DIFFUSION OF Cd(II), Pb(II) AND Zn(II) ON CALCIUM ALGINATE BEADS

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Abstract

Effective diffusion coefficients ($D_e$) for different heavy-metal salts: Cd, Pb, Zn in calcium alginate beads were determined. Their values depend 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.

Nomenclature

$A_s$ – biosorbent bead area [m$^2$],
$C_i$ – initial sorbate concentration in solution [g·L$^{-1}$],
$C_L$ – sorbate concentration in solution at time $t$ [g·L$^{-1}$],
$C_S$ – sorbate concentration in sorbent pores at time $t$ [g·L$^{-1}$],
$C_{S0}$ – sorbate concentration in sorbent pores for $t=0$ [g·L$^{-1}$],
$C_{eq}$ – equilibrium concentration of sorbate in solution [g·L$^{-1}$],
$D_e$ – effective coefficient of sorbate diffusion in sorbent pores [m$^2$/s],
$D_{aq}$ – coefficient of diffusion in dilute aqueous solution [m$^2$/s],
$K$ – partition ratio [–],
$N$ – number of sorbent bead,
$P_t$ – conductivity of solution after time $t$ [µS],

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Introduction

Heavy metals have a proven harmful effect on many forms of life. Lead and cadmium are known to be especially harmful to man and the environment (Meena et al. 2008). Wastewater that contains zinc is harmful for both irrigational and industrial applications (Lai et al. 2008). Lead, copper and zinc are generally present in water as a result of industrial pollution of rivers and reservoirs, and/or by dissolution of natural sources. The World Health Organization in the guidelines for drinking water has recommended a desirable limit concentration of 0.01 mg·L$^{-1}$ for lead and 3 mg·L$^{-1}$ for zinc. Cadmium compounds are potentially carcinogenic to humans, being the recommended levels of 0.003 mg·L$^{-1}$. The European Union Council Directive on water quality set the permissible levels in drinking water for Pb to 10 µmol·L$^{-1}$ (2 mg·L$^{-1}$) and for Cd to 5 µmol·L$^{-1}$ (0.56 mg·L$^{-1}$).

Various methods have been suggested and applied for the removal of toxic heavy metals from aqueous solutions, such as chemical precipitation, evaporation, ion-exchange, adsorption, solvent extraction, electrolysis and reverse osmosis (Dhaka L et al. 2005, Lai et al. 2008, Chand et al. 2009). These conventional processes face several constraints and have certain disadvantages like high cost, environmental impact, technical efficiency (Wang et al. 2016), generation of large volumes of sediment, problems with recycling and with the reuse of adsorbents or ion exchangers (Ghimire et al. 2003, Dhaka L et al. 2005, Chand et al. 2009), that limit their use. Therefore, there is a growing interest in the search for low cost, easily available and environmentally friendly biologically-derived materials suitable for the efficient removal of these toxic substances (Lai et al. 2008, Iqbal, Saeed 2002). Biosorption, an alternative technology, is based on the properties of inactive and dead biomass, which can bind and concentrate hazardous ions from aqueous solutions (Ruiz et al. 2013). Biosorption on materials of natural origin seems to provide 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

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$P_\infty$ – conductivity of solution after time $\infty$ [µS],
$q_n$ – a parameter, defined by Equation (5) [-],
$r$ – bead radial coefficient,
$R$ – sorbent bead radius [m],
$t$ – time [s],
$V_L$ – volume of the solution which contains the sorbate [ml],
$\alpha$ – a parameter, defined by Equation (6) [-],
$\beta$ – porosity [-],
$\varphi$ – diffusion retardation coefficient [-],
$\tau$ – tortuosity factor [-].
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.

The process of sorption with biomass can be linked to various organic species, e.g. chitosan (DEMEY et al. 2017, DEMEY et al. 2018 b) or alginate.

Pollutants do not only include toxic, cancerogenic and mutagenic metals (such as cadmium, lead) but also metals of economic value (such as silver, gold, platinum), therefore, possibilities of their recovery have become another important issue. Once again, biosorption has appeared to be 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: VOLESKY, HOLAN 1995, Hu et al. 1996, VEGLIO, BEOLCHI 1997, KRATOCHVIL, VOLESKY 1998, ECLES 1999, FIGUEIRA et al. 2000, VOLESKY 2001, JEON et al. 2002, VOLESKY 2003, RINCON et al. 2005, PAPAGEORGIOU et al. 2006, 2008, CHOJNACKA 2010). The studies have demonstrated that marine algae, which are acquired at a rather low cost, have a considerable sorption capacity.

Alginate as one of the major components of brown algae (KAWAI, MURATA 2016), whose high affinity for heavy metals has been confirmed by many studies. The sorption properties of alginates have been investigated since 1990’s (PAPAGEORGIOU et al. 2006, 2008, JANG et al. 1990, 1991, DEANS, DIXON 1992, CHEN et al. 1993, JANG 1994, LEWANDOWSKI, ROE 1994, JANG et al. 1995a, 1995b, CHEN et al. 1997, KONISHI et al. 1998, AKSU et al. 1992, IBANEZ, UMETSU 1999, 2000, VEGLIO et al. 2002, LAI et al. 2008, DEZE et al. 2012, PLAZINSKI 2012, NASTAJ et al. 2016). Alginates are linear copolymers of β-D-mannuronate (M) and α-L-guluronate (G) residues in (1→4)-linkage, arranged in a block-wise pattern along the linear chain (DAVIS et al. 2003). 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 (PAPAGEORGIOU et al. 2006). 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) (KWIAKTOWSKA-MARKS et al. 2011a) with a simultaneous recovery of metals. Their other advantages also include: biodegradability, hydrophilicity and the presence of carboxylic groups (ARICA et al. 2004). Owing to all these advantages, alginates are regarded as the most-promising category of biosorbents of heavy metals (APEL, TORMA 1993, NESTLE, KIMMICH 1996, PAPAGEORGIOU et al. 2006, 2008).

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 (IBANEZ, UMETSU 1999, 2000). 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:

\[
D_e = \frac{D_{aq} \cdot \beta}{\tau} \quad (1)
\]

The tortuosity factor (\( \tau \)) 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, \( \beta \), is known. Formulas for calculating the tortuosity are presented in the paper SOBIESKI and LIPIŃSKI (2017).

In the case of alginate gels, it is convenient to use the diffusion retardation coefficient, \( \phi \):

\[
\phi = \frac{D_e}{D_{aq}} = \frac{\beta}{\tau} \quad (2)
\]

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

The rate of diffusion has hitherto been determined based on changes in sorbate concentration in the solution during the sorption process. Measurements of the diffusion coefficient can be made in either an open or a closed system. The closed system is used more often 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) (JANG et al. 1991, LEWANDOWSKI, ROE 1994, ARAUJO, TEIXEIRA 1997) or the linear absorption model (LAM) (CHEN et al. 1993, ARAUJO, TEIXEIRA 1997, PAPAGEORGIOU et al. 2006).

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
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The case of low concentrations of metals in solution (PAPAGEORGIOU et al. 2006). 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 (KWIAKTOWSKA-MARKS et al. 2011b). 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:

– preparation of calcium alginate beads from sodium alginate solution;
– to determine by the conductometric method the effective diffusion coefficient for different heavy-metal salts: Cd, Zn and Pb in calcium alginate beads;
– to 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. Six different heavy-metal salts were examined: CdCl$_2$, CdSO$_4$, ZnCl$_2$, ZnSO$_4$, Zn(NO$_3$)$_2$, Pb(NO$_3$)$_2$.

Preparation of the alginate beads

Calcium alginate beads were prepared by dropwise addition of a viscous, aqueous sodium alginate solution to 0.05 mol·L$^{-1}$ of CaCl$_2$ 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 CaCl$_2$ solution and a cross-linked Ca-alginate was formed. The gelation process was continued for 0.5 hr. The beads were then placed in a new 0.05 mol·L$^{-1}$ portion of CaCl$_2$ 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 the analysis to ensure 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 mol·L$^{-1}$ 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 at a constant temperature of 25°C± 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. Conversely, 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:
\[
\frac{\partial C_S}{\partial t} = D_e \left( \frac{\partial^2 C_S}{\partial r^2} + \frac{2 \partial C_S}{r \partial r} \right)
\]

(3)

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:

\[
\begin{align*}
& t=0 \quad 0<r<R \quad C_S = \text{const.} \\
& t=0 \quad r>R \quad C_S = 0 \\
& t>0 \quad r=0 \quad \frac{\partial C_S}{\partial r} = 0 \\
& t>0 \quad r=R \quad V_L \frac{\partial C_L}{\partial t} = K A_S D_e \frac{\partial C_S}{\partial r} \big|_{r=R}
\end{align*}
\]

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 (Arnaud et al. 1992, Somers et al. 1989):

\[
C_L = \left( \frac{C_{S_0}}{1 + \alpha} \right) \left\{ 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1)}{9 + 9\alpha + q_n^2\alpha^2} \exp \left( -\frac{q_n^2 D_e t}{R^2} \right) \right\}
\]

(4)

Where \( q_n \) represents positive, non-zero roots of Equation (5):

\[
tgq_n = \frac{3q_n}{3 + \alpha q_n^2}
\]

(5)

and parameter \( \alpha \) is defined by Equation (6):

\[
\alpha = \frac{3V_L}{4N\pi R^3 K}
\]

(6)

\( C_\infty \) (the sorbate’s equilibrium concentration in the solution) is linked with \( C_{S_0} \) (sorbate’s concentration in the beads for \( t=0 \)) as follows:

\[
C_\infty = \frac{C_{S_0}}{1 + \alpha}
\]

(7)

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

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

(8)

By selecting suitable experimental conditions (\( \alpha \geq 100 \), which means that the sorbent sample volume is at least 100 times smaller than 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 $q_n$):

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

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):

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

where:

- $P_t$ – conductivity of the solution after the time $t$,
- $P_\infty$ – conductivity of the solution after the time $\infty$.

A strictly defined sample of alginate beads, saturated with the test metal salt was placed in a beaker filled with distilled water. The content 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 smaller than 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

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Fig. 1. Setup for determination of effective diffusion coefficient:
A – to thermostat, B – from thermostat, C – conductometer; description in the text
the total volume was not higher than 1 ml, were dropped in 100 ml of distilled water while the magnetic stirrer and a stopper were started. A constant temperature of 25°C ± 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 1. It was composed of a 120 ml 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**

Conducted experiments confirmed that dependence of the solution’s conductivity on the given test-metal salt concentration is linear, and performed analysis 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 $P_t/P_\infty$ on the process duration is shown in Figure 2.

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

![Fig. 2. Dependence of $P_t/P_\infty$ on the process duration for diffusion of cadmium sulfate from alginate beads with a dry weight of 1.5%](image-url)
values of $D_e$. Conversely, an increase in the process temperature contributes to an increase in the values of the effective diffusion coefficient.

Sulfates, chlorides and nitrates of 3 heavy metals: Cd, Zn 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.

**Cadmium(II) salt diffusion**

Table 1 and Figure 3 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 $\phi$ is shown.

<table>
<thead>
<tr>
<th>Alginate content in beads [wt %]</th>
<th>Effective diffusion coefficient $D_e \cdot 10^{-9}$ [m$^2$/s]</th>
<th>Correlation coefficient $r^2$</th>
<th>Retardation coefficient $\phi = \frac{D_e}{D_{aq}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CdCl}<em>2$ ($D</em>{aq} = 1.26 \cdot 10^{-9}$ m$^2$/s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>0.73</td>
<td>0.978</td>
<td>0.58</td>
</tr>
<tr>
<td>3.7</td>
<td>0.67</td>
<td>0.989</td>
<td>0.53</td>
</tr>
<tr>
<td>5.7</td>
<td>0.59</td>
<td>0.987</td>
<td>0.47</td>
</tr>
<tr>
<td>$\text{CdSO}<em>4$ ($D</em>{aq} = 0.86 \cdot 10^{-9}$ m$^2$/s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>0.47</td>
<td>0.996</td>
<td>0.55</td>
</tr>
<tr>
<td>3.7</td>
<td>0.40</td>
<td>0.995</td>
<td>0.46</td>
</tr>
<tr>
<td>5.7</td>
<td>0.37</td>
<td>0.994</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Fig. 3. Dependence of retardation coefficient on alginate content in beads for cadmium salts
All the values of $D_e$, obtained by the conductometric method, are lower than the calculated diffusion coefficients in a highly dilute aqueous solution of the given this 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 CdSO$_4$, was 35% lower in comparison with the value obtained for 1.5% alginate and the diffusion of CdCl$_2$).

Both the retardation coefficient $\phi$ 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 $\phi$ decreased by 19% and 22% for CdCl$_2$ and CdSO$_4$, respectively.

Also in this case, literature data (Tab. 2) indicated significant differences between the values of $D_e$, as obtained by the SCM (KLIMIUK, KUCZAJOWSKA-ZADROŻNA 2002) and LAM (PAPAGEORGIOU et al. 2006) methods.

### Table 2

<table>
<thead>
<tr>
<th>$D_e \cdot 10^{-9}$ [m$^2$/s]</th>
<th>$\phi$</th>
<th>pH</th>
<th>temperature [°C]</th>
<th>$C_i$ [mg·L$^{-1}$]</th>
<th>other</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>0.42</td>
<td>no data</td>
<td>no data</td>
<td>100</td>
<td></td>
<td>as calculated according to SCM, sorbate: CdSO$_4$</td>
</tr>
<tr>
<td>0.6</td>
<td>0.83</td>
<td>4.0</td>
<td>no data</td>
<td>no data</td>
<td>no data</td>
<td></td>
</tr>
<tr>
<td>1.9</td>
<td>2.64</td>
<td>4.5</td>
<td>25°C</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>6.26</td>
<td>4.5</td>
<td>25°C</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0134</td>
<td>0.02</td>
<td>5.0</td>
<td>23°C</td>
<td>51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.208</td>
<td>0.29</td>
<td>4.0</td>
<td>20°C</td>
<td>33.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^b$ for Cd(II) ions at a temperature of 298 K: $D_{aq}=0.719 \cdot 10^{-9}$ m$^2$/s VOLESKY (2003).
Zinc(II) salt diffusion

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

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

Also in this instance, all of the values of De, as obtained by the conductometric method, are lower than the diffusion coefficients in a given, highly dilute aqueous solution this salts ($D_{aq}$). The retardation coefficient (Fig. 4) and

<table>
<thead>
<tr>
<th>Alginate content in beads [wt %]</th>
<th>Effective diffusion coefficient $D_e \times 10^{-9}$ [m$^2$/s]</th>
<th>Correlation coefficient $r^2$</th>
<th>Retardation coefficient $\phi = \frac{D_e}{D_{aq}}$</th>
</tr>
</thead>
<tbody>
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<td>1.5</td>
<td>0.77</td>
<td>0.977</td>
<td>0.62</td>
</tr>
<tr>
<td>3.7</td>
<td>0.73</td>
<td>0.982</td>
<td>0.59</td>
</tr>
<tr>
<td>5.7</td>
<td>0.66</td>
<td>0.982</td>
<td>0.53</td>
</tr>
<tr>
<td>ZnCl$<em>2$ ($D</em>{aq}$ = 1.25 $\times$ 10$^{-9}$ m$^2$/s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>0.44</td>
<td>0.962</td>
<td>0.52</td>
</tr>
<tr>
<td>3.7</td>
<td>0.37</td>
<td>0.988</td>
<td>0.43</td>
</tr>
<tr>
<td>5.7</td>
<td>0.24</td>
<td>0.967</td>
<td>0.28</td>
</tr>
<tr>
<td>ZnSO$<em>4$ ($D</em>{aq}$ = 0.85 $\times$ 10$^{-9}$ m$^2$/s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>0.84</td>
<td>0.985</td>
<td>0.69</td>
</tr>
<tr>
<td>3.7</td>
<td>0.63</td>
<td>0.981</td>
<td>0.52</td>
</tr>
<tr>
<td>5.7</td>
<td>0.50</td>
<td>0.966</td>
<td>0.41</td>
</tr>
<tr>
<td>Zn(NO$_3$)$<em>2$ ($D</em>{aq}$ = 1.22 $\times$ 10$^{-9}$ m$^2$/s)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 4. Dependence of retardation coefficient on alginate content in beads for zinc salts](image-url)
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 lead nitrate**

Lead nitrate was used for the tests because both lead sulfate and lead chloride are difficult to dissolve in water. The results of calculation are shown in Table 4.

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 four times as high, have a retardation coefficient of just more than 13% lower (down from 0.52 to 0.45).

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

### Table 4

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

<table>
<thead>
<tr>
<th>Alginate content in beads [wt %]</th>
<th>Effective diffusion coefficient $D_e \cdot 10^{-9}$ [m$^2$/s]</th>
<th>Correlation coefficient $r^2$</th>
<th>Retardation coefficient $\phi = \frac{D_e}{D_{aq}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(NO$_3$)$<em>2$ ($D</em>{aq} = 1.41 \cdot 10^{-9}$ m$^2$/s)</td>
<td>1.5</td>
<td>0.74</td>
<td>0.980</td>
</tr>
<tr>
<td>3.7</td>
<td>0.70</td>
<td>0.994</td>
<td>0.49</td>
</tr>
<tr>
<td>5.7</td>
<td>0.64</td>
<td>0.991</td>
<td>0.45</td>
</tr>
</tbody>
</table>

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. Significantly 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 highly dilute aqueous solution of the given this salt, $D_{aq}$. 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.

References


Diffusion of Cd(II), Pb(II) and Zn(II) on Calcium Alginate Beads


