



## **DETERMINATION OF THE EFFECTIVE DIFFUSIVITY OF CADMIUM(II) IN CALCIUM ALGINATE BEADS**

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### **ABSTRACT**

Effective diffusivity ( $D_e$ ) of cadmium compounds was calculated in the beads. The study was carried out using two methods: a shrinking core model (SCM) method and a newly developed method named conductometric. It turned out to be a simple and effective method for the calculation of effective diffusivity of Cd(II) in alginate sorbents. The  $D_e$  values obtained by the two methods depended on the alginate content in the beads. However, SCM, in contrast to the conductometric method, gave  $D_e$  values increasing with increasing alginate levels in the beads and lower than the molecular diffusivity of Cd(II), this being inconsistent with the mechanism of diffusion in porous carriers. Hence, the conductometric method can be considered as one giving more reliable results, compared with the SCM method. Moreover, diffusion retardation coefficients for the alginate beads were calculated. Enhanced content of the biopolymer in the beads caused retardation of Cd(II) diffusion in the beads due to the decreasing calculated retardation coefficients with the increasing alginate contents in the beads.

Keywords: cadmium ions, alginate beads, effective diffusivity

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### **INTRODUCTION**

Heavy metals, due to their accumulation in living organisms and non-biodegradability have been considered as being extremely hazardous to humans and other living organisms. Among them, cadmium has been found to be hazardous due to its strong toxicity. It has been classified among the top hazardous substances as being extremely carcinogenic. Moreover, it impairs kidneys, causes anemia, skeletal disorders (e.g., osteoporosis), smell disturbances, has a

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detrimental influence on the circulatory system and leads to some other diseases and ailments. Furthermore, cadmium(II) ions replace zinc(II) ions in some enzymes, thus inhibiting their activity [1]. The most toxic are freely water-soluble cadmium salts.

Cadmium compounds penetrate to the environment from many industrial effluents, in particular, those from the dye industry, manufacturing of Cd-Ni cells, cadmium batteries, cadmium alloys, and agricultural fertilizers. Cadmium(II) chloride has been used as a pesticide, and cadmium(II) nitrate(V) in the manufacture of plastics and dyes. Therefore, the removal of cadmium(II) from industrial effluents is mandatory. There are chemical and physical procedures for the removal of heavy metals, including cadmium, from wastewaters. Unfortunately, traditional ones are either ineffective or very expensive for heavy metal concentrations falling below  $100 \text{ mg/dm}^3$  [2]. Recent studies [3-5] have shown that biosorbents are an advantageous alternative of the physico-chemical methods of removing heavy metals from dilute solutions. Among the biosorbents, particularly effective are alginates [6] including alginic acid, its salts and derivatives.

Alginic acid is a copolymer of two uronic acids,  $\beta$ -D-mannuronic and  $\alpha$ -L-guluronic (Fig. 1), occurring in the form of long, straight chains.

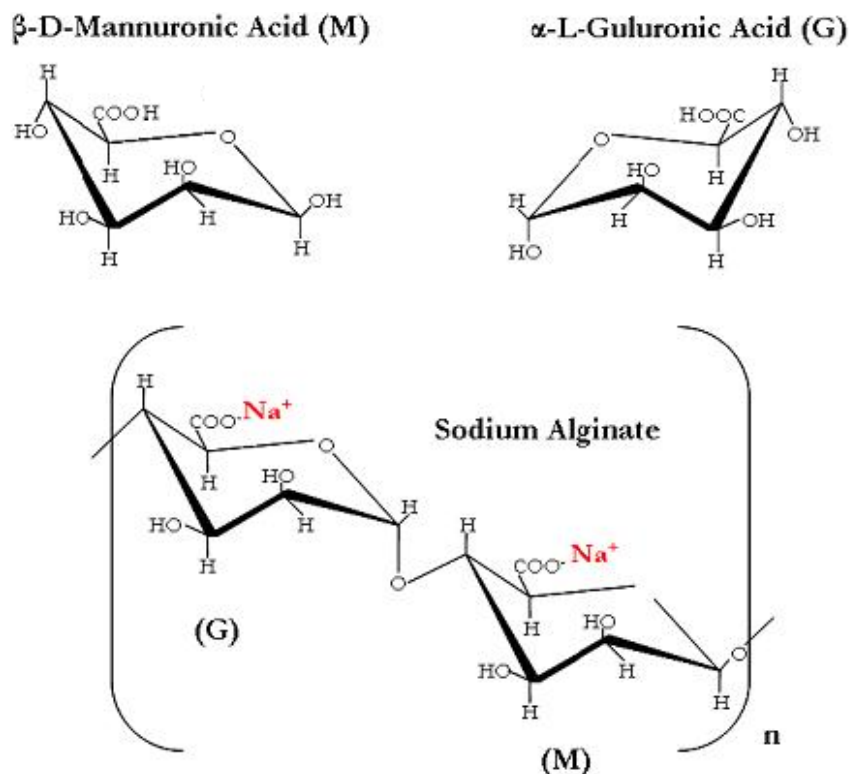


Fig. 1. Structure of sodium alginate and mannuronic and guluronic acids.

As the alginates produced from brown algae (Fig. 2) are widespread in the food and chemical industries, they are cost-effective. Moreover, after appropriate treatment of the alginates and conversion to spherical beads they can be used in identical processes and equipment as are ion exchangers. Their other advantage is the possibility of repeated use after regeneration. Owing to their numerous advantages, alginate biosorbents have been extensively studied [6-11].

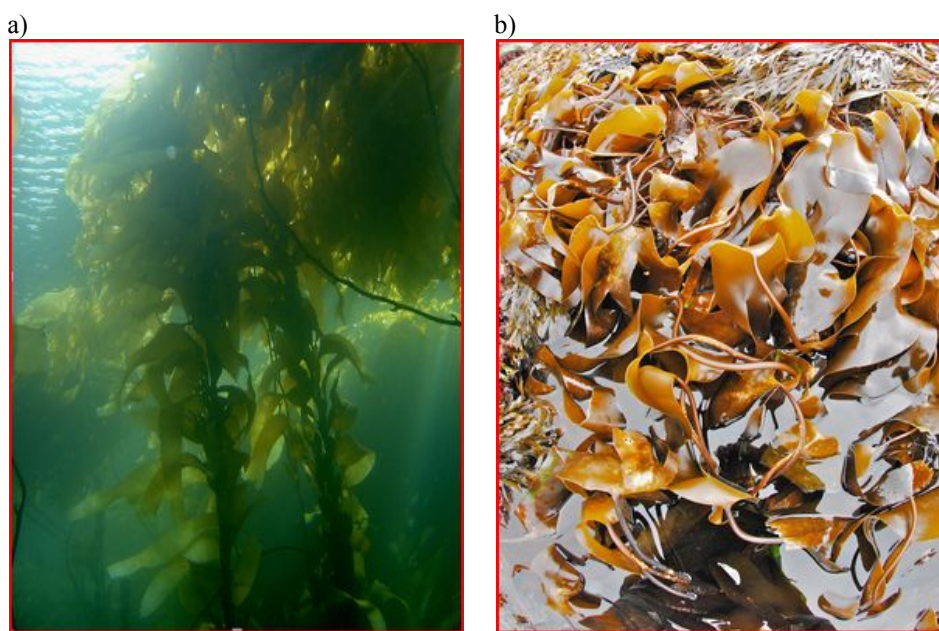


Fig. 2. Brown algae: a) *Macrocystis pyrifera*, b) *Laminaria Digitala* ([www.algaebase.org](http://www.algaebase.org)).

The rate of the processes occurring in biosorbent beads is usually restricted by resistance arising from internal diffusion [12-14] characterized by the effective diffusivity coefficient,  $D_e$ . The coefficient was thought to generalize all the diffusion phenomena taking place in porous beads of complex geometry. The coefficient is also related to the molecular diffusivity coefficient,  $D_m$ , by the following equation:

$$D_e = \frac{D_m \cdot \beta}{\tau} \quad (1)$$

In the above equation, the tortuosity factor,  $\tau$ , accounts for the shape irregularity as well as the variable cross-section of the pores in a bead. Usually its value ranges between 3 and 4 [15] and can be determined given the porosity  $\beta$ . With alginate gels, it is convenient to use the following relationship:

$$\frac{D_e}{D_m} = \frac{\beta}{\tau} = \varphi \quad (2)$$

because factor  $\varphi$ , which is present in the equation, enables it to be stated whether or not the results obtained are in agreement with the mechanism of diffusion in porous carriers. The value of the diffusion retardation coefficient,  $\varphi$ , ought to be lower than  $D_m$  and not exceed 1 ( $\varphi = 1$  denotes that  $D_e = D_m$ , while  $\varphi > 1$  denotes  $D_e > D_m$ ).

As the sorption rate usually determines the rate of diffusion within the pores of a sorbent, knowledge of effective diffusivity is necessary for equipment design. For the determination of the effective diffusivity in those carriers where sorption processes take place in addition to diffusion, either the shrinking core model (SCM) or the linear absorption model (LAM) have been used. In the former, it is assumed that in a spherical bead there is a non-reacted core coated with a reacted material. Diffusion of the metal ions proceeds across the layer of the reacted material towards the core to cause gradual shrinking. The LAM model is used less frequently due to complicated numerical calculations. Because both models often give contradictory results and require time-consuming procedures for the determination of metal concentrations, a new method has been developed for the determination of effective diffusivity in porous sorbents using conductometry [16]. It is based on the measurement of conductance variations depending on the concentration of metal ions in solution and relation these measurements with the effective diffusivity. It is called the conductometric method.

The primary purpose of this contribution was to compare the effective diffusivity of Cd(II) in the alginate beads determined by SCM and conductometric methods. Moreover, the influence of the biopolymer content on the retardation of diffusion was estimated.

## EXPERIMENTAL

### Preparation of calcium alginate beads

The starting material for the preparation of the beads was a low-viscosity sodium alginate (SIGMA-Aldrich). Although the alginate itself had a low viscosity as compared with that of other alginates, viscosity of its aqueous solutions was so high that the maximum attainable calcium alginate concentration in the beads was only 6.4 wt %.

All the alginate beads were prepared using the same procedure wherein only the quantities of sodium alginate, which was dissolved in distilled water, were varied. The aqueous solution of sodium alginate was added dropwise to a  $0.05 \text{ mol/dm}^3$   $\text{CaCl}_2$  solution used as a cross-linking medium. During a 30-min gelation period, Ca(II) ions were bonded to the alginate beads. To attain an equilibrium between Ca(II) in the solution and the ions adsorbed on the beads, they were placed in a  $0.05 \text{ mol/dm}^3$   $\text{CaCl}_2$  solution for 24 hrs. The beads, which were 2.6 to 4.3 mm in diameter, differed from one another in the alginate content in the gel (from 1.5 to 6.4 wt%). They were stored in a refrigerator in a solution containing  $0.01 \text{ mol/dm}^3$  of KCl and  $0.001 \text{ mol/dm}^3$  of  $\text{CaCl}_2$ . The

amount of sodium alginate used for the production of beads and the characteristics of the obtained calcium alginate beads are compiled in Table 1.

Table 1. Characteristics of calcium alginate beads.

amount of sodium alginate [g]	amount of water [g]	alginate content of the beads [wt%]	diameter of the beads after 24 hrs gelation [mm]
1.1	98.9	1.5	2.6
2.2	97.8	2.7	3.7
3.3	96.7	3.7	3.2
4.5	95.5	5.0	4.0
5.2	94.8	5.7	2.8
6.8	93.2	6.4	4.3

Prior to carrying out the measurements of the effective diffusivity by the conductometric method, calcium(II) ions in the beads were substituted by cadmium(II) ions. The number of beads used in the experiment depended on their diameter, since the total volume of the pellets should be 1 cm<sup>3</sup> (in order to satisfy the condition  $\alpha \geq 100$ ). For saturation with cadmium, an appropriate quantity of the calcium alginate beads were placed in a 0.1 mol/dm<sup>3</sup> CdCl<sub>2</sub> solution and the mixture was stirred with a magnetic stirrer. After a 2-hr saturation period, the beads were transferred to a fresh volume of the 0.1 mol/dm<sup>3</sup> CdCl<sub>2</sub> solution where they were stirred for 24 hrs. After saturation with Cd(II), the beads shrank in volume by *ca.* 8%, probably owing to the exchange of the calcium(II) for the cadmium(II) ions.

## Determination of effective diffusivity

### The SCM method

The effective diffusivity,  $D_e$ , was determined from Equation (3) reported by Rao and Gupta [17] and quite frequently cited in the literature [10, 12]

$$F_X(t) = \left[ 1 - 3(1 - X)^{2/3} + 2(1 - X) \right] = \frac{6D_e}{A_d R^2} \int_0^t C_t dt \quad (3)$$

where  $X$  is the extent to which a final equilibrium is attained and is defined by the following equation:

$$X = \frac{C_0 - C_t}{C_0 - C_\infty} \quad (4)$$

and parameter  $A_d$  is the average binding site density of the beads calculated as:

$$A_d = \frac{(C_0 - C_\infty) \cdot V_L}{N \cdot \frac{4}{3} \cdot \pi \cdot R^3} \quad (5)$$

The apparatus used for the measurements is shown in Fig. 3. It consisted of an 800-cm<sup>3</sup> glass reactor (2) filled with a cadmium(II) solution and alginate beads (3), and a magnetic stirrer (4). The reactor was placed in a thermostated water jacket (1).

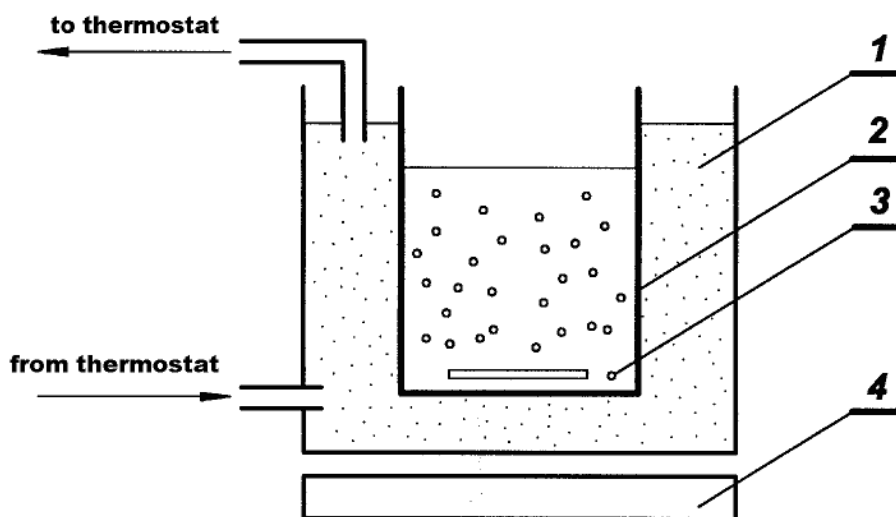


Fig. 3. Schematic diagram of the apparatus for the determination of effective diffusivity by the SCM method.

The sorption process was carried out for 24 hrs in a closed system. One hundred and five beads were placed in the reactor filled with 500 cm<sup>3</sup> of a standardized solution containing 0.001 mol/dm<sup>3</sup> of CaCl<sub>2</sub> and 0.01 mol/dm<sup>3</sup> of KCl. The reactor was thermostated at 25±0.5°C with stirring. After attaining a constant temperature, 0.5 cm<sup>3</sup> of a 0.5 mol/dm<sup>3</sup> CdCl<sub>2</sub> solution was added to the reactor containing the alginate beads to initiate sorption. At the same time, a stop-watch was started. During the experiments, the Cd(II) concentration was measured by taking 1 cm<sup>3</sup> of aliquots of the solution at set time intervals. The Cd(II) content in the aliquots was then determined by atomic absorption spectroscopy.

During the experiments the diameter of the alginate beads gradually diminished and by the end of the experiment it was *ca.* 2.5% smaller than at the beginning. Therefore, for the calculation of effective diffusivity an averaged diameter, i.e., the arithmetic mean of the beads' diameter before and after the experiment, was assumed.

### Conductometric method

The method was based on carrying out the measurements in a closed system. In a beaker with distilled water, a known quantity of a Cd(II)-saturated alginate was placed and the suspension was vigorously agitated to eliminate the

internal diffusion resistance and to ensure ideal mixing in the system. Under such conditions, the Cd(II) ions present in the pores of the sorbent diffuse to the distilled water, the rate of the process being controlled by effective diffusivity. An increasing Cd(II) concentration in the solution results in an increase in conductance, as measured with a conductometer. During elaboration of the model of sorbate diffusion into the solution. the following assumptions were made:

- the sorbent is present in the form of spheres with the radius R,
- the total volume of the beads is made up of that of the solid and the pore volume,
- during sorption, the pores are completely filled with the solvent,
- the mass transfer occurs exclusively by diffusion within the space of the pores,
- the sorbate concentration in the liquid is uniform (a homogeneous solution),
- the volume of the liquid does not change,
- desorption of the sorbate ions from the sorbent is not taking place.

The mass transfer in the solvent pores is a transient process and can be described by Fick's second equation under the assumption that effective diffusivity is constant. When the beads of a homogeneous sorbate are spherical, the total mass balance for diffusion of a substance in spherical beads (for the transient state) is in the form

$$\frac{\partial C_s}{\partial t} = D_e \left( \frac{\partial^2 C_s}{\partial r^2} + \frac{2}{r} \frac{\partial C_s}{\partial r} \right) \tag{6}$$

If  $N$  sorbate-containing beads are immersed in a vigorously agitated sorbate-free solution of a definite volume, then the initial and boundary conditions are as follows:

$$\begin{array}{lll} t = 0 & 0 < r < R & C_s = \text{const} \\ t = 0 & r > R & C_t = 0 \\ t > 0 & r = 0 & \frac{\partial C_s}{\partial r} = 0 \\ t > 0 & r = R & V_L \frac{\partial C_t}{\partial t} = K A_s D_e \frac{\partial C_s}{\partial r} \Big|_{r=R} \end{array}$$

Under the assumption that the sorbate is uniformly distributed within the whole bead and the beads are in an equilibrium with the liquid phase, the rate of diffusion of the sorbate from the sorbent beads into the solution is given by Equation (7) describing diffusion of the starting materials onto the outside of the sphere

$$C_t = \left( \frac{C_{s0}}{1 + \alpha} \right) \left\{ 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1)}{9 + 9\alpha + q_n^2 \alpha^2} \exp\left( -q_n^2 \frac{D_e t}{R^2} \right) \right\} \tag{7}$$

as  $C_\infty$  and  $C_{s0}$  are interrelated by

$$C_\infty = \frac{C_{s0}}{(1 + \alpha)} \tag{8}$$

Equation (7) can be rewritten as

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

where  $q_n$  represents non-zero roots of Equation (10)

$$tgq_n = \frac{3q_n}{3+\alpha q_n^2} \quad (10)$$

and parameter  $\alpha$  is defined by Equation (11)

$$\alpha = \frac{3V_L}{4N\pi R^3 K} \quad (11)$$

by selecting appropriate experimental conditions ( $\alpha \geq 100$ , *i.e.*, the volume of the sorbent is at least 100 times as small as that of distilled water). Equation (9) can be shortened to the form derived for the open system (the arduous calculation of successive  $q_n$  values is thus eliminated).

$$\frac{C_L}{C_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot \exp\left(-\frac{D_e n^2 \pi^2 t}{R^2}\right) \quad (12)$$

Because in the new conductometric procedure, determination of effective diffusivity is based on the measurement of conductance of a solution into which the sorbate diffuses (under assumption of a linear relationship between the conductance and concentration), transformation of the equation for transient diffusion leads to Equation (13)

$$\frac{P_t}{P_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-D_e n^2 \pi^2 t}{R^2}\right) \quad (13)$$

The apparatus for the determination of effective diffusivity is shown in Fig. 4. It consists of a 120-cm<sup>3</sup> beaker (2), thermostated water jacket (1), magnetic stirrer (4), thermometer (5), and a conductometer with an electrode (6). Number 3 denotes the alginate beads.

Conductance of the solution was measured on a microcomputer-assisted CPC-551 (ELMETRON) conductometer. Cadmium(II)-saturated beads of a volume smaller than 1 cm<sup>3</sup> were placed in 100 cm<sup>3</sup> of distilled water with simultaneous starting the magnetic stirrer and a stop-watch. The temperature was held at 25±0.5°C throughout. The conductance of the solution was measured at set time intervals up to reaching constant readings on the conductometer (usually within 60 minutes).



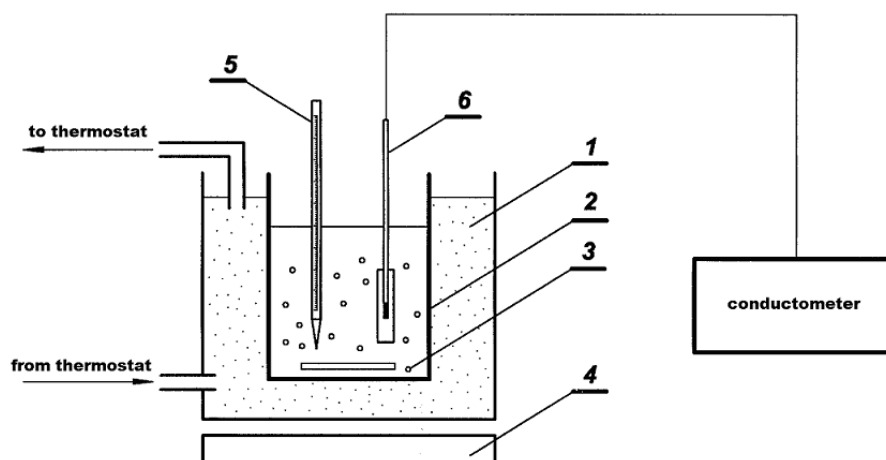


Fig. 4. Schematic diagram of the apparatus for determination of effective diffusivity by the conductometric method.

## RESULTS AND DISCUSSION

### Effective diffusivity SCM method

Beads containing 2.7 to 6.4% of the alginate were examined. Effective diffusivity was calculated using Equation (3). The  $D_e$  values for all the alginate beads tested are compiled in Table 2. According to literature, molecular diffusivity,  $D_m$ , for Cd(II) ions in a very dilute aqueous solution is  $0.72 \cdot 10^{-9} \text{ m}^2/\text{sec}$  at  $25^\circ\text{C}$  [18].

Table 2. Effective diffusivity of  $\text{CdCl}_2$ , as calculated by the SCM method for the beads with various alginate contents.

Alginate content of beads [wt%]	Effective diffusivity $D_e \cdot 10^9 \text{ [m}^2/\text{sec]}$	$\varphi = \frac{D_e}{D_m}$
2.7	0.75	1.04
5.0	1.82	2.53
6.4	1.99	2.76

Both the  $D_e$  and  $\varphi$  values were dependent on the alginate content of the beads. Upon increasing the content, diffusivity also increased and in each case  $D_e$  was larger than  $D_m$ , this being incompatible with the mechanism of diffusion in porous carriers [15]. The calculated retardation coefficients fell in the range 1.04 – 2.76.

### Conductometric method

Beads containing 1.5 to 5.7% of the alginate were examined. Effective diffusivity was calculated from Equation (13) using the Levenberg-Marquardt optimization procedure of non-linear regression contained in the Slide Write Plus program. Effective diffusivity of  $\text{CdCl}_2$  in beads of various alginate contents as well as correlation coefficients and retardation coefficients are compiled in Table 3.

Table 3. Effective diffusivity of CdCl<sub>2</sub> and retardation coefficients in alginate beads of various alginate content.

Alginate content of the beads [wt%]	Effective diffusivity $D_e \cdot 10^9$ [m <sup>2</sup> /sec]	Correlation coefficient	$\varphi = \frac{D_e}{D_m}$
1.5	0.73	0.978	0.58
3.7	0.67	0.989	0.53
5.7	0.59	0.987	0.47

Calculated using the Nernst equation, molecular diffusivity,  $D_m$ , for CdCl<sub>2</sub> in a very dilute aqueous solution is  $1.26 \cdot 10^{-9}$  m<sup>2</sup>/sec at 25°C.

All the  $D_e$  values obtained by the conductometric method are smaller than those of  $D_m$ . Moreover, there is a distinct decrease in the  $D_e$  values as the alginate content increases. This finding is compatible with the mechanism of diffusion in porous carriers. A fairly good accordance of the experimental results with the mathematical model has been noted, as highlighted by high correlation coefficients. The calculated retardation coefficients,  $\varphi$ , fall in the range 0.47 to 0.58 and decrease with an increasing alginate content of the beads.

The beads used for the conductometric method were different from those used for the SCM method because fresh beads were to be prepared for each analysis.

A comparison of the effective diffusivities, as calculated by the SCM and the conductometric methods is presented in Fig. 5. It is clear that the results obtained by the SCM method are much different from those obtained by the conductometric method. The difference is especially noticeable for higher alginate contents in the beads. Moreover, in the SCM method, higher alginate contents in the beads are accompanied by higher values of the effective diffusion coefficient  $D_e$ . In an extreme case (6.4% of the bead), the value of  $D_e$ , as calculated by that method, is nearly 3 times as high as that of  $D_m$ .

In contrast, for the conductometric method, an increase in the alginate content in the beads leads to lower values of the effective diffusion coefficient  $D_e$ , while in no case is  $D_e$  higher than  $D_m$ .

As the magnitude of effective diffusivity is affected by a number of environmental conditions such as the pH of the sorbate solution, the initial sorbate concentration and the biosorbent content in the beads, usually it is difficult to compare literature data because their authors often fail to report the experimental conditions. However, most authors claim that internal diffusion is a process which controls the rate of biosorption of heavy metals [12-14, 19]. On the other hand, the literature effective diffusivities of Cd(II) in the alginates differ markedly from one another depending on the calculation procedures used. For instance, Appel and Torma [14] obtained  $D_e = 0.0134 \cdot 10^{-9}$  m<sup>2</sup>/sec, a value one order of magnitude smaller than that of  $D_m$ . Again, in papers by Papageorgiou *et al.* [20, 21], the  $D_e$  values are  $1.9 \cdot 10^{-9}$  m<sup>2</sup>/sec and  $4.5 \cdot 10^{-9}$  m<sup>2</sup>/sec, these being one order of magnitude higher than  $D_m$ . Our effective diffusivities of Cd(II) in calcium alginate beads, as determined by the conductometric method, are most similar to the

values obtained by Klimiuk ( $D_e = 0.3 \cdot 10^{-9} \text{ m}^2/\text{sec}$  [22]) and by Volesky [18] ( $D_e = 0.6 \cdot 10^{-9} \text{ m}^2/\text{sec}$  for  $\text{Cd}^{2+}$ ).

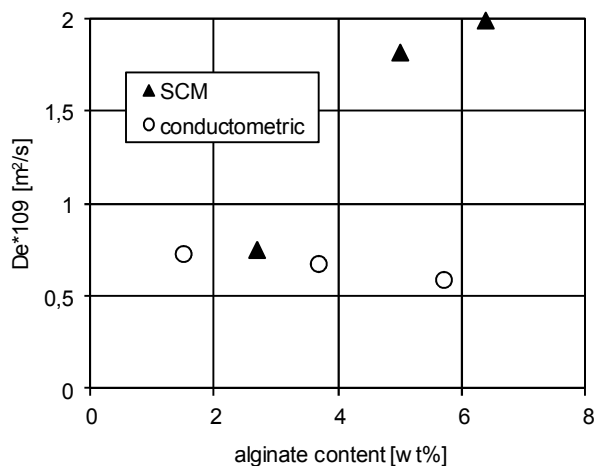


Fig. 5. Comparison of effective diffusivities, as calculated by the SCM and the conductometric methods.

## CONCLUSIONS

1. The SCM method gave  $D_e$  values, increasing with an increase in the alginate content in the beads, this being incompatible with the mechanism of diffusion in porous carriers.
2. The conductometric method turned out to be a simple and effective one for the calculation of effective diffusivity of Cd(II) in alginate sorbents. All the effective diffusivity values,  $D_e$ , obtained by the conductometric method, were lower than those of  $D_m$ .
3. The effective diffusivity values obtained by the conductometric method for diffusion of Cd(II) ions were found to be dependent on the alginate contents in the beads. An increase in the alginate content from 1.5 to 5.7 wt% was accompanied by a decrease in  $D_e$  from  $0.73 \cdot 10^{-9}$  to  $0.59 \cdot 10^{-9} \text{ m}^2/\text{sec}$ . This was in accordance with the mechanism of diffusion in porous carriers.
4. An enhanced content of the biopolymer in the beads caused retardation of Cd(II) diffusion in the beads owing to the decreasing of the calculated retardation coefficients with increasing alginate contents in the beads.

## LIST OF SYMBOLS

- $A_d$  – average binding site density of the beads,  
 $A_s$  – surface of the bead,  
 $C_S$  – concentration of Cd(II) ions in bead pores at time  $t$ ,  
 $C_{S0}$  – concentration of Cd(II) ions in bead pores at time  $t = 0$ ,

- $C_0$  – initial Cd(II) ions concentration in solution,  
 $C_\infty$  – final equilibrium concentration of Cd(II) ions in solution,  
 $C_t$  – concentration of Cd(II) ions in solution at time  $t$ ,  
 $D_e$  – effective diffusivity,  
 $D_m$  – molecular diffusivity,  
 $K$  – partition coefficient,  
 $m_s$  – dry mass of sorbent,  
 $N$  – number of alginate beads,  
 $P_t$  – conductance of solution after time  $t$ ,  
 $P_\infty$  – equilibrium conductance of solution,  
 $q_n$  – parameter defined by Equation (10),  
 $R$  – radius of alginate beads (m),  
 $s$  – slope of a straight line,  
 $t$  – time (s),  
 $V_L$  – volume of solution, containing of Cd(II) ions.

### Greek Symbols

- $\alpha$  – parameter defined by Equation (11),  
 $\beta$  – porosity,  
 $\tau$  – tortuosity factor,  
 $\varphi$  – retardation coefficient,

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