likewise the synthetic ones, they exhibit the amphyphylic character that results from the presence of a hydrophobic part (non-polar) and non-ionic hydrophilic part (polar) in a molecule. The hydrophobic part is usually constituted by long-chain fatty acids and hydroxy fatty acids containing from 8 to 20 carbon atoms in a molecule, whereas the hydrophilic fraction is made of carbohydrates, amino acids, peptides, phosphates, carboxyl acids, or alcohols [35].

Various species of micro-organisms are capable of biosurfactants synthesis with the use of cheap and easily available substrates including sugars, vegetable oils, fatty acids, and alcohols [36]. Compared to biosurfactants synthesized by micro-organisms, those of plant origin are known to a smaller extent. Their most recognized representatives include saponin—a triterpene glycoside isolated i.e. from soap bark tree (*Quillaja bark*), tannin—a natural plant pigment, constituting a mixture of gallic acid and glucose, aescin—isolated from chestnut tree (*Aesculus hippocastanum*), and L-a-phosphatidylcholine—isolated from soybean seeds [37].

Biosurfactants were used for the removal of kerosene products from soils. Recently, however, a number of reports have appeared on the feasibility of their application for metals removal from and soil polluted bottom deposits [35,38,39]. In the literature, there are no reports on the use of biosurfactants to leaching of metals from biosorbents to their repeated use. There is a need for a more exhaustive identification of mechanisms of metals removal from biosorbent and for determination of operation conditions of this process.

The innovative character of the presented study results from the use of a biosorbent being a combination of a waste product—activated sludge from a wastewater treatment plant, and sodium alginate in which the activated sludge was immobilized. Furthermore, polyvinyl alcohol (PVA) was added to sodium alginate, which ensures the improvement of the mechanical properties of the biosorbent by increasing its mechanical resistance and sedimentation properties compared to the activated sludge alone.

In this study, the authors investigated desorption of cadmium, zinc, and copper and their mixtures with the use of biosurfactants—saponin, JBR 515, JBR 425, and with nitric acid—from activated sludge immobilized in 1.5% sodium alginate and 0.5% PVA. It served to better understand the desorption of Cd^{2+}, Zn^{2+}, and Cu^{2+} during the leaching phase and exchange with the solution at equilibrium. Experimental data of desorption of single metals and their mixtures were fitted to various desorption models. Two types of kinetic models (pseudo-first and pseudo-second one) were used to describe the release phase. The study allowed to determine constants in kinetic equations of desorption, which are key elements in designing processes of metal recovery using biotechnological methods.

2. Materials and methods

2.1. Heavy metal biosorption studies

2.1.1. Preparation of the metal ion solutions

Adsorption was analyzed with the use of hydrated nitrate salts of cadmium, zinc, and copper with mixtures of equal proportions of each of these metals. Stock solutions of $Cd(NO_3)_2·4H_2O$, $Zn(NO_3)_2·6H_2O$ and $Cu(NO_3)_2·3H_2O$ (Sigma-Aldrich) metals were prepared at a concentration of 20 g L^{-1}.

2.1.2. Preparation of biosorbent

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 4,500 rpm, and dried in a water bath at 50˚C for 48 h. Dried sludge was placed in a porcelain mortar and sieved through a screen with a mesh diameter of 0.01 mm. The activated sludge was immobilized to alginate as follows: 0.5 g of PVA was dissolved in 80 g of distilled water and placed in a water bath at a temperature of 60˚C until dissolved. The PVA solution was cooled to room temperature, 1.5 g of sodium alginate was dissolved, followed by 2 g of the activated sludge, and finally distilled water was added to a weight of 100 g. A homogenous sol was instilled to a solution of 0.1 M $CaCl_2$ in a saturated solution of boric acid. The grains that formed were left to gelatinize for 24 h, and afterwards were rinsed with distilled water in order to wash out chlorides.

2.1.3. FT-IR analysis of biosorbent

The samples without and with addition of metals were analyzed. The IR spectra of samples were determined using a FT-IR spectrometer (Alpha FTIR Spectrometer—Candela) over the range 4,000–400 cm^{-1}.

2.1.4. Batch biosorption studies

Analyses of cadmium, zinc, and copper desorption from activated sludge immobilized in a mixture of 1.5% sodium alginate with 0.5% PVA were preceeded by 12 h adsorption of metals.

The adsorption experiment was carried out in 1,000 mL reaction vessel, by adding 40 g (5.84 g dw L^{-1}) of biosorbent to 500 mL of a metal solution at concentration of 300 mg L^{-1}. Adsorption was performed at a constant initial pH of 6.0 and 170 rpm under a controlled temperature of 22˚C. The pH was adjusted using 0.1 M NaOH and 0.1 M HNO_3 solutions. The reaction vessel was placed on a magnetic stirrer for 12 h. After adsorption, the biosorbent was rinsed several times with distilled water, dried, and used for desorption study.

The residual concentration of metal ions was determined using atomic adsorption spectrometer AA 280FS (Varian). The amount of metal ion adsorbed by immobilized activated sludge (Q_{ad}) was calculated according to the following equation:

$$Q_{ad} = \frac{(C_0 - C_{ad})}{m} \tag{1}$$

where C_0—initial concentration of metal in the solution (mg L^{-1}); C_{ad}—concentration of metal in the solution in the equilibrium state after adsorption (mg L^{-1}); and m—concentration of biosorbent (g L^{-1}).

2.2. Preparation of the desorbents

Metals leaching from immobilized biomass were analyzed with the use of saponin (Sigma-Aldrich cat. No. 84510). According to elementary analysis conducted at the Institute of Organic Chemistry of the Polish Academy of Sciences in Warsaw, saponin contained: 42.3% of carbon, 6.2% of hydrogen, 0.2% of nitrogen, and 51.3% of oxygen.

Preparations of biosurfactant with commercial names: JBR 425 and 515, being technical products (*Jeneil Biosufactant Co.*, LLC, USA), were, respectively, 25 and 15% aqueous solutions of rhamnolipids produced during fermentation process by *Pseudomonas aeruginosa* bacteria under aerobic conditions.

Nitric acid was used as a desorbent (puriss. p.a. ≥69% with density of 1.413 g L^{-1} at 20˚C by Sigma-Aldrich) at the concentration from 0.5 to 15%.

2.2.1. Effect of pH and concentration of desorbents

In analysis devoted to finding the effect of pH value and doses of desorbent on metals desorption, adsorption was conducted with solutions of single metals in the concentration of 100 mg L^{-1}.

Biosorbent (1 g) saturated with metal was placed in a reaction vessel, which was then filled with 50 mL of desorbent. Next, the samples were placed on a Gerhardt-type shaker and shaken for 2 h at a constant speed of 170 rpm. For saponin and nitric acid, the analyzed range of pH was from pH 1 to 12, whereas for the analyzed rhamnolipids, JBR 515 and 425, it was between pH 5 and 12.

The concentration of desorbent ranged from 0 to 25 g 100 mL^{-1} for biosurfactants, and from 0 to 12.6 g 100 mL^{-1} for nitric acid.

2.3. Effect of time on desorption

Analyses of metals desorption from activated sludge immobilized in a mixture of alginate with PVA included determination of the time necessary to reach reaction equilibrium. To obtain it, biosorbent (10 g) saturated with metal was put into a 1,000 mL reaction vessel, which was next filled with 500 mL of a desorbent solution. Experiments were carried out with 5% solutions of saponin, JBR 515 and 425, and with 1 M HNO_3. The reaction vessel was placed on a magnetic stirrer and samples were collected after 0, 5, 10, 15, 30, 60, 90, and 120 min to determine the concentration of metals released from the biosorbent to the solution.

2.4. Desorption kinetics experiment

The kinetic study of all metal ions and their mixtures was carried out at optimum: pH, desorbent dose, and contact time for each desorbent.

Desorption kinetics was analyzed with the use of solutions of single metals at concentrations of 300 mg L^{-1} and with their mixture in the ratio of 100:100:100 mg L^{-1}.

Desorption was performed at a constant initial pH (pH 5 for saponin; pH 6 for JBR 515 and 425; pH 1 for nitric acid) and 170 rpm under a controlled temperature of 22°C. The pH was adjusted using 0.1 M NaOH and 0.1 M HNO_3 solutions. The reaction vessel was placed on a magnetic stirrer. The samples were collected after 0–120 min. The amount of metal ion desorbed by immobilized activated sludge (Q_d) was calculated according to the following equation:

$$Q_d = \frac{C_d}{m} \tag{2}$$

where C_d—concentration of metal in the eluate (mg L^{-1}), m—concentration of biosorbent mass (g L^{-1}) .

The effectiveness of desorption (η_d) as influenced by the pH value was based on the percentage content of metal in the adsorbent and was calculated from the following equation:

$$\eta_d = \left(1 - \frac{Q_d}{Q_{ad}}\right) \cdot 100 \tag{3}$$

where Q_{ad}—content of metal in the adsorbent after adsorption (mg g^{-1} dm^{-1}); Q_d—content of metal in the adsorbent after desorption (mg g^{-1} dm^{-1}).

2.5. Kinetic models

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:

$$\frac{dQ_t}{dt} = k_1(Q_d - Q_t) \tag{4}$$

where k_1—rate constant of pseudo-first-order desorption (1 m^{-1}).

Model of pseudo-second-order reaction:

$$\frac{dQ_t}{dt} = k_2(Q_d - Q_t)^2 \tag{5}$$

where k_2—rate constant of pseudo-second-order desorption (mg g^{-1} min^{-1}).

2.5.1. Statistical analyses

The kinetic expression with the best fit to the experimental data was determined using the coefficient of correlation, R^2 [40], which is defined as:

$$R^2 = \frac{\Sigma(q_{cal} - \bar{q}_{exp})^2}{\Sigma(q_{cal} - \bar{q}_{exp})^2 + \Sigma(q_{cal} - q_{exp})^2} \tag{6}$$

where q_{cal} is the theoretical Me^{2+} desorbed from biosorbent (mg g^{-1}), q_{exp} is the experimental Me^{2+} desorbed (mg g^{-1}), and $\bar{q}_{exp}$ is the average experimental Me^{2+} desorbed (mg g^{-1}). A high value of R^2 is perceived as implying a causal relationship between the variables.

3. Results and discussion

3.1. FT-IR analysis of biosorbent

Fig. 1 presents FT-IR spectra for sodium alginate, PVA, and activated sludge that were constituents of the biosorbent.

A wide band from 3,660 to 3,004 cm^{-1} may be observed in sodium alginate spectrum which indicates vibration of –OH groups. The peak at 1,602 cm^{-1} is typical of sodium alginate and indicative of stretching vibrations of C=O. Asymmetric adsorption band at 1,403 cm^{-1} appeared in response to vibrations of COO– groups and suggested the presence of carboxyl groups in a molecule of sodium alginate. The peak at 1,296 cm^{-1} is induced by vibration of C–O, whereas the vibration band at 1,035 cm^{-1} shows the presence of –COC groups [41]. The spectrum of PVA also possesses a wide band at 3,600–3,100 cm^{-1} which indicates the presence of –OH groups. Another peak at 2,900–2,940 cm^{-1} may be linked with a vibration band of –CH group of alkyl groups. The peak at 1,713 cm^{-1} appeared as a result of stretching vibrations of C=O of the acetate group. The adsorption band at 1,141–1,096 cm^{-1} was probably linked with the presence of C–O functional groups [42]. The spectroscopic FT-IR analysis of activated sludge shows a wide adsorption band of the –OH group (3,600–3,200 cm^{-1}). The peak at 2,922–2,852 cm^{-1} may be linked with the –CH group. In turn, the band at 1,639 cm^{-1} confirms the presence of proteins in activated sludge and is likely to be induced by stretching vibrations of COO, C=O and C–N. The peak at 1,443 cm^{-1} indicates vibrations of C–O and O–H groups of phenolic compounds. In addition, the spectrum of activated sludge shows a band at 1,004 cm^{-1} which confirms the presence of uronic acids and a peak at 827 cm^{-1} which indicates the presence of functional groups containing phosphorus and sulfur [43,44].

3.2. Effect of pH

Analyses of metals desorbed from activated sludge immobilized in 1.5% alginate with 0.5% PVA were conducted at pH 1–12 for saponin and at pH 5–12 for JBR 515 and 425. In the latter case, the boundary value was adopted at pH 5 owing to the fact that decreasing pH below this value caused precipitation of rhamnolipid (JBR 515 and 425) from the solution.

Experimental data depicting the effectiveness of the desorption process for the analyzed biosurfactants and nitric acid depending on pH value are presented in Fig. 2.

The study demonstrated that upon the use of saponin, the effectiveness of desorption of all three examined metals was similar in a pH range of 1–5. Process effectiveness decreased significantly at pH > 5, especially in the case of cadmium (6.4%). In the case of zinc and copper, the effectiveness of desorption was also observed to decrease, to 70 and 59%, respectively, (Fig. 2(a)). pH 5.0 was adopted for further analyses.

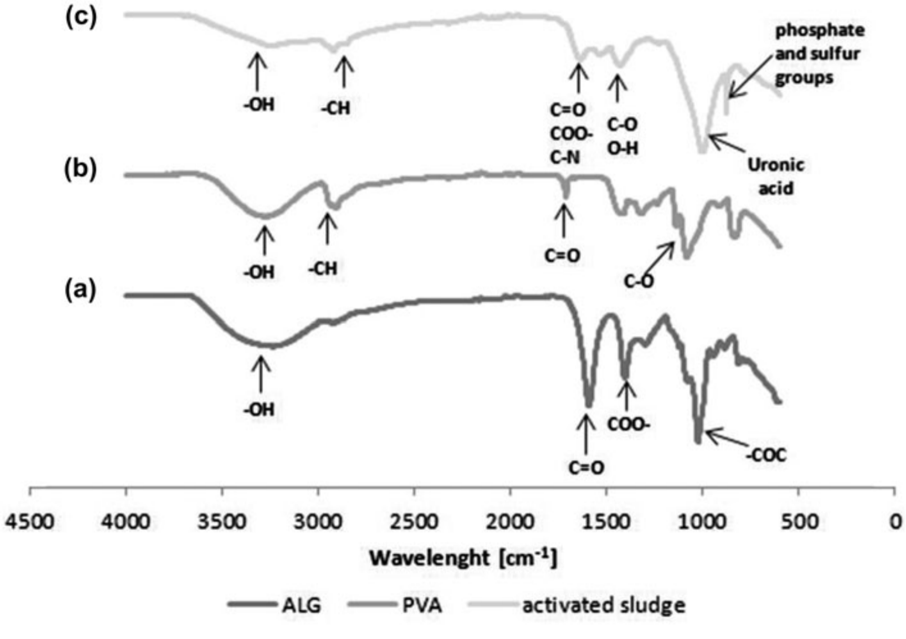

Fig. 1. FT-IR spectrum of: (a) sodium alginate, (b) PVA, and (c) activated sludge.

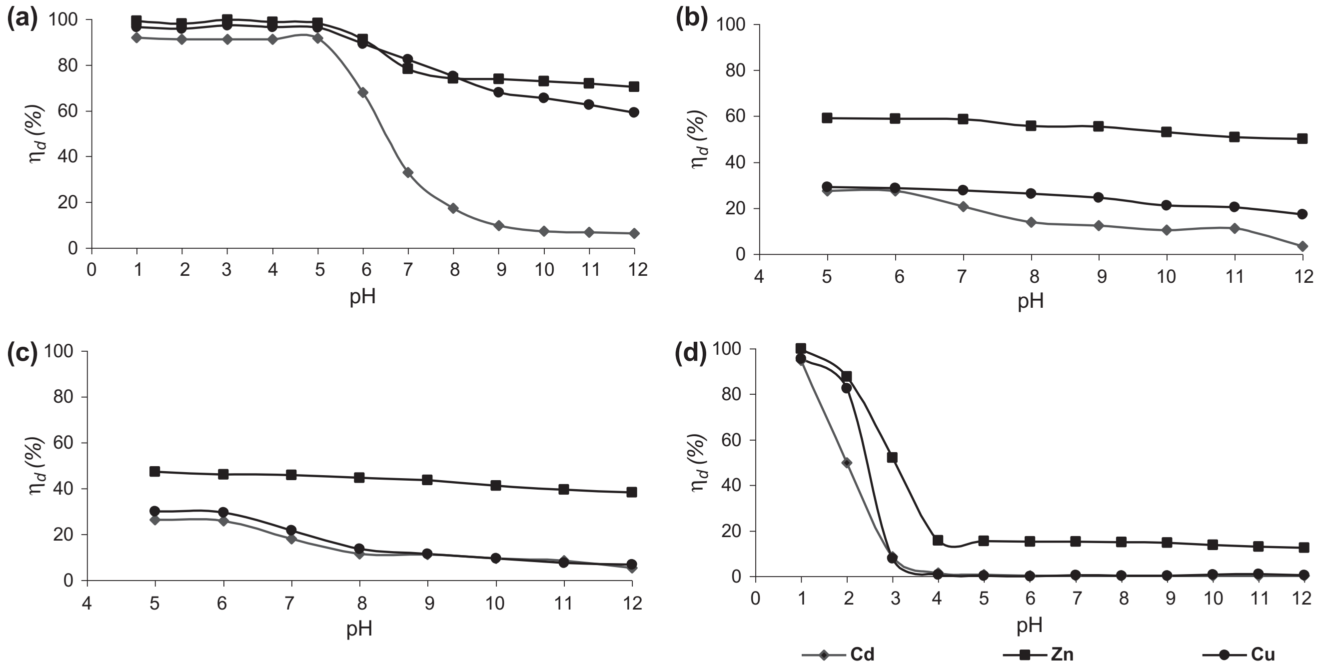

Fig. 2. Effectiveness of metals leaching from biosorbent at various pH values with solutions of: (a) saponin, (b) JBR 515, (c) JBR 425, and (d) HNO_3.

An overview of the literature indicates that saponin is more effective in desorption of heavy metals at lower pH values [38,45]. It was showed that lower pH values were more efficient in removing heavy metals using saponin for different adsorption materials as: soil and kaolin. For instance, Hong et al. [46] investigated desorption of copper, zinc, and cadmium with saponin and achieved the most effective leaching of copper and zinc at pH 3 and 100% desorption of cadmium at pH 3.9. At pH above 6, the process practically did not proceed. In contrast, Rahman and Gakpe [36] report that the highest effectiveness of copper desorption from kaolin by saponin was achieved in a pH range of 2–8. The maximum Cu desorption (over 90%) was obtained by these authors at pH 2; however, the optimal pH was established at 6.5 (83% desorption of Cu).

The effect of pH on the effectiveness of metal recovery with the use of rhamnolipids JBR 515 and 425 was more complex in character and depended on metal type (Fig. 2(b) and (c)). In the case of cadmium, both biosurfactants displayed the highest effectiveness of metal leaching in a pH range of 5–6 (26.7% on average). Increasing the pH value to 12 had a negative effect on the effectiveness of cadmium release with the use of JBR 515 and 425, decreasing it to 3.3 and 5.4%, respectively.

The effectiveness of zinc leaching with the use of rhamnolipids did not depend on the pH value and accounted for 55 and 43% on average in the case of JBR 515 and 425, respectively. Experiments with copper leaching from the biosorbent demonstrated that the rhamnolipids were the most effective at pH 5–6 (29.5%). pH increase to 12 had a negligible effect in the case of JBR 515, contrary to JBR 425 for which the effectiveness of copper release from the biosorbent dropped to 6.8% at a strongly alkaline pH value. Taking into account the effectiveness of metals removal from biosorbent using both analyzed rhamnolipids, the pH value of 6 was adopted as optimal.

A pH value of 6.8 was also the most effective in leaching cadmium from kaolin with the use of JBR 425 [47]. Consistently, Mulligan and Wang [48] report that the rhamnolipid was able to remove 73.2% Cd and 68.1% Ni from polluted soil, and that a change of pH from 6.8 to 10.0 did not improve the process.

In the case of nitric acid, the highest effectiveness of metals removal from biosorbent was achieved at pH 1. The increase in pH value resulted in diminished effectiveness of desorption process, regardless of the type of metal.

Analyses of desorption induced by changes in pH value were conducted for the optimal pH values determined in earlier study, i.e. saponin—pH 5.0 and rhamnolipids JBR 515 and 425—pH 6.0. To exclude the possibility that pH is the only condition responsible for removing metals from biosorbents, distilled water at pH 5 and 6 was applied. Fig. 3 clearly shows that

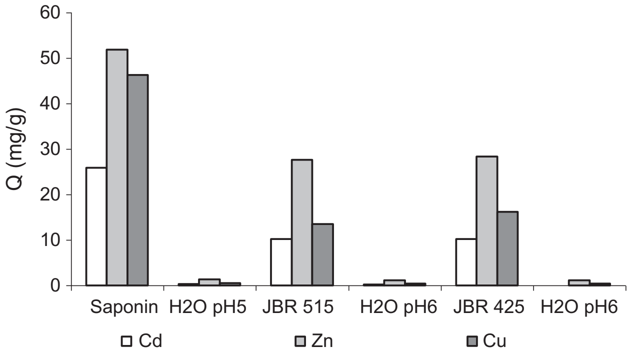

Fig. 3. Effectiveness of metals leaching from biosorbent as a result of using various biosorbents and pH values.

pH alone has no effect on metal removal. Only biosurfactants at pH 5 and 6 are capable of desorption.

3.3. Effect of desorbents concentration

In this study, we also analyzed the effect of the type and dose of applied desorbent on the quantity of cadmium, zinc, and copper released from the biosorbent. Fig. 4 presents the quantities of released metals as affected by the applied dose of desorbents.

Experimental data show that amongst the investigated biosurfactants, saponin (Fig. 4(a)) was more effective in leaching metals compared to the rhamnolipids JBR 515 and 425 (Fig. 4(b) and (c)). Nitric acid had the highest capability for metal removal from the immobilized activated sludge (Fig. 4(d)).

The analysis of desorbent concentrations enabled to determine the optimal dose of it, i.e. a dose above which process effectiveness was no longer increasing. Taking into account the extent of metal removal from the immobilized activated sludge, the optimal dose for saponin and both rhamnolipids was found at 5 g 100 mL^{-1} (≈5% solution), whereas for nitric acid—at 6.3 g 100 mL^{-1} (1 M solution).

3.4. Effect of contact time

Experimental data for the four analyzed desorbents depicting the mass (Q_d) of single metals released from the biosorbent to the solution as a function of time are presented in Fig. 5.

Experimental data demonstrated that the shortest time to reach the equilibrium concentration, i.e. 30 min (Fig. 5(d)), was achieved when 1 M HNO_3 solution was applied to wash out cadmium, zinc, and copper from the biosorbent. For the analyzed biosurfactants and metals, the time to reach equilibrium was significantly longer and reached 120 min (Fig. 5(a)–(c)).

In the solutions of single metals, the leaching of zinc and copper from the biosorbent after $t = 120$ min was the highest and comparable for saponin and nitric acid, whereas in the case of rhamnolipids JBR 515 and 425, it was lower regardless of metal type.

The desorption of the three metals from biosorbent showed typical biphasic kinetics with rapid desorption in the first 30 min for biosurfactants and in the 10 min for nitric acid, and then, the desorption capacity slowly reached equilibrium. This is because initially abundant desorbent is available for desorption and metal concentration (in biosorbent) gradient is high. Afterwards, few surface active sites with metal are available and difficult to be occupied due to repulsive forces between the biosorbent and desorbent. Therefore, very slow increase in metals desorption is observed.

The effectiveness of zinc and copper recovery as a result of saponin application reached 95 and 87%, respectively, whereas their release from biosorbent upon the use of nitric acid reached 86 and 96%, respectively (Table 1).

It was showed that desorption is usually induced by pH changes and depends on the type of desorbent. Zhang and Wang [49] investigated desorption of cadmium from calcination-modified coal waste using HCl. The effectiveness of Cd^{2+} desorption reached 92.12 and 96.43% depending on the type of adsorbent modification. Chen and Hsiao [39] were examining metal desorption from copper(II)/nickel(II)-spiked kaolin as a soil component using plant-derived saponin biosurfactant. Effectiveness of metals removal was ≈83% of the copper and ≈85% of the nickel. Dahrazma and Mulligan [50] evaluated the removal of heavy metals (copper, zinc, and nickel) from sediments by rhamnolipid (a glycolipid biosurfactant JBR 215). The efficiency of heavy metals from sediments was up to 37% for Cu, 13% for Zn, and 27% for Ni.

Experimental data demonstrating the mass (Q_d) of a mixture of metals released from biosorbent to solution depending on time are presented in Fig. 6.

Analysis of experimental data demonstrated that the time necessary to reach the equilibrium concentration was the same for mixtures and single metals in the case of all analyzed desorbents (Fig. 6).

The highest effectiveness of metal recovery from the mixture with the use of all analyzed desorbents was obtained for zinc, which ranged from 92.7% for saponin to 51.1% for JBR 425 (Table 2).

3.5. Desorption kinetics

Determination of technological parameters required for metal removal from wastewaters with the adsorption method requires the knowledge of process rate.

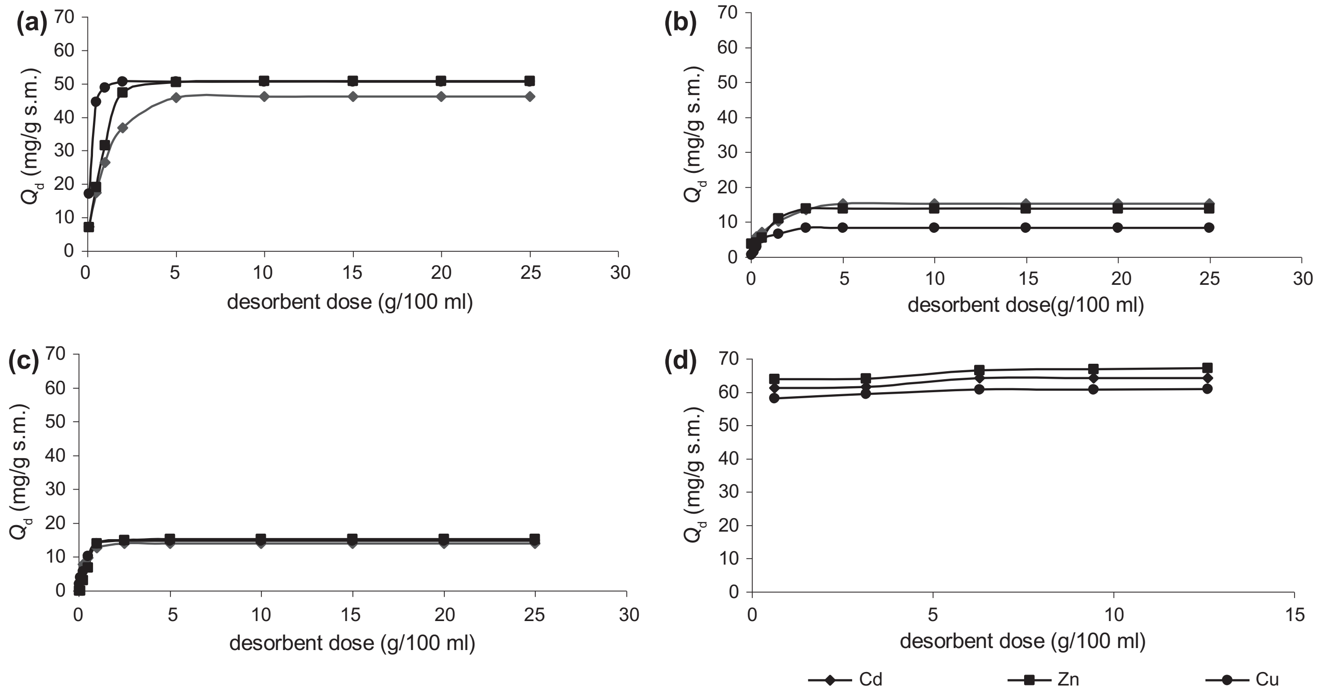

Fig. 4. Effectiveness of metals leaching from biosorbent depending on the concentration of desorbent: (a) saponin, (b) JBR 515, (c) JBR 425, and (d) nitric acid.

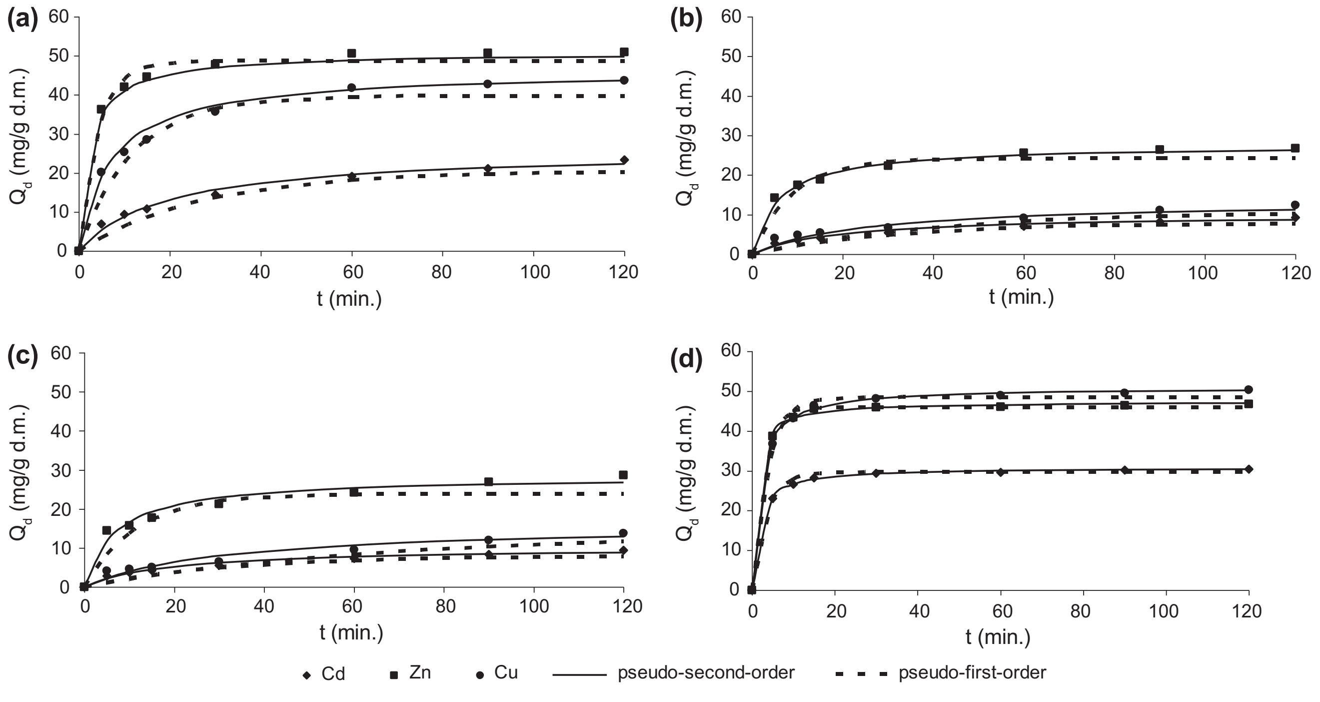

Fig. 5. Correlation between the mass of desorbed metals and time of desorption for single metals desorbed from solutions: (a) saponin, (b) JBR 515, (c) JBR 425, and (d) nitric acid.

Table 1
Effectiveness of metal recovery from biosorbent (solutions of single metals)

	Desorption (%)			
Metal	Saponin	JBR 515	JBR 425	HNO_3
Cd	51.2	20.4	20.7	65.3
Zn	94.8	49.7	53.3	85.7
Cu	86.5	24.6	27.2	96.2

Table 2
Effectiveness of metal recovery from biosorbent (metal mixtures)

	Desorption (%)			
Metal	Saponin	JBR 515	JBR 425	HNO_3
Cd	43.1	19.8	17.6	52.7
Zn	92.7	61.6	51.1	89.0
Cu	73.6	19.4	15.4	85.0

The knowledge of the values of kinetic constants enables to determine the required time of reaction and reactor's volume, especially when the process is run with the batch adsorption method in a bath, namely under conditions of dosing the adsorbent into a specified batch of adsorbate, and stirring the whole mixture.

When designing a cyclic process of desorption, the knowledge of its kinetics is especially significant because the successive cycles might result in mechanical damage to carrier structure or—after metals binding—in conformational changes in the biosorbent biopolymeric structure. In such circumstances, the rate of unitary processes in the subsequent cycles may differ, which in turn may lead to a decrease in process effectiveness.

Analyses of desorption kinetics were carried out with the use of activated sludge immobilized in a mixture of 1.5% alginate with 0.5% PVA for single metal solutions of 300 mg L^{-1} and in the ratio of 100:100:100 mg L^{-1} for their mixture. Desorbents used in the study were 5% solutions of saponin, JBR 515 and 425, as well as 1 M HNO_3.

The evaluation of desorption effectiveness consisted in determining desorption kinetics, i.e. the order of reaction and rate constants. Overview of the literature data shows that desorption kinetics was usually described using both pseudo-first-order and pseudo-second-order reactions [51–53].

The kinetic constants, i.e. rate constants of pseudo-first-order (k_1) and pseudo-second-order (k_2) desorption, and the mass of metals desorbed in the

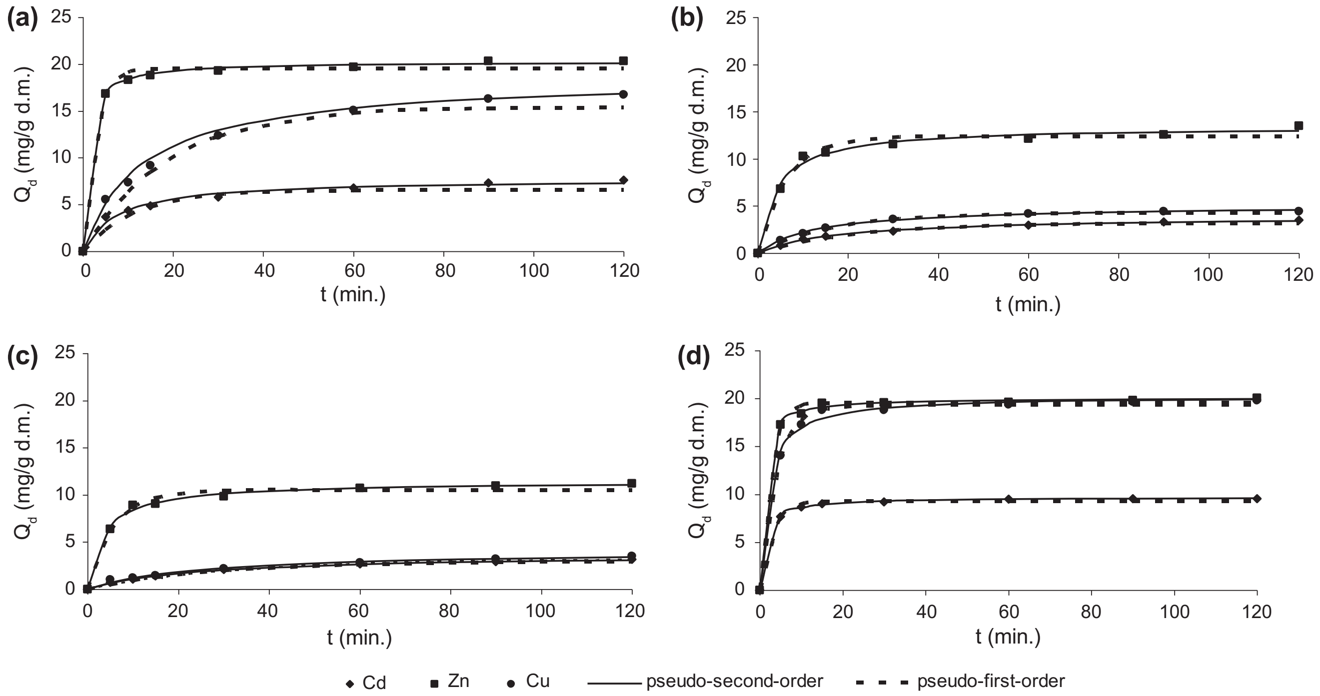

Fig. 6. Correlation between mass of metals desorbed from a mixture and desorption time: (a) saponin, (b) JBR 515, (c) JBR 425, and (d) nitric acid.

equilibrium state (Q_d) for single metals are presented in Table 3.

Based on the determined constants (Table 3), the conclusion is that in the case of all analyzed biosurfactants, the process of desorption proceeded according to the pseudo-second-order reaction, whereas in the case of HNO_3, both the pseudo-first-order and pseudo-second-order reaction described experimental results, which was indicated by the determined R^2 values.

Table 3
Values of kinetic constants of single metals desorption from solutions

Cd	Pseudo-first-order		
	k_1 (1 min^{-1})	Q_d (mg g^{-1} dm^{-1})	R^2
Saponin	0.037	20.440	0.9865
JBR 515	0.032	7.970	0.9817
JBR 425	0.032	8.040	0.9807
HNO_3	0.279	29.470	0.9974
	Pseudo-second-order		
	k_2 (mg g^{-1} min^{-1})	Q_d (mg g^{-1} dm^{-1})	R^2
Saponin	0.002	25.897	0.9928
JBR 515	0.005	10.164	0.9880
JBR 425	0.005	10.247	0.9873
HNO_3	0.020	30.826	0.9971
Zn	Pseudo-first-order		
	k_1 (1 min^{-1})	Q_d (mg g^{-1} dm^{-1})	R^2
Saponin	0.232	48.740	0.9926
JBR 515	0.112	24.290	0.9815
JBR 425	0.086	23.850	0.9627
HNO_3	0.355	46.000	0.9993
	Pseudo-second-order		
	k_2 (mg g^{-1} min^{-1})	Q_d (mg g^{-1} dm^{-1})	R^2
Saponin	0.008	51.860	0.9997
JBR 515	0.006	27.603	0.9961
JBR 425	0.005	28.324	0.9839
HNO_3	0.021	47.361	0.9993
Cu	Pseudo-first-order		
	k_1 (1 min^{-1})	Q_d (mg g^{-1} dm^{-1})	R^2
Saponin	0.084	39.720	0.9862
JBR 515	0.025	10.730	0.9725
JBR 425	0.016	13.590	0.9792
HNO_3	0.259	48.530	0.9974
	Pseudo-second-order		
	k_2 (mg g^{-1} min^{-1})	Q_d (mg g^{-1} dm^{-1})	R^2
Saponin	0.003	46.251	0.9966
JBR 515	0.003	13.542	0.9761
JBR 425	0.002	16.230	0.9714
HNO_3	0.011	50.957	0.9995

The recovery of zinc and copper with the use of saponin reached 51.86 and 46.25 mg g^{-1} dm^{-1}, whereas the application of nitric acid enabled their recovery at 46.0 and 50.96 mg g^{-1} dm^{-1}, respectively.

The highest values of kinetic constants k_1 and k_2 were obtained for nitric acid irrespective of reaction order and metal type.

The obtained values of kinetic constants, i.e. rate constants of pseudo-first-order (k_1) and pseudo-second-order (k_2) desorption, and the mass of metals from a mixture desorbed in the equilibrium state (Q_d) are presented in Table 4.

Based on the constants listed in Table 4, it can be concluded that in the case of all analyzed desorbents, the process of metals leaching from immobilized activated sludge proceeded according to the pseudo-second-order reaction, as indicated by the R^2 values.

The determination of kinetic constants of metals desorption from a mixture (Table 4) demonstrated that the quickest adsorption occurred for zinc, which was demonstrated by values of k_2 constant. The mass of zinc released from biosorbent was also the highest and fitted within the range of 11.4–20.2 mg g^{-1} dm^{-1}.

The R^2 values obtained for the pseudo-first-order were lower than the values obtained with the pseudo-second-order kinetic equation. Therefore, the pseudo-second-order model better represents the desorption kinetic, and thus supports the assumption that the overall desorption rate is proportional to the square of the difference between the equilibrium Me^{2+} uptake and the actual uptake amount $(q_e–q)^2$ [54]. This suggested that the overall rate of the Me^{2+} biosorption process is controlled by a chemical process as the rate-controlling mechanism. An external surface mass transfer or film diffusion process possibly controls the early stages of the desorption process.

3.6. Mechanism of metals leaching from biosorbent with the use of alkaline biosurfactants

The molecules of the biosurfactant from dissociated micelles may easily adsorb on the interfacial surface. After some time, they are a subject of desorption and re-form micelles in the aqueous solution. This means, a dynamic equilibrium is being established. This process enables acid–base and electrostatic interactions of charges between hydrophilic anions of biosurfactants and cations of metals bound at the active sites of the sorbent. Additionally, non-ionic hydrophilic polar groups of the biosurfactant molecules and sorbent–surface interactions occur, at which no sorption of metals occurred, until the moment of the formation of a biosurfactant monolayer covering the sorbent. Next competitive adsorption of biosurfactant molecules and

Table 4
Values of kinetic constants of desorption from a mixture of metals

Cd	Pseudo-first-order		
	k_1 (1 min^{-1})	Q_d (mg g^{-1} dm^{-1})	R^2
Saponin	0.086	6.570	0.9736
JBR 515	0.047	3.200	0.9917
JBR 425	0.038	2.950	0.9969
HNO_3	0.328	9.330	0.9978
	Pseudo-second-order		
	k_2 (mg g^{-1} min^{-1})	Q_d (mg g^{-1} dm^{-1})	R^2
Saponin	0.017	7.732	0.9912
JBR 515	0.014	3.936	0.9979
JBR 425	0.011	3.723	0.9993
HNO_3	0.082	9.684	0.9998
Zn	Pseudo-first-order		
	k_1 (1 min^{-1})	Q_d (mg g^{-1} dm^{-1})	R^2
Saponin	0.371	19.570	0.9963
JBR 515	0.156	12.380	0.9912
JBR 425	0.170	10.520	0.9915
HNO_3	0.410	19.580	0.9984
	Pseudo-second-order		
	k_2 (mg g^{-1} min^{-1})	Q_d (mg g^{-1} dm^{-1})	R^2
Saponin	0.047	20.266	0.9996
JBR 515	0.018	13.417	0.9944
JBR 425	0.024	11.387	0.9975
HNO_3	0.063	20.090	0.9995
Cu	Pseudo-first-order		
	k_1 (1 min^{-1})	Q_d (mg g^{-1} dm^{-1})	R^2
Saponin	0.053	15.410	0.9936
JBR 515	0.061	4.310	0.9987
JBR 425	0.032	3.180	0.9900
HNO_3	0.248	19.320	0.9979
	Pseudo-second-order		
	k_2 (mg g^{-1} min^{-1})	Q_d (mg g^{-1} dm^{-1})	R^2
Saponin	0.004	18.746	0.9982
JBR 515	0.015	5.074	0.9991
JBR 425	0.010	4.090	0.9929
HNO_3	0.025	20.254	0.9986

metal ions on the sorbent proceed at head–head and tail–tail positions. It is claimed that interruption of interactions between metal ions adsorbed on the sorbent results from a high gradient of voltage induced by a biosurfactant film on the sorbent's surface [55]. The last stage begins with the spatial translocation of a biosurfactant film at the sorbent–water interface, thus causing the leaching of metal ions and their unassisted binding into metal–biosurfactant complexes as a result of chemi-micelle aggregation on the top of the monolayer and, finally, desorption of metal–biosurfactant complexes. The development of chemi-micelles into complete micelles proceeds spontaneously due to increased electrostatic interactions with neighboring molecules of chemi-micelles and/or cation exchange inside the double layer. Finally, there occurs desorption of micelles formed and/or metal–biosurfactant aggregates from the sorbent, with constant transfer of metal ions to the solution as a result of electrostatic repulsion and surface diffusion by detachment from the negatively charged biosurfactant film occurring on the surface of the sorbent [39].

4. Conclusions

Activated sludge immobilized in 1.5% sodium alginate with 0.5% PVA was an excess sludge after methane fermentation obtained from a wastewater treatment plant in Olsztyn. The desorption of heavy metal from immobilized activated sludge depends strongly on the pH of solution, biosorbent dose, and contact time. Saponin showed the highest effectiveness of metals leaching at pH 1–5, whereas rhamnolipids—at pH 5–6. The optimal biosorbent dose was found at 5 g 100 mL^{-1} (≈5% solution) for all the biosurfactants, whereas for nitric acid, the optimal dose was determined at 6.3 g 100 mL^{-1} (1 M solution). The shortest time—30 min to reach the equilibrium concentration—was achieved for 1 M HNO_3, whereas for biosurfactants, this period was longer and reached 120 min. Such results were achieved in desorption process of both single metals and their mixtures. The kinetic study results showed that pseudo-second-order kinetic model gave the best correlation coefficient. The highest values of adsorption kinetic constants (Q_{ad} and k) were obtained for zinc removal from both a solution of single metal and from a metal mixture. The highest values of desorption kinetic constants (Q_d, k) were achieved for zinc with saponin and nitric acid used as leaching agents. In contrast, the lowest values of kinetic constants of adsorption and desorption processes were obtained for cadmium, irrespective of the adsorbent applied. Saponin was found to be comparable to nitric acid in its effectiveness in the recovery of zinc and copper from biosorbent, which was at a level of ca. 90%. This suggests the feasibility of using saponin as a desorbing agent.

Acknowlegments

This research was financially supported by the grant: KBN N N523 452936 (Poland). The present study was carried out at Warmia and Mazury University in Olsztyn in Poland in the years 2011–2012.

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