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DIFFUSIVE PROPERTIES OF ALGINATE BIOSORBENTS

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Abstract: Effective diffusion coefficients for different heavy-metal salts: Cu, Cd, Zn, Cr, Pb in calcium alginate beads were determined. Their values depended on the metal type, anion from the metal salt, and the alginate content in the beads. The results of calculations indicate a decrease in the values of D_e , caused by an increase in the alginate content in the alginate sorbent beads. This is in agreement with the mechanism of the diffusion process taking place in porous carriers. Experimental data were found to be in good agreement with the mathematical model, as indicated by high values of the correlation coefficient.

Keywords: effective diffusion coefficients, heavy-metal salts, calcium alginate beads

Introduction

Many kinds of industrial liquid waste, such as those arising in the metallurgic, chemical, mining, tanning industries, are rich in toxic heavy metals [1-3] having a proven harmful effect on many forms of life. Of these, lead, cadmium, copper, mercury and zinc are known to be especially harmful to man and the environment [4].

Heavy metals are eliminated from liquid waste by means of a number of techniques, such as: chemical precipitation, ion exchange, reverse osmosis, membrane techniques, and adsorption [5, 6]. In spite of being highly efficient, the above methods have certain disadvantages, including: high cost, generation of large volumes of sediment, problems with recycling and with the reuse of adsorbents or ion exchangers [5-7]. This encourages searching for alternative sorbents. Biosorption on materials of natural origin seems to be providing the most prospective results: in addition to being highly efficient, it enables elimination of the entire content of metal ions, even if they are present at very low concentrations in the liquid waste. Biosorption is based on sorbents in the form of readily available materials of natural origin or on waste products arising in industry or agriculture: such sorbents have a high sorption capacity and are rather inexpensive, in comparison with high-priced synthetic sorbents.

Pollutants do not only include toxic, cancerogenic and mutagenic metals (such as chromium, lead, mercury), but also metals of economic value (such as silver, gold,

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platinum), therefore, possibilities of their recovery have become another important issue. Once again, biosorption has appeared to be an efficacious though low-cost solution for the recovery of heavy metals. For the above reasons, sorption on materials of natural origin has become the subject of extensive studies (described, for instance, in [8-21]). The studies have demonstrated that marine algae, which are acquired at a rather low cost, have a considerable sorption capacity.

The sorption properties of algal biomass are connected with its biopolymeric content, therefore, such biopolymers could be used for the biosorption of heavy metals after being separated. The cell walls of numerous species of brown algae (including *Macrocystis*, *Laminaria*, *Ectocarpus*, *Chorda*, *Fucus*, *Nereocystis*, *Alaria*) are built of alginates - macromolecular polysaccharides containing uronic acid radicals. This group of compounds include alginic acid - a linear copolymer of two uronic acids (D-mannuronic and L-guluronic acids), connected by β -1,4 glycoside bonds (Fig. 1). The sorption properties of alginates have been investigated since 1990's [9-11, 15, 22-33].



Fig. 1. Structure of alginic acid

Major advantages of the use of alginates as biosorbents include: efficiency, selectivity, and non-toxicity. Being readily available in large volumes because of their numerous applications, they are also low-priced. Alginates are biopolymers with high sorption capacity for heavy metals, even at low concentrations of the metals in solutions. Their sorption capacities are much higher than those of commonly used metal sorbents, such as active carbon. A very simple technology provides a biosorbent in the form of beads, which are easily separated from the sorbate solution. Moreover, alginate sorbents have the added advantage of being reusable after regeneration (typically, by means of a dilute acid solution) [27] with a simultaneous recovery of metals. Their other advantages also include: biodegradability, hydrophilicity and the presence of carboxylic groups [28]. Owing to all these advantages, alginates are regarded as the most-promising category of biosorbents of heavy metals [9, 10, 29].

The alginate biosorbents are typically prepared in the form of spherical beads of calcium alginate. In aqueous solutions, heavy metal ions show higher affinity and displace calcium ions, and are combined with the alginates. Sorption of metals takes place throughout the structure of the alginate beads, therefore, they can be regarded as a porous ion exchanger of high permeability and capacity [25]. Moreover, they can be applied in identical process and equipment solutions as ion exchangers.

The sorption of metal ions on alginates takes place at a very fast rate and is only limited by diffusion phenomena. Therefore, according to the commonly accepted belief, the rate of sorption with this type of sorbent is limited by internal diffusion. In order to use the quantitative approach to the diffusive-mass movement within the porous beads having a complicated geometrical structure, the notion of effective diffusion coefficient D_e has

been introduced. Since the rate of sorption on alginate beads is determined by the rate of diffusion in the sorbent pores, it is essential to know the effective diffusion coefficient to design the equipment.

The effective diffusion coefficient D_e is connected with the diffusion coefficient for highly dilute aqueous solution D_{aq} by the following relationship:

$$D_e = \frac{D_{aq} \cdot \beta}{\tau} \tag{1}$$

The tortuosity factor τ in the relationship takes into account the irregular shape, tortuosities, and variable bead pore sizes. Its values are typically in the range from 1 to 3 and can be found if porosity β is known.

In the case of alginate gels, it is convenient to use the diffusion retardation coefficient φ :

$$\varphi = \frac{D_e}{D_{aa}} = \frac{\beta}{\tau} \tag{2}$$

The value of the diffusion retardation coefficient is preferably not higher than 1 ($\varphi = 1$ means that $D_e = D_{aq}$; and $\varphi > 1$ means that $D_e > D_{aq}$).

The rate of diffusion has historically been found from changes in sorbate concentrations in the solution in the course of the sorption process. Measurements of the diffusion coefficient can be made in either the open or the closed system. The closed system is more often used because of its simplicity and a much greater abundance of reference material for the diffusion coefficients, found for that system previously. Measurements of D_e can be performed regardless of the sorption process, by measuring the rate of diffusion from the beads into the solution. If, during the experiments, diffusion is accompanied by sorption, then the effective coefficient of diffusion in carriers is usually found using the shrinking core model (SCM) [23, 30] or the linear absorption model (LAM) [9, 22, 30].

It should be noted that the effective diffusion coefficient calculating by SCM or by LAM method will provide different values of D_e . Moreover, LAM will fail in the case of low concentrations of metals in solution [9]. The SCM and LAM methods often provide unsatisfactory results (for instance, the calculated value of D_e is higher than the effective diffusion coefficient of the same metal in water), moreover, they are connected with the use of labor-consuming procedures in measuring the metal concentrations.

The known calculation models have had numerous disadvantages, therefore, a new method of determination of the effective diffusion coefficient was proposed [31]. Known as the conductometric method, it is based on measuring changes in the metal-salt solution conductivity (which depends on the solution's concentration) and correlating them with the effective diffusion coefficient.

The main objectives of this research work are: (i) preparation calcium alginate beads from sodium alginate solution, (ii) determine by the conductometric method the effective diffusion coefficient for different heavy-metal salts: Cu, Cd, Zn, Cr, Pb in calcium alginate beads, (iii) determine the effect of the metal type, anion from the metal salt and the alginate content in the beads on the D_e value.

Materials and methods

Reagents

The alginate beads were made of the sodium alginate from KELCO. Nine different heavy-metal salts were examined: CuCl₂, CuSO₄, CdCl₂, CdSO₄, ZnCl₂, ZnSO₄, Zn(NO₃)₂, Pb(NO₃)₂, Cr(NO₃)₂.

Preparation of the alginate beads

Calcium alginate beads were prepared by dropwise addition of a viscous, aqueous sodium alginate solution to 0.05 M of CaCl₂ solution. All the beads were prepared in the same way, only the concentration of the aqueous solution of sodium alginate was varied. During the gelation process, the sodium alginate reacted with the Ca ion from the CaCl₂ solution and a cross-linked Ca-alginate was formed. The gelation process was continued for 0.5 h. The beads were then placed in a new 0.05 M portion of CaCl₂ for 24 hours to establish an equilibrium between the calcium ions that remained in the solution and those adsorbed by the beads. The resultant beads differed in their alginate gel contents (from 1.3 to 6.1 wt.%). The beads were kept in the refrigerator.

The beads were washed with distilled water prior to analysis to make sure the bead pores contained no calcium ions, otherwise, the solution's conductivity could be affected. The beads were then saturated with a selected heavy-metal salt for 24 hours. A 0.1 M solution of the selected heavy-metal salt solution was prepared and a suitable amount of calcium alginate beads was immersed in it. The solution was stirred with a magnetic stirrer. Conductivity of metal salts was determined using the microcomputer conductometer model CPC-551 from ELMETRON. All the experiments were performed at a constant pH of the solution (5.0) into which the heavy-metal salts diffused, and a constant temperature of 25 \pm 0.5 °C.

The conductometric method for determination of effective diffusion coefficient

The LAM and SCM methods are based on the diffusion of metal ions from the solution into the beads and their sorption therein; therefore, the coefficient calculated according to LAM and SCM relates to the diffusion of the given metal ions. On the other hand a reversed situation takes place in the conductometric method: the biosorbent beads are saturated with the test metal salt and dropped into distilled water, where diffusion of the metal salt molecules from the bead pores into the solution containing the beads takes place. An increase in the metal salt content of the solution leads to an increase in the solution's conductivity. In the conductometric method, conductivity of the solution into which the test metal salts diffuse is measured. The conductivity varies with the effective diffusion coefficient. The experiment is carried out for a diffusion in the closed system.

In modeling diffusion of the metal salts from the alginate bead pores into the solution, it was assumed that:

- 1. The alginate beads are spheres with a radius *R*.
- 2. The total volume of the beads is a sum of the solid volume and the pore volume.
- 3. During the diffusion, the pores are entirely filled with the aqueous solution of the metal salt.
- 4. Mass transport takes place only due to diffusion within the pores.
- 5. The metal salt concentration in water is uniform (the solution is homogeneous).

- 6. The liquid volume does not change.
- 7. Desorption of the metal ions from the alginate beads does not take place.

The metal salt diffusion in the alginate beads is a non-stationary process and, assuming that the effective diffusion coefficient is a constant value, it can be described with Fick's second equation. When the homogeneous alginate beads are spherical, the general mass balance for the diffusion of substances in the spherical beads (for non-stationary state) takes the following form:

$$\frac{\partial C_s}{\partial t} = D_e \left(\frac{\partial^2 C_s}{\partial r^2} + \frac{2}{r} \frac{\partial C_s}{\partial r} \right)$$
(3)

where C_s is sorbate concentration in sorbent pores at time *t*; *r* is bead radial coefficient; and *t* is time.

If N beads which contain the dissolved substance are immersed in a well stirred solution containing no sorbate and has a strictly defined volume, then the following initial and boundary conditions apply:

$$t = 0 \qquad 0 < r < R \qquad C_{S} = \text{const}$$

$$t = 0 \qquad r > R \qquad C_{L} = 0 \qquad C_{L} = 0$$

$$t > 0 \qquad r = 0 \qquad \frac{\partial C_{s}}{\partial r} = 0$$

$$t > 0 \qquad r = R \qquad V_{L} \frac{\partial C_{L}}{\partial t} = KA_{s}D_{e} \frac{\partial C_{s}}{\partial r}$$

where: A_s - biosorbent bead area, C_L - sorbate concentration in solution at time t, K - partition ratio, R - sorbent bead radius, V_L - volume of the solution which contains the sorbate.

Assuming that the sorbate is uniformly distributed within the bead and the beads are in equilibrium with the liquid phase, the rate of the sorbate's diffusion from the sorbent beads into the solution is expressed by the following equation, describing the substrates' diffusion outside the sphere in the closed system [34]:

$$C_{L} = \left(\frac{C_{S0}}{1+\alpha}\right) \left\{ 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1)}{9+9\alpha+q_{n}^{2}\alpha^{2}} \exp\left(-q_{n}^{2}\frac{D_{e}t}{R^{2}}\right) \right\}$$
(4)

Where q_n represents positive, non-zero roots of equation:

$$tgq_n = \frac{3q_n}{3 + \alpha q_n^2}$$
(5)

 $|_{r=R}$

and parameter α is defined by equation:

$$\alpha = \frac{3V_L}{4N\pi R^3 K} \tag{6}$$

 C_{∞} (the sorbate's equilibrium concentration in the solution) is linked with C_{S0} (sorbate's concentration in the beads for t = 0) as follows:

$$C_{\infty} = \frac{C_{S0}}{(1+\alpha)} \tag{7}$$

therefore, equation (4) can be described as follows:

$$\frac{C_L}{C_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(1+\alpha)}{9+9\alpha+\alpha^2 q_n^2} \cdot \exp\left(-q_n^2 \frac{D_e t}{R^2}\right)$$
(8)

By selecting suitable experimental conditions ($\alpha \ge 100$, which means that the sorbent sample volume is at least 100 times as small as that of distilled water), it is possible to simplify equation (8) into the form which was derived for the open system (thus avoiding the troublesome calculation of the consecutive values of q_n):

$$\frac{C_L}{C_{\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot \exp\left(-\frac{D_e n^2 \pi^2 t}{R^2}\right)$$
(9)

In the new, conductometric method, determination of the effective diffusion coefficient is based on measurements of conductivity of the solution into which the sorbate diffuses; therefore, assuming that dependence of conductivity on concentration is linear, the following equation is obtained (by transforming the non-stationary diffusion equation):

$$\frac{P_{t}}{P_{\infty}} = 1 - \frac{6}{\pi^{2}} \sum_{n=1}^{\infty} \frac{1}{n^{2}} \exp\left(\frac{-D_{e}n^{2}\pi^{2}t}{R^{2}}\right)$$
(10)

where: P_t - conductivity of the solution after the time t, P_{∞} - conductivity of the solution after the time ∞ .



Fig. 2. Setup for determination of effective diffusion coefficient: A - to thermostat, B - from thermostat, C - conductometer with electrode (6), thermostated water jacket (1), beaker containing distilled water (2), alginate beads (3), magnetic stirrer (4), thermometer (5)

A strictly defined sample of alginate beads, saturated with the test metal salt was placed in a beaker filled with distilled water. The contents of the beaker was thermostated and stirred vigorously to eliminate external diffusion resistance and provide an ideal mixing in the system. The metal salt molecules in the sorbent pores diffused into distilled water and the process rate was determined by the effective diffusion coefficient. An increase in the metal ion concentration in the solution was observed to lead to an increase in conductivity, as measured with the conductometer. The sorbent sample volume was more than 100 times

as small as that of distilled water and conductivity was in linear dependence on concentration, therefore, the effective diffusion coefficient was calculated using equation (10). The amount of the beads, to be used for the test, depended on their diameter. After being saturated with the metal salt, the beads, of which the total volume was not higher than 1 cm³, were dropped in 100 cm³ of distilled water while the magnetic stirrer and a stopper were started. A constant temperature of 25 ± 0.5 °C was maintained throughout the experiment. After a defined time (1, 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 60 min, etc., until the value of conductivity was constant), the solution's conductivity was measured.

The setup for determination of the effective diffusion coefficient is shown in Figure 2. It was composed of a 120 cm³ beaker (2) containing distilled water and alginate beads (3), saturated with the test metal salt. A thermostated water jacket (1), magnetic stirrer (4), thermometer (5), and conductometer with electrode (6).

Results and discussion

Experiments were carried out which confirmed that dependence of the solution's conductivity on the given test-metal salt concentration is linear, and an analysis was carried out which enabled the authors to find that satisfactory accuracy of the results is obtained by using the initial 6 terms of equation (10) for determination of the effective diffusion coefficient for the metal salt diffusion in the calcium alginate beads.

After measuring conductivity of the solution into which the test metal salt ions diffused from the beads, the measurement data were used for determination of the effective diffusion coefficient. The coefficient was calculated from equation (10), using the Levenberg-Marquardt non-linear regression optimization procedure, incorporated in the SLIDE WRITE Plus software.

A typical dependence P_t/P_{∞} on the process duration is shown in Figure 3.



Fig. 3. Dependence of P_r/P_{∞} on the process duration for diffusion of cadmium sulfate from alginate beads with a dry weight of 1.5 %

The value of effective diffusion coefficient depends on temperature and the alginate content in the biosorbent beads. According to the mechanism of diffusion in porous carriers, an increase in the alginate content in the beads leads to lower values of D_e . On the other hand, an increase in the process temperature contributes to an increase in the values of the effective diffusion coefficient.

Sulfates, chlorides and nitrates of 5 heavy metals: Cu, Cd, Zn, Cr and Pb, were examined. The diffusion coefficients of all the heavy-metal salts for a highly dilute aqueous solution (D_{aq}) for a temperature of 25 °C were calculated using the Nernst equation.

Copper(II) salt diffusion

The effective diffusion coefficients, correlation coefficients, and retardation coefficients for copper chloride and sulfate are shown in Table 1. High correlation coefficients were obtained, which indicates good agreement between the experimental data and the mathematical model.

Table 1

Alginate content in beads [wt.%]	contentEffective diffusion coefficientCorrelation coefficient $\%$] $D_e \cdot 10^9 [m^2/s]$ r^2		Retardation coefficient $f = \frac{D_e}{D_{aq}}$
	$CuCl_2 (D_{aq} =$	$1.29 \cdot 10^{-9} \mathrm{m^2/s}$	
1.3	0.99	0.991	0.77
2.6	0.91	0.993	0.70
3.5	0.88	0.994	0.68
6.1	0.85	0.984	0.66
	$CuSO_4 (D_{aq} =$	$0.87 \cdot 10^{-9} \mathrm{m^2/s})$	
1.5	0.52	0.986	0.59
3.7	0.45	0.987	0.52
5.7	0.41	0.985	0.47

Dependence of effective diffusion coefficient on alginate content in beads for copper salts



Fig. 4. Dependence of retardation coefficient on alginate content in beads for copper salts

D . 109	<i>m</i> ¹	Environmental conditions				
$\begin{bmatrix} D_e \cdot 10 \\ [m^2/s] \end{bmatrix}$	φ [-]	рН [-]	Temp. [°C]	C_i [mg/dm ³]	Other	Source
0.98	1.31	no data	25	63.5	as calculated according to SCM sorbent: 3 % alginate beads	[23]
1.08	1.45	no data	25	63.5	as calculated according to LAM sorbent: 3 % alginate beads	[23]
1.2	1.61	no data	no data	no data	as calculated according to SCM	[22]
0.45	0.60	no data	no data	no data	as calculated according to LAM	[22]

Values of effective diffusion coefficient for Cu(II) ions in the alginate beads according to literature

¹ for Cu(II) ions at a temp. of 298 K, as calculated from the Nernst formula: $D_{aq} = 0.745 \cdot 10^{-9} \text{ m}^2/\text{s}$. According to the literature, D_{aq} as found experimentally for copper(II) ions by different authors using different methods, is in the range 0.62-0.75 $\cdot 10^{-9} \text{ m}^2/\text{s}$ [22]

The values of D_e and φ were observed to decrease due to an increase in the alginate content in the sorbent beads. This is in agreement with the mechanism of the diffusion process taking place in porous carriers. The effective diffusion coefficients, as calculated for CuCl₂, were considerably higher (nearly twice as high), in comparison with CuSO₄.

The retardation coefficient φ was also found to depend on the alginate content in the beads (Fig. 4). However, even though the values of φ for CuCl₂ were higher than those for CuSO₄, the differences were not as pronounced as in the case of D_e . A more-than four-fold increase in the alginate content in the beads caused a decrease in the value of the retardation coefficient by merely 14 % for copper(II) chloride, and by merely 20 % for copper(II) sulfate.

Each D_e value, obtained by the conductometric method is lower than the calculated diffusion coefficient in a highly dilute aqueous solution of a given salt. More often than not, the condition is not satisfied in literature reports (Table 2) using the conventional methods (SCM, LAM). Moreover, literature reports indicate a significant divergence between the values of D_e obtained by SCM and those obtained by LAM. Those values of D_e calculated by Lewandowski and Roe [23] using SCM are more than twice as high as the effective diffusion coefficient calculated by the LAM methods and reported by Chen et al. [22].

Cadmium(II) salt diffusion

Table 3 and Figure 5 show the results of calculation for cadmium chloride and cadmium sulfate. The effect of alginate content in the biosorbent beads on the effective diffusion coefficient D_e and retardation coefficient φ is shown.

All the values of D_e , obtained by the conductometric method, are lower than the calculated diffusion coefficients in a highly dilute solution of the given test salt, D_{aq} . As in the case of copper salts, the values of D_e were observed to decrease for increased alginate contents in the sorbent beads. The effective diffusion coefficients, as calculated for cadmium chloride, were higher than those for cadmium sulfate but, when compared with copper salts, the differences were slightly less pronounced (for instance, D_e , calculated for 1.5 % calcium alginate in the case of CdSO₄, was 35 % lower in comparison with the value obtained for 1.5 % alginate and the diffusion of CdCl₂).

Table 2

Table 3

Dependence of effective diffusion coefficient on alginate content in beads for cadmium salts

Alginate content in beads [wt.%]	inate content in beadsEffective diffusion coefficient $D_{\ell} \cdot 10^9 [\text{m}^2/\text{s}]$		Retardation coefficient $f = \frac{D_e}{D_{aq}}$				
	$CdCl_2 (D_{aq} =$	$1.26 \cdot 10^{-9} \mathrm{m^2/s})$					
1.5	0.73	0.978	0.58				
3.7	0.67	0.989	0.53				
5.7	0.59	0.987	0.47				
$CdSO_4 (D_{aa} = 0.86 \cdot 10^{-9} \text{ m}^2/\text{s})$							
1.5	0.47	0.996	0.55				
3.7	0.40	0.995	0.46				
5.7	0.37	0.994	0.43				



Fig. 5. Dependence of retardation coefficient on alginate content in beads for cadmium salts

Table 4

Values of effective diffusion coefficient for Cd(II) ions in the alginate beads according to literature

D 109	1						
$[m^{2}/s]$	φ [-]	рН [-]	Temp. [°C]	$\overline{C_i}$ [mg/dm ³]	Other	Source	
0.30	0.42	no data	no data	100	as calculated according to SCM sorbate: CdSO ₄ sorbent: 2 % alginate beads	[32]	
0.6	0.83	4.0	no data	no data	no data	[35]	
1.9	2.64	4.5	25	100	as calculated according to LAM, sorbate: CdSO ₄ sorbent: 2 % alginate beads	[9]	
4.5	6.26	4.5	25	100	sorbate: CdSO ₄ sorbent: 2 % alginate beads	[10]	
0.0134	0.02	5.0	23	51	sorbate: Cd(NO ₃) ₂	[29]	

¹ for Cd(II) ions at a temp. of 298 K: $D_{aq} = 0.719 \cdot 10^{-9} \text{ m}^2/\text{s}$ [35]

Both the retardation coefficient φ and the effective diffusion coefficient also depended on the alginate content in the beads; when the alginate content in the beads increased from 1.5 to 5.7 %, the value of φ decreased by 19 and 22 % for CdCl₂ and CdSO₄, respectively.

Also in this case, literature data (Table 4) indicated significant differences between the values of D_e , as obtained by the SCM [32] and LAM [9] methods.

Zinc(II) salt diffusion

Diffusion was tested for 3 zinc salts: chloride, sulfate and nitrate. Tables 5 shows the calculated values of the effective diffusion coefficient and the retardation coefficient for all of the zinc(II) salts tested.

Table 5

		Ū.					
Alginate content in beads [wt.%]	Alginate content in beadsEffective diffusion coefficient $[wt.\%]$ $D_e \cdot 10^9 [m^2/s]$		Retardation coefficient $f = \frac{D_e}{D_{aq}}$				
	$ZnCl_2 (D_{aq} =$	$1.25 \cdot 10^{-9} \mathrm{m^2/s})$					
1.5	0.77	0.977	0.62				
3.7	0.73	0.982	0.59				
5.7	0.66	0.982	0.53				
	$ZnSO_4 (D_{aq} =$	$0.85 \cdot 10^{-9} \mathrm{m^2/s})$					
1.5	0.44	0.962	0.52				
3.7	0.37	0.988	0.43				
5.7	0.24	0.967	0.28				
$Zn(NO_3)_2 (D_{aq} = 1.22 \cdot 10^{-9} \text{ m}^2/\text{s})$							
1.5	0.84	0.985	0.69				
3.7	0.63	0.981	0.52				
5.7	0.50	0.966	0.41				





Fig. 6. Dependence of retardation coefficient on alginate content in beads for zinc salts

No information has been found in the literature on the effective coefficient of diffusion of zinc ions in the alginate beads.

Also in this case, all of the values of D_e , as obtained by the conductometric method, are lower than the diffusion coefficients in a given, highly dilute test salt. The retardation coefficient (Fig. 6) and the effective diffusion coefficient were found to decrease with an increase in the alginate content in the beads. The lowest diffusion coefficients and the lowest retardation coefficients were obtained for zinc sulfate, the highest were obtained for zinc chloride.

Diffusion of chromium nitrate

The effective diffusion coefficients were calculated for chromium nitrate (Table 6). The beads with the lowest alginate content (1.5 wt. %), have been omitted from the calculations because they disintegrated in the course of the experiment.

Table 6

Alginate content in beads [wt.%]	Effective diffusion coefficient D _e ·10 ⁹ [m ² /s]	Correlation coefficient r ²	Retardation coefficient $f = \frac{D_e}{D_{aq}}$
	$Cr(NO_3)_3$ ($D_{aq} = 1$	$1.23 \cdot 10^{-9} \mathrm{m^2/s}$	
3.7	0.31	0.966	0.25
5.7	0.19	0.976	0.16

Dependence of effective diffusion coefficient on alginate content in beads for chromium salt

Table 7

Values	of e	ffective	diffusio	1 coefficient	for (Cr(III)	ions in	the alginate	beads	according to	literature
	~ ~ ~										

D . 10 ⁹	<i>"</i> 1					
$\begin{bmatrix} D_e \cdot 10 \\ [m^2/s] \end{bmatrix}$	φ [-]	рН [-]	Temp. [°C]	C _i [mmol]	Other	Source
2.39	4.02	no data	10	0.2	as calculated according to SCM sorbent: 6.2 % beads	[20]
0.47	0.79	no data	10	0.2	as calculated according to LAM sorbent: 6.2 % beads	[30]

¹ for Cr(III) ions at a temp. of 298 K as calculated from the Nernst formula: $D_{aq} = 0.594 \cdot 10^{-9} \text{ m}^2/\text{s}$

The results for the bead types tested by the authors are comparable with those obtained for salts of the other metals tested; this means that an increase in the alginate content in the beads leads to a decrease in the values of D_e and φ .

Once more, a significant divergence is observed between the results for the SCM and LAM methods (Table 7). The differences are best visible in the case of chromium: the value of D_e obtained by SCM was nearly 5-times as high as that contained by LAM, even though same conditions were applied.

Diffusion of lead nitrate

Lead nitrate was used for the tests because both lead sulfate and lead chloride are hard to dissolve in water. The results of calculation are shown in Table 8. For lead nitrate, the retardation coefficient decreases with an increase in the alginate content in the beads, however, its decrease is not very pronounced because the alginate beads, of which the alginate content is nearly 4-times as high, have a retardation coefficient of just more than 13 % lower (down from 0.52 to 0.45).

Alginate content in beads [wt.%]	Effective diffusion coefficient $D_e \cdot 10^9 \text{ [m^2/s]}$	Correlation coefficient r^2	Retardation coefficient $f = \frac{D_e}{D_{aq}}$
	$Pb(NO_3)_2 (D_{aq} = 1.41)$	$\cdot 10^{-9} \mathrm{m^2/s})$	
1.5	0.74	0.980	0.52
3.7	0.70	0.994	0.49
5.7	0.64	0.991	0.45

Dependence of the effective retardation coefficient on alginate content in the beads for lead salt

In the literature [33] the values of the diffusivity coefficient were found several orders of magnitude lower than the self-diffusivity of Pb(II) $(D_{aq} = 1.41 \cdot 10^{-9} \text{ m}^2/\text{s})$ and is $D_e = 0.72 \cdot 10^{-12} \text{ m}^2/\text{s}$ for air-dried beads (as calculated according to SCM, pH = 4, temp. = 25 °C, $C_i = 100 \text{ mg/dm}^3$). This confirms that the resistance to intraparticle diffusion plays a significant role in the control of uptake kinetics.

For all tested metal salts the value of the effective diffusion coefficient is affected by the metal salt anion. In the case of sulfates, the highest values of D_e were obtained for the Cu salts, the lowest - for the Zn sulfate. For the chlorides, the highest values of D_e were obtained also for Cu, and the lowest - for Cd; the values of D_e for Zn were not much higher than those calculated for Cd. For the nitrate salts, the lowest diffusion coefficients were those for chromium. Much higher values of D_e were recorded for zinc nitrate and the highest (with the exception of the 1.5 % alginate beads), were those for lead nitrate.

Conclusions

The experimental results clearly indicate a decrease in the values of D_e , caused by an increase in the alginate content in the sorbent beads. This is in agreement with the mechanism of the diffusion process taking place in porous carriers. Good agreement between the experimental data and the mathematical model was obtained, as shown by the high values of correlation coefficients.

The value of the effective diffusion coefficient is affected by the metal salt anion, therefore, it should also be taken into account in the calculations.

All the values of D_e , obtained by the conductometric method, are lower than the calculated diffusion coefficients in a given, highly dilute salt. More often than not, the condition is not satisfied in literature reports, especially in calculations by conventional methods (SCM, LAM).

The conductometric method is simple and it provides good results in calculating the effective diffusion coefficients for heavy metals in alginate sorbents.

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