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Adsorption kinetics of Cd(II), Zn(II) and Cu(II) and their mixtures from an aqueous solution onto immobilized activated sludge

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ABSTRACT

In this study, we determined the kinetics of cadmium, zinc, and copper removal by an activated sludge immobilized in 1.5% sodium alginate with 0.5% polyvinyl alcohol. The adsorption of metals from solutions of both single metals and their mixtures was found to follow the pseudo-second-order reaction. In the solutions of single metals cadmium was most effectively adsorbed (96.10 mg g^{-1} d.m.); whereas in metal mixtures, it was copper (37.38 mg g^{-1} d.m). It was also observed that the presence of copper in a mixture of metals impaired the sorption of cadmium and zinc.

Keywords: Heavy metals; Mixture of metals; Sorption kinetics

1. Introduction

Effective methods of heavy metal ions removal from aqueous solutions include adsorption and chemisorption, with the most popular and documented in literature adsorbents including zeolites [1], silica gels [2] and activated carbons [3]. However, a search is underway for novel materials of biological origin to be used for metal ions removal from multi-component solutions as economical, effective and easily available sorbents.

Biosorbents can be divided into adsorbents with high and low costs of obtaining them.

The first group includes microorganisms, which are specially bred and propagated for biosorption. Because of the costs, they should be characterized by high metal adsorption efficiency from solutions and easy desorption with the use of cheap desorbents.

The second group contains materials, which can be directly obtained from the environment such as algae [4,5], moss [6], fungi [7] and industrial waste products f.e. yeast from the process of fermentation [8] or breweries [9]. Equally, effective biosorbent is the biomass of microorganisms which is a waste product of wastewater treatment activated sludge. It consists of microorganisms of various kinds, mainly bacteria, fungi, yeast, algae, and protozoa. This biosorbent is easy in access to the sewage treatment plant and has big sorption abilities [10]. Interaction between metals and biomass leads to heavy metal binding depending on functional groups such as carboxyl, hydroxyl, amino, phosphate, sulfhydryl, thioether, carbonyl, imidazole, sulfate or sulfonate which are in cell walls or biopolymers of dead organisms [11].

The disadvantage of biosorbents, which occur in the form of free biomass is small mechanical resistance and difficulty in separating the biosorbent from the solution. The usage of the immobilized biomass particles provides bigger application possibilities as well as enables easy recovery of biomass from wastewater, the possibility of regeneration and high metal elimination efficiency [12,13].

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An overview of literature indicates that alginates are not only good carrier used for immobilization of biomass, but also an effective adsorbent of metals [14,15]. Alginate sorbents are, however, characterized by low mechanical resistance and a relatively low stability, which is one of the reasons limiting their more common application. For this reason, in this study, the biomass is a waste product (namely excess activated sludge after methane fermentation of wastewaters at the municipal wastewater treatment plant in Olsztyn), was immobilized with 1.5% sodium alginate and 0.5% polyvinyl alcohol (PVA).

One of the basic adsorbent usefulness criteria is maximal adsorption capacity. In the research adsorptions of single metals and their mixtures were analyzed based on isotherms of adsorption and maximum volume determined from Langmuir and Freundlich equations.

The usage of the new biosorbent requires the knowledge of parameters having an influence on the process of adsorption such as pH and the contact time. The adsorption of metal on biosorbent must also include external mass transfer, intramolecular diffusion, and adsorption.

The main purpose of the research was to determine the adsorption kinetics of cadmium, zinc and copper and their mixtures on immobilized activated sludge with 1.5% alginate and 0.5% PVA. In the work, the order, the adsorption rate constants and the influence of external and internal diffusion on its efficiency were determined.

2. Materials and methods

2.1. Preparation of activated sludge

The experiment was conducted with excess activated sludge that had been methane fermented in the wastewater treatment plant in Olsztyn. To dehydrate the sludge, it was rinsed twice with acetone, centrifuged for 10 min at 4,500 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.

2.2. Preparation of immobilized activated sludge

To immobilize the dehydrated sludge, a solution was prepared containing 0.5 g of PVA in 80 g of distilled water (60°C). The PVA solution was cooled to room temperature, then 1.5 g of sodium alginate was dissolved in it, followed by 2 g d.m. of the sludge. Distilled water was added until the total weight reached 100 g. This homogenous solution was dropped into a 0.1 M $CaCl_2$ solution that was saturated with boric acid. The grains that formed were left to gelatinize for 24 h and afterward were rinsed with distilled water.

2.3. Fourier transform infrared spectroscopy analysis of biosorbent

Fig. 1 presents Fourier transform infrared spectroscopy (FTIR) spectra for sodium alginate, PVA and activated sludge that was constituents of the biosorbent.

A wideband from 3,660 to 3,004 cm^{-1} may be observed in the 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 [16]. The spectrum of PVA also possesses a

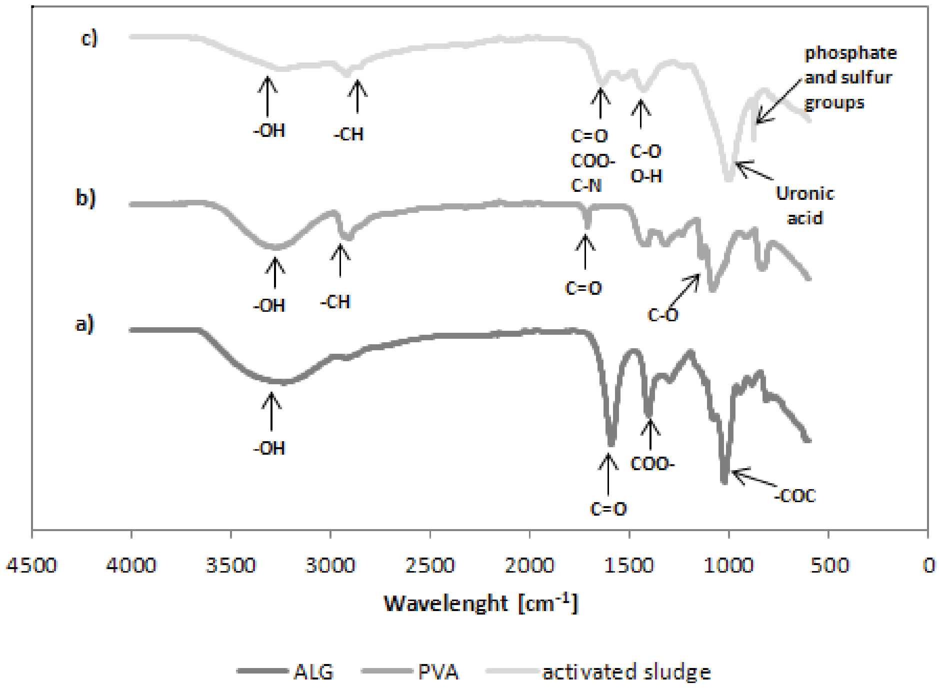

Fig. 1. FTIR spectrum of (a) sodium alginate, (b) polyvinyl alcohol, and (c) activated sludge.

wide band at 3,600–3,100 cm^{-1} which indicates the presence of –OH groups. Another peek 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 [17]. The spectroscopic FTIR 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 [18,19].

2.4. Metal solution preparation

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

2.5. Effect of pH on the adsorption of the metal

To determine if the optimal pH value for the adsorption reaction test were carried out at seven pH values, pH = 3, 4, 5, 6, 7, 8, and 9. To this end, 4 g of a biosorbent was added to 50 cm^3 (5.84 g d mL^{-1}) of a metal solution with a specified pH value that was adjusted by 0.1 and 1 N NaOH or 0.1 N HNO_3. Samples were shaken with a shaker for 120 min at 170 rpm.

2.6. Determination of equilibrium adsorption time

To determine the time necessary to reach reaction equilibrium, biosorbent (8 g–5.84 g d mL^{-1}) was weighed into a reaction vessel, which was next filled with 100 cm^3 of a cadmium, zinc, and copper solution at a concentration of 300 mg L^{-1} or with a mixture of these metals at a ratio of 100:100:100 mg L^{-1}.

The reaction vessel was placed on a magnetic stirrer. Next, after periods of 0, 5, 10, 15, 30, 60, 90, and 120 min, samples were collected and the concentration of metals in the solution was determined.

2.7. Determination of the maximum adsorption capacity

To determine the adsorption capacity of the activated sludge immobilized in sodium alginate with the addition of PVA, solutions of metals were prepared in concentrations from 1 to 600 mg L^{-1}. Next, 100 cm^3 of these prepared solutions of either single metals or their mixtures at a ratio of 1:1:1 were added to 250 cm^3 reaction flasks along with 8 g (5.84 g d mL^{-1}) of the biosorbent. The flasks were shaken with a shaker for 2 h at 180 rpm. Next, the concentration of metals left in the solution after sorption was determined.

3. Results and discussion

3.1. Effect of adsorption pH on its effectiveness

The effect of the pH value on adsorption effectiveness (η_s) was evaluated based on the percentage content of metal in the adsorbent and computed from the following formula:

$$\eta_{ad} = \frac{C_0 - C_{ad}}{C_0} \times 100 \tag{1}$$

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

The adsorption capability of the biosorbent depended on the pH value applied, respective results are presented in Fig. 2.

The study demonstrated that the effectiveness of cadmium adsorption reached 94% at a pH of 5.0 to 9.0. A reduction in the pH value to 4.0 caused a decrease in adsorption effectiveness to 80%, whereas a further decrease in pH to 3.0 resulted in a significant decline of effectiveness to merely 56%.

In analyses of zinc adsorption dependence on the pH value, the optimal pH value of zinc adsorption fitted within the range of 5.0–7.0. The highest effectiveness of the process (83%) was noted at pH 6.0. Increasing the pH value above 7.0 and its reduction to 3.0 caused a significant decrease in adsorption effectiveness to ca. 50%.

The greatest impact of pH value on adsorption effectiveness was observed in the case of copper. The optimal pH fitted within the range of 5.0–6.0, where the effectiveness of metal removal reached 91%. A significant change in copper adsorption was noted in a pH range of 7.0–9.0, when the effectiveness of copper removal from the solution accounted for 86% and 45%, respectively.

The concentration of hydrogen ions is one of the most important factors that determine biosorption effectiveness. Based on the correlation between adsorption effectiveness and pH, Madrid and Cámara [19] have distinguished three classes of metal ions. Metals analyzed in our study belong to the first class which is characterized by the highest process effectiveness at a pH close to neutral. Low pH values (pH < 2) inhibit the removal of these metals and enable their

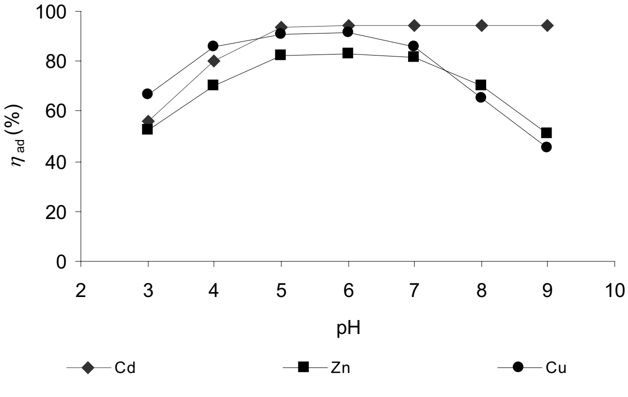

Fig. 2. Effectiveness of metals adsorption at different pH (pH 6.0 and temperature 25°C).

easy recovery from the bisorbent. However, each sorbent is characterized by a varied optimum of action, hence optimal pH ought to be adjusted individually. In the analysis of cadmium, zinc and copper adsorption from an aqueous solution by activated sludge immobilized in 1.5% alginate with 0.5% PVA, the optimal pH range is between 5.0 and 7.0. These values were used for further experiments in this study.

3.2. Internal and external diffusion

The results of these experiments and literature data related to mechanisms of metals sorption served to formulate equations that were used to approximate measuring points of changes in the concentrations of metals and their mixtures over time. It was assumed that metals removal by the adsorbent might be impaired by the rate of the following processes:

- external diffusion,
- internal diffusion,
- sorption,

In this work, the rate of these processes was determined based on results presenting the changes in the concentrations of the metals and their mixtures in time.

The rate constant of external diffusion may be computed from Eq. (2) [21].

$$\frac{dC_t}{dt} = -\beta_L S\left(C_t - C_s\right) \tag{2}$$

where β_L is the external coefficient of mass transfer (cm s^{-1}); S is the specific surface (cm); and C_t is the metal concentration in the solution (mg L^{-1}) in time t (s).

The values of these coefficients were determined to assume that metal concentration at the liquid-sorbent interface (C_s) is insignificant at time $t = 0$, and metal concentration in the solution does not change much from the initial concentration C_0, and finally, the internal diffusion is insignificant. For this reason, the equation was simplified to the form:

$$\left(\frac{dC_t / C_0}{dt}\right)_{t\to 0} = -\beta_L S \tag{3}$$

The initial rate of sorption $-\beta_L S$ (s^{-1}) was determined by C_t/C_0 linearization depending on time. It was assumed that the specific surface would correspond to the external surface and that the particles would be oval. By this means, S was computed according to the formula:

$$S = \frac{6m}{d \times \rho} \tag{4}$$

where m is the sorbent mass concentration in the solution, 80 (g L^{-1}); d is the particle size diameter (m); and ρ is the apparent volume mass of the sorbent, 1.0879 (g L^{-1}). The specific surface area reached 176.5 (m^{-1}).

The coefficient of internal diffusion was determined using an equation provided by Urano and Tachikawa [21]. This model assumed that the rate of adsorption was independent of the speed of mixing and that the external diffusion coefficient was insignificant with respect to the low total sorption rate. The kinetics of sorption was described with the following model:

$$f\left(\frac{Q_t}{Q_{\text{ad}}}\right) = -\left[\log\left(1-\left(\frac{Q_t}{Q_{\text{ad}}}\right)^2\right)\right] = \frac{4\pi^2 D_i t}{2.3d^2} \tag{5}$$

where Q_t and Q_{ad} (mg g^{-1} d.m.) is the solute concentration in the solid at t and equilibrium ($t \to \infty$) in the previous experimental condition; d is the particle diameter (m), and D_i is the diffusion coefficient in the solid (m^2 s^{-1}) t (s). Linearization was carried out using the initial time of contact between 0 and 15 min in the case of zinc and copper, and between 0 and 30 min in case of cadmium.

Experimental results achieved for changes in concentrations of metals over time, and constants of external and internal diffusion determined on their basis were presented in Figs. 3 and 4, and in Table 1.

The external (β_L) and internal (D_i) diffusion coefficients for Cu^{2+} was highest, both without other metals in solution and a mixture.

Determined values of the external and internal diffusion coefficients for three examined metals in case of adsorption from single solutions have not shown a significant difference. Lower values obtained for cadmium can be explained with

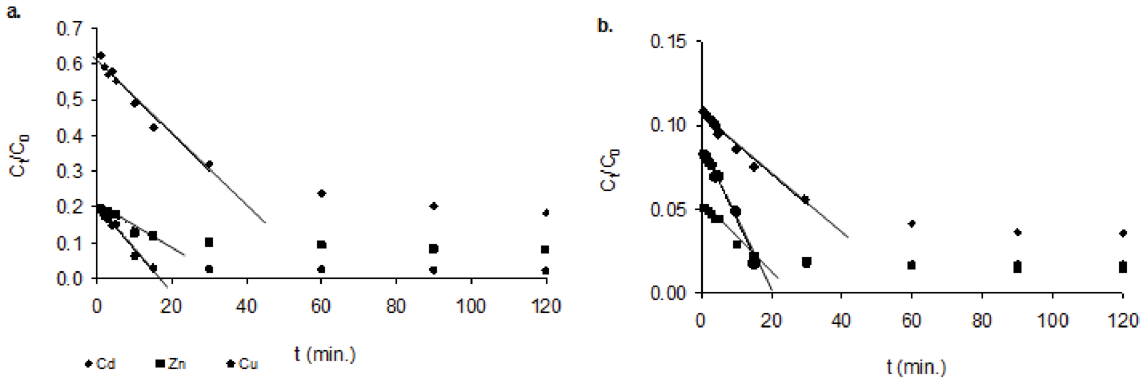

Fig. 3. Changes in metals concentration in time (a) single metals and (b) metal mixture (pH 6.0 and temperature 25°C).

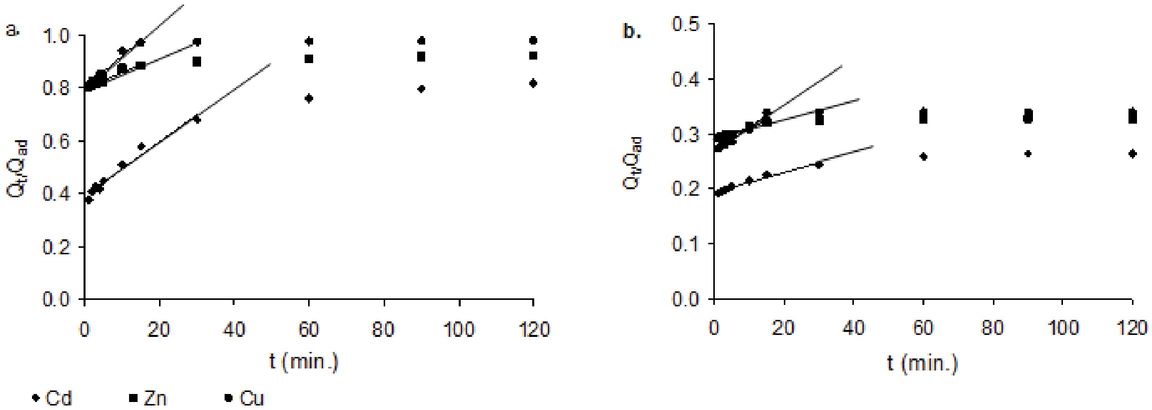

Fig. 4. Changes in the amount of adsorbed single metals and their mixture in time (a) single metals and (b) metal mixture (pH 6.0 and temperature 25°C).

Table 1
Constants of external and internal diffusion for single metals and their mixture

Metal ions	External diffusion	Internal
Single metals	β_L (m^{-1})	D_i ($m^2\ s^{-1}$)
Cd	5.84×10^{-5}	1.76×10^{-11}
Zn	6.18×10^{-5}	1.86×10^{-11}
Cu	6.91×10^{-5}	2.09×10^{-11}
Metal mixture		
Cd	1.02×10^{-5}	0.308×10^{-11}
Zn	1.25×10^{-5}	0.376×10^{-11}
Cu	2.55×10^{-5}	1.64×10^{-11}

higher molecular weight. Molecular weights of the remaining tested metals – zinc and copper are comparable and about twice lower in comparison to cadmium.

In the case of adsorption from the mixture of metals considerably the highest values of the external and internal diffusion coefficients were obtained for copper. In the case of the external diffusion, the value was about twice higher in comparison to cadmium and zinc, in internal diffusion around 5 times higher. Differences in the external and internal diffusion coefficients might be a result of different features of the adsorbent. The research shows that tested adsorbent is the most effective in adsorption of copper.

3.3. Analyses of adsorption kinetics of cadmium, zinc, and copper under static conditions

To determine technological parameters for designing systems for metal removal from wastewater by adsorption, it is essential to know the process rate. Knowledge of kinetic constants enables the determination of the required reaction time and reactor volume, especially when the process is run with the batch adsorption method in a bath, that is, by adding the adsorbent to a specific batch of adsorbate and stirring the mixture.

Adsorption kinetics were analyzed with the use of activated sludge immobilized in a mixture of 1.5% alginate with 0.5% PVA for solutions containing single metals at a concentration of 300 mg L^{-1} and for a mixture of cadmium, zinc, and copper at a ratio of 100:100:100 mg L^{-1} (the entire amount of metal in solution was also equal 300 mg L^{-1}) To evaluate adsorption effectiveness the reaction order and rate constants were determined. An overview of literature data indicates that adsorption kinetics have been described as both pseudo-first-order and pseudo-second-order reactions [23–26].

Reaction rate constants were calculated with Lagergren's equation commonly applied to this end, which consists in the analysis of correlations between the mass of metal adsorbed by 1 g of adsorbent and time, and is defined as the pseudo-n-order reaction. The order of reaction was determined by using determination coefficients (R^2) as selection criteria.

Equation for a pseudo-first-order reaction:

$$\frac{dQ_t}{dt} = k_1 \left(Q_{\text{ad}} - Q_t\right) \tag{6}$$

where k_1 is the rate constant for a pseudo-first-order adsorption (1 min^{-1}).

Model of pseudo-second-order reaction:

$$\frac{dQ_t}{dt} = k_2 \left(Q_{\text{ad}} - Q_t\right)^2 \tag{7}$$

where k_2 is the rate constant for pseudo-second-order adsorption (mg L^{-1} min^{-1}).

The relationships between the mass of single metals adsorbed and time are presented in Fig. 5; the rate constants determined from the pseudo-first-order and pseudo-second-order equation are presented in Table 2.

The time for the adsorption reaction to reach equilibrium was greatly affected by the type of metal, both for solutions of single metals and for their mixtures. Copper and zinc both reached equilibrium after 15 min; 46.6 mg g^{-1} d.m. of copper was removed, 51.5 mg g^{-1} d.m. of zinc. After 15 min, only 38.0 mg g^{-1} d.m. of cadmium had been removed; this solution reached equilibrium after 90 min. (Fig. 5a).

In the metal mixtures, the adsorption of Cu and Zn took longer to reach equilibrium (30 min.), whereas Cd reached equilibrium faster (60 min) than in its single metals (Fig. 5b).

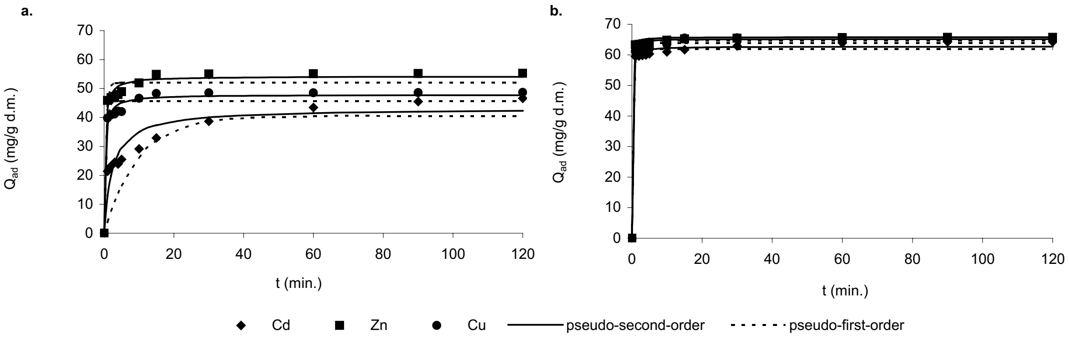

Fig. 5. Relationships between the mass of adsorbed metals and time of adsorption (a) solutions of single metals and (b) metal mixture.

Table 2
Values of kinetic constants of adsorption from solutions of single metals and their mixture

Metal ions	Pseudo-first-order		
Single metals	k_1 (min^{-1})	Q_{ad} (mg g^{-1} d.m.)	R^2
Cd	0.103	40.48	0.9228
Zn	1.890	51.96	0.9976
Cu	1.772	45.68	0.9744
	Pseudo-second-order		
	k_2 (mg g^{-1} min^{-1})	Q_{ad} (mg g^{-1} d.m.)	R^2
Cd	0.010	43.10	0.9459
Zn	0.068	54.17	0.9920
Cu	0.069	47.82	0.9909
Metal ions	Pseudo-first-order		
Mixture	k_1 (min^{-1})	Q_{ad} (mg g^{-1} d m)	R^2
Cd	3.198	61.80	0.9854
Zn	3.784	64.68	0.9989
Cu	3.081	63.83	0.9958
	Pseudo-second-order		
	k_2 (mg g^{-1} min^{-1})	Q_{ad} (mg g^{-1} d m)	R^2
Cd	0.190	62.71	0.9976
Zn	0.353	65.18	0.9995
Cu	0.375	64.81	0.9981

The study demonstrated that the adsorption of single metals proceeded according to the pseudo-second-order reaction (Eq. (7)). It is in agreement with the findings of other authors [27–29].

Calculations made for adsorption effectiveness showed that cadmium and zinc were adsorbed more effectively from solutions of single metals than from the mixture of metals. In contrast, in case of copper adsorption from the mixture with cadmium and zinc, the effectiveness of its removal was higher compared to the effectiveness of copper removal from the solution of single metals and reached 99.6% and 94.5%, respectively (Fig. 6).

The determined external and internal diffusion coefficients confirm that. In the case of cadmium and zinc around 5 times, a lower value of β_L and D_i was noted in comparison with the values determined for the single metal solutions. In the case of values of β_L and D_i determined for copper significantly lower decrease (around 2 times lower values) was noted.

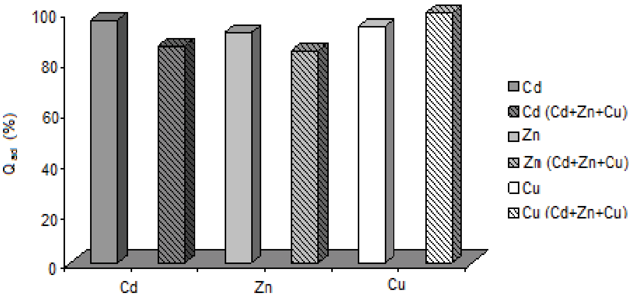

Fig. 6. Effectiveness of metals removal from solutions of single metals and from their mixture.

In analyzing reaction rate constants, it may be concluded that adsorption of Cd^{2+} and Zn^{2+} proceeded faster from the mixture of metals, whilst Cu ions were adsorbed with a comparable rate from both solutions of single metals and their mixtures.

Particularly significant increase in the speed of reaction was observed in case of adsorption of cadmium, for which the constant value of k_2 for adsorption from single solution was equal 0.010 mg g^{-1} min^{-1} and for adsorption from a mixture of three metals it increased to 0.025 mg g^{-1} min^{-1}. The values of constants k_2 determined for zinc and copper were comparable in case of adsorption from single solutions as well as from mixtures.

3.4. Adsorption

Adsorption of metals under equilibrium conditions was evaluated based on the course of adsorption isotherms and the maximum adsorption capacity determined from the Langmuir's equation for single metals and their mixtures at the Cd:Zn:Cu ratio of 1:1:1. In this study, we also determined the effect of cadmium, zinc and copper competition during adsorption from aqueous solutions for active sites of the biosorbent on the effectiveness of the adsorption of the analyzed metal.

The process of adsorption continues until the adsorption equilibrium is reached between the adsorbent and the adsorbate, which may be expressed as in Eq. (8):

$$q = f(C,T) \tag{8}$$

where q is the quantity of adsorbate adsorbed in the surface layer of 1 g of adsorbent (mg g^{-1} d.m.), C is the equilibrium concentration of adsorbate (mg L^{-1}), and T is the temperature (°C).

At a constant temperature, under equilibrium conditions, the dependency $q = f(C)$ is mathematically described with the use of adsorption isotherms, most frequently these of Langmuir's (10) or Freundlich's (11).

The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The Langmuir isotherm is given by:

$$Q = \frac{q_{\max} \times C \times b}{1 + b \times C} \tag{9}$$

where C is the equilibrium concentration in solution (mg L^{-1}), $q_{\max}$ (mg g^{-1} d.m.) and b are the Langmuir constants (L mg^{-1}), representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively.

The Freundlich isotherm model [11] is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of metal adsorbed per unit mass of adsorbent, Q (mg g^{-1} d.m.), and the concentration of the metal at equilibrium, C.

$$Q = K_F \times C^{\frac{1}{n}} \tag{10}$$

where K_F and n are the Freundlich constants ((mg g^{-1} d.w.)/(dm^3 mg$^{-1/n}$), the characteristics of the system. K_F and n are indicators of the adsorption capacity and adsorption intensity, respectively.

Experimental results achieved for the quantity of adsorbed metal depending on the concentration of metal left in the solution as well as Langmuir and Freundlich isotherms determined on their basis are presented in Fig. 7. The $q_{\max}$ and b as well as K_F and n constants determined from Eqs. (9) and (10) for single metals and their mixture were presented in Table 3.

The coefficient of determination (R^2) was adopted as a measure of curve fit (at adopted parameters) to experimental data.

The study demonstrated that the Langmuir model served well to describe the adsorption of single metals and mixtures of metals onto the analyzed biosorbent, and the Freundlich model was describing well adsorption of single metals only, which was indicated by the determined R^2 values (Table 3).

Experimental data indicate that during adsorption from solutions of single metals the highest adsorption effectiveness

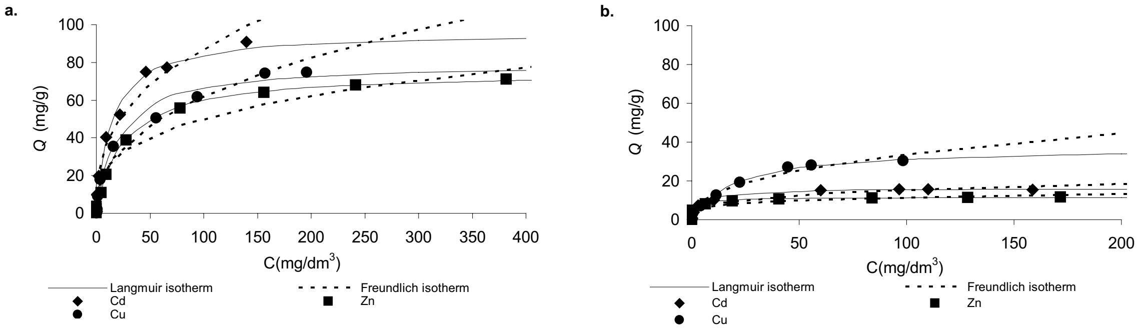

Fig. 7. Experimental results of cadmium, copper and zinc adsorption on the biosorbent, and Langmuir and Freundlich isotherms (a) single metals and (b) metal mixture.

Table 3
Values of constants in Langmuir and Freundlich equations

Metal ions	Langmuir			Freundlich		
Single metals	$q_{\max}$ (mg g^{-1})	B (dm^3 mg^{-1})	R^2	K_F (mg g^{-1}) (dm^3 g^{-1})$^{-1-n}$	n	R^2
Cd	96.10	0.07	0.9941	15.99	0.370	0.9856
Zn	75.00	0.039	0.9968	12.06	0.310	0.9831
Cu	79.63	0.047	0.9917	9.39	0.410	0.9882
Metal mixture						
Cd	16.00	0.250	0.9964	4.41	0.270	0.9737
Zn	11.59	0.350	0.9928	4.53	0.200	0.9466
Cu	37.38	0.060	0.9960	5.09	0.410	0.9897

was noted for cadmium –96.10 mg g^{-1} d.m. In the case of the other two metals, the adsorption capacity of the immobilized activated sludge was lower and reached 75.00 mg g^{-1} d.m. for zinc and 79.63 mg g^{-1} d.m. for copper. During metals adsorption from the mixture, the highest adsorption capacity was determined for copper –a 37.38 mg g^{-1} d.m.

During Cd, Zn and Cu adsorption from the mixture on the immobilized activated sludge, the total adsorption capacity of the biosorbent reached 64.97 mg g^{-1} d.m. and was lower than biosorbent capacity determined for solutions of individual metals.

When analyzing the adsorption capacities of the biosorbent, it may be speculated that the presence of copper in a metal mixture impaired the sorption of cadmium and zinc. The quantity of copper bound in the biosorbent was 3.23-fold and 2.34-fold higher than that of, respectively, zinc and cadmium.

The process of adsorption of three metals on immobilized in alginate activated sludge might be influenced by various factors. The different mechanism of adsorption for solutions of single metals and mixtures of metals was stated. The type of adsorbed metal also influenced the process of adsorption. Determined values of external and internal diffusion coefficients, reaction order and isotherms of adsorption with adsorption volume for three metals determined on their basis confirmed that.

4. Conclusions

The effectiveness of metals adsorption depended on the pH. The optimal pH range for the adsorption process turned out to be between 5.0 and 7.0. The external (β_L) and internal (D_i) diffusion coefficients for Cu^{2+} was highest, both without other metals in solution and a mixture. The adsorption of cadmium, zinc, and copper onto biosorbent followed the pseudo-second-order reaction. The highest values of adsorption kinetics constants (Q_{ad} and k) were obtained for zinc removed from both the solution of single metal and from the metal mixture. The adsorption capacity of the analyzed biosorbent, namely an activated sludge immobilized in a mixture of 1.5% alginate with 0.5% PVA, was high for both individual solutions of cadmium, zinc, and copper and their mixture. This biosorbent may, thus, be successively applied for the removal of metals from multi-component solutions.

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