HYDROGEL NANOCOMPOSITES BASED ON CALCIUM ALGINATE AND CLAY MINERALS

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Abstract. Methods for the synthesis of calcium alginate gels (in the form of beads and fibers) and hydrogel composites based on alginates and clay minerals (Laponite and Montmorillonite) have been developed. The structure of the synthesized gels and composites was characterized using FT-IR spectroscopy. Their kinetics of swelling in water, saline, and phosphate buffer was studied and inherent to them Fick type of diffusion was determined using the Peppas-Ritter equation.

The complex of sorption and diffusion properties inherent to the synthesized hydrogel composites determines their high potential as soil conditioners for agrotechnological purposes, providing remediation of soils contaminated with toxic substances and pathogenic microorganisms, increased water retention and aeration, as well as prolonged release of plant protection products.

Key words. Hydrogels, calcium alginate, ionotropic cross-linking, laponite, clay minerals, soil conditioners, montmorillonite, swelling, diffusion.

Анотація. Розроблено методи синтезу гелів альгінату кальцію (у вигляді кульок і волокон) та гідрогелевих композитів на основі альгінатів і глинистих мінералів (лапоніту та монтморилоніту). Структуру синтезованих гелів та композитів охарактеризовано за допомогою ІЧ-спектроскопії. Вивчено кінетику їх набухання у воді, фізіологічному розчині та фосфатному буфері і визначено притаманний їм тип дифузії за Фіком з використанням рівняння Пеппаса-Ріттера.

Сукупність сорбційних і дифузійних властивостей, притаманних синтезованим гідрогелевим композитам, обумовлює їх високий потенціал як ґрунтових кондиціонерів агротехнологічного призначення, що забезпечує ремедіацію ґрунтів, забруднених токсичними речовинами і патогенними мікроорганізмами, підвищену водоутримання та аерацію, а також пролонговане вивільнення засобів захисту рослин.

Ключові слова. Гідрогелі, альгінат кальцію, іонотропне зшивання, лапоніт, глинисті мінерали, кондиціонери ґрунту, монтморилоніт, набухання, дифузія.

Alginates are natural polysaccharides, polyanionic polymers derived from brown marine algae, and some bacteria (e.g. Pseudomonas and Azotobacter) [1]. The polymer chains of alginates consist of β-D-mannuronic acid (M-blocks) and α-L-guluronic acid (G-blocks) connected by (1→4) glycosidic bonds [2]. The interaction of alginates with multivalent cations, primarily calcium cations, leads to the formation of biodegradable gels. Polymerization is based on crosslinking of copolymers through ionic bonds between Ca^{2+} cations and alginate anions. Each Na^+ cation ionically binds to only one carboxyl group of the alginate chain, while the Ca^{2+} cation interacts with two carboxyl groups located in different polymer chains [3]. The exchange of Na+ ions in sodium alginate for Ca^{2+} ions occurs when an aqueous solution of sodium alginate mixes with a solution containing calcium ions. It should be emphasized that only G-blocks are involved in the crosslinking process. To increase the sorption capacity of calcium-alginate gels, clay minerals, such as natural montmorillonite and synthetic laponite, were incorporated into their structure. Let us analyze their properties.

Laponite is disks with a diameter of about 25-30 nm and a thickness of about 1 nm [4] with a structure similar to that of natural hectorite and empirical composition $Na_{0.7}(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4$. MMT is a natural clay mineral belonging to the smectite group. It is a dioctahedral 2:1 phyllosilicate constituted by two tetrahedral sheets and one octahedral sheet (T:O:T). Chemically, the MMT consist of isomorphic substitutions in the tetrahedral sheet of Si^{4+} by Al^{3+} and Al^{3+} by Mg^{2+} in the octahedral ones [5].

Materials

Alginic acid sodium salt (SA, viscosity 450-550 cP (1 % in H_2O, Glentcham Life Science, №1), LAPONITE®RD (Lap, Rockwood Additives Ltd., Widnes, U.K.), Montmorillonite K 10 (MMT, Bulk density 300 - 370 kg/m³, Sigma-Aldrich), Calcium chloride (CaCl$_2$, 97 %, Sigma-Aldrich), were used as received without further purification. Distilled water was used as a solvent in all experiments.

Synthesys

Calcium-alginate gels, particularly those filled by nanoclays, have been synthesized by two different methods. The first one involves extrusion of sodium alginate by continuous flow into solution of crosslinking agent - calcium chloride. The gel formed in the form of fibers is then subjected to repeated mechanical grinding and sieving to form a powder with a particle size of about 1 mm. An alternative method involves extruding sodium alginate into the crosslinking agent solution in a dropwise manner, using a pipette, syringe or peristaltic pump. The size of the resulting beads can be controlled by varying the diameter of the nozzle.

Swelling degree, Q, (g/g) of hydrogels were studied in distilled water, saline and phosphate buffer using the gravimetric method and calculated according to the following formula:

$$Q = \frac{m_{(t)} - m_d}{m_d}, \quad (1)$$

where $m_{(t)}$ is the mass of swollen sample at the time (t); m_d is the mass of the gel after drying. All swelling measurements were performed in triplicate.

Fig.1. Changes in the size of hydrogel beads based on calcium-alginate and laponite (C$_{alg}$=2 %, C$_{lap}$=0.5 %, C$_{CaCl2}$=0.5%) during processing (a-after synthesis; b-after swelling; c-after drying)

The FTIR spectra were recorded in the range of 400–4000 cm^{-1} (internal reflection spectroscopy, with resolution of 4 cm^{-1} and accumulations of 40 scans) using a Shimadzu IRAffinity-1S spectrometer equipped with GS10800-X QuestsR ATR Diamond accessory, while Micrographs of alginate gels were obtained using a Kerui 1600X Zoom USB microscope (China).

Fig.2. shows the FTIR spectra of Lap, SA, calcium Alginate, and hybrid gels based on calcium Alginate with incorporated Lap and MMT. For the pristine Lap, the broadband 950−1010 cm^{-1} with a maximum at ≈970 cm^{-1} corresponds to the asymmetric stretch vibrations of Si − OH bond in different environments in layered silicates [6]. The absorption bands around 470 cm^{-1} are caused by skeletal and outskeletal vibrations of the -Si-O-Si-, -Si-O- bonds of the crystal lattice of the mineral nanodisks, and the peak at 650 cm^{-1} corresponds to the vibrational oscillations of the -Si-O-Me- bonds [7].

MMT is characterized by signals in the range from 3600 to 4000 cm^{-1} with a low-intensity peak at 3624 cm^{-1} caused by valence vibrations of the O-H in the silanol group, and the peak at 911 cm^{-1} is the result of strain vibrations of the O-H group. The valence asymmetric and symmetric vibrations of Si-O-Si cause bands with peaks at 1028 cm^{-1} and 800 cm^{-1}, and the strain vibrations of the same bonds absorb at 420 cm^{-1}. The absorption peak at 520 cm^{-1} is caused by -Si-O-Al- group [8].

Spectra of SA and ionically cross-linked calcium alginate are characterized by symmetrical valence vibrations of -C-O- bonds in the rings of guluronic and mannuronic acids, which are overlapped with valence vibrations of (1→4) glycosidic bonds with the formation of a broad band with a peak at 1005...1025 cm^{-1}. The band at 1590 cm^{-1} corresponds to the carboxyl group of carboxylic acid salts, deformation scissor vibrations of the C-H bonds of the carbon skeleton of alginate cause absorption at 1410 cm^{-1}, and deformational skeletal vibrations of these bonds shows up at 1294 cm^{-1}. Hydroxyl group signals of sodium alginate appear at 3246 cm^{-1} and 810 cm^{-1}, which corresponds to the valence and strain vibrations of O-H bonds. Ionic crosslinking of sodium alginate enhances the intensity of the vibrations of its

functional groups, probably due to an increase in the dipole moment of the hydrogel macromolecule.

The FTIR spectrum of the nanocomposites based on calcium-alginate gel and clays shows a combination of absorption bands characteristic for these individual components. At the same time, the intensity of vibrations of the corresponding functional groups of both components increases notably, indicating a synergistic interaction between them.
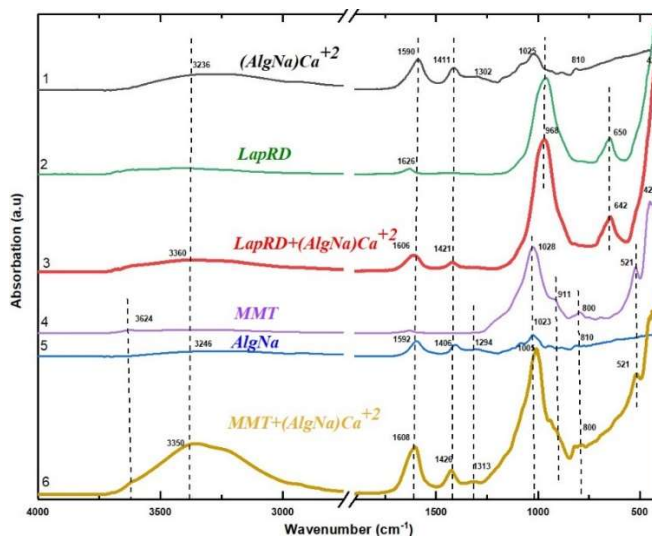

Fig. 2. FTIR spectra of calcium-alginate gel, Lap, composite based on Ca-alginate gel and Lap, MMT, SA, and composite based on Ca-alginate gel and MMT

The swelling of Ca-alginate and Lap - based nanocomposites is described by standard saturation curves, with the reaching of the equilibrium swelling degree in about 24 hours. Visualization of dry alginate-laponite bead swelling during the first three hours is demonstrated on the Fig. 3. At SA concentrations less than 0.5%, even if a gel is formed, it is very heterogeneous and with poor mechanical properties, which is probably due to the insufficient content of G-blocks. For the same reason, swelling degree of the corresponding nanocomposites rise with increasing of SA (Fig.4). Effect of Lap content on the swelling of nanocomposites is not so unambiguous and needs further investigation.
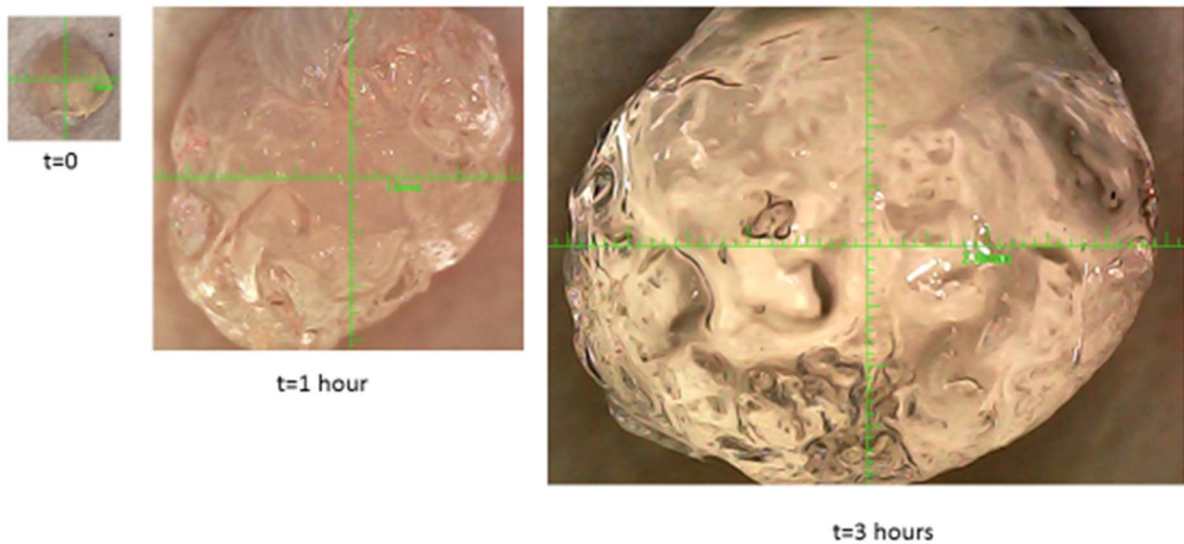
Fig.3. Visualization of dry alginate-laponite (C_{lap}=1% wt.; C_{Alg}=2 % wt.; C_{CaCl2}=0.25 % wt.) bead swelling during the first three hours

Swelling degree of nanocomposites based on alginate gels and clays nanoparticles strongly depends on the crosslinking density of gel networks determined by the concentration of $CaCl_2$, and growth of the crosslinking agent concentration led to the predictable transition of the hydrogel to a denser conformation, with the most significant decrease in swelling observed in the range of $CaCl_2$ concentrations of 0.25-0.5 % wt. (Fig. 5). It is worth noting that at higher concentrations of the cross-linking agent, the degree of swelling of calcium alginate gels with incorporated laponite nanoparticles is an order of magnitude less (Fig. 5b).

Clay nanocomposites based on alginate and MMT exhibit similar behavior when swelling in water - swelling degree decreases with the increase of $CaCl_2$ concentration and rise with growth of MMT content.
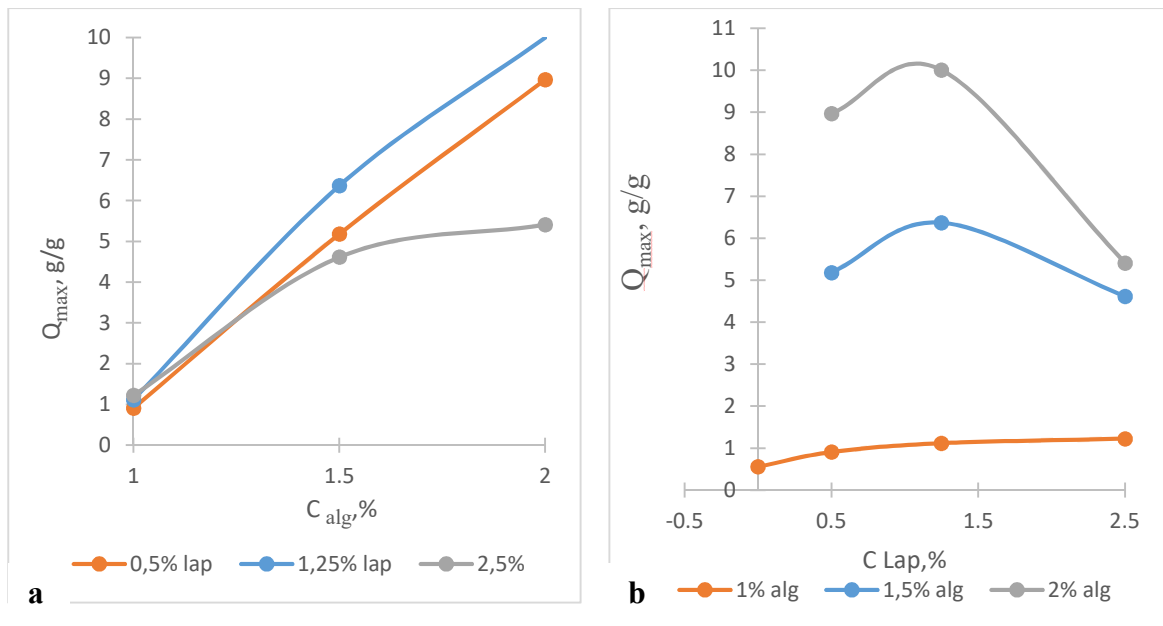
Fig. 4. Effect of Alginate (a) and Laponite (b) content on the swelling of nanocomposites based on them (C_CaCl2=0,5% wt.)

Swelling kinetics

When a glassy hydrogel is exposed to contact with water, it diffuses into the hydrogel and the hydrogel expands. Diffusion involves the migration of water into pre-existing or dynamically formed spaces between the hydrogel chains. Swelling of the hydrogel involves more extensive segmental movements, which ultimately leads to an increase in the distance between the hydrogel chains [9].
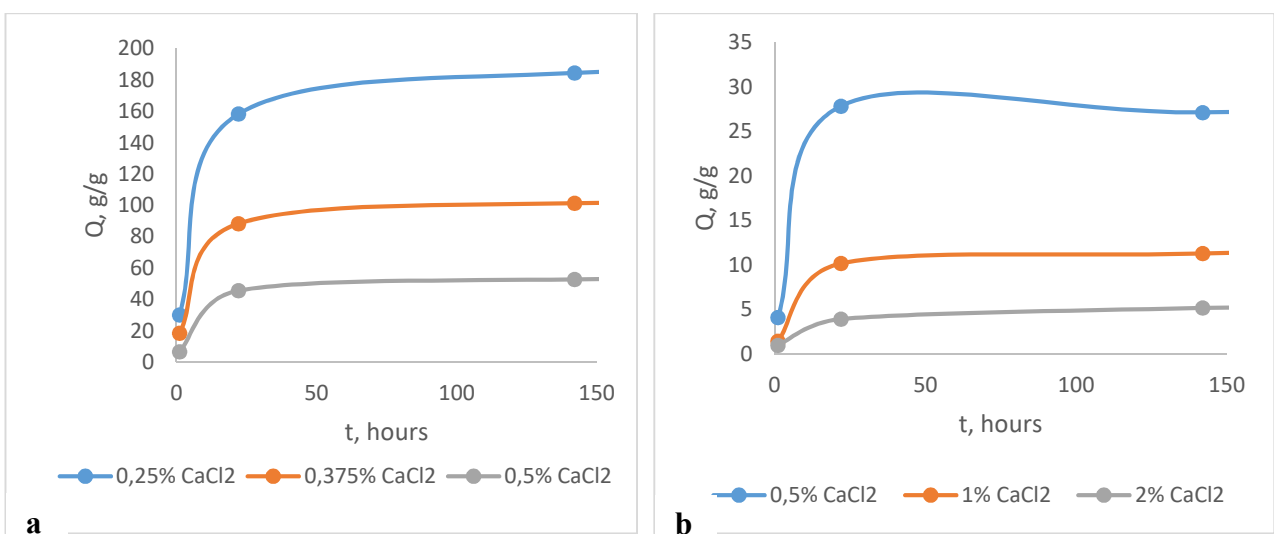

Fig. 5. Swelling kinetics of nanocomposites based on calcium alginate and Lap at low (a) and high (b) CaCl₂ concentrations (C_Alg=2 % wt.; C_Lap=1 % wt.)

To describe this process in 1987 Peppas and Ritger introduced a simple exponential equation (2):

$$M_t/M_\infty = kt^n, \quad (2)$$

that describes the diffusion mechanism of a polymeric system [10]. In these equation M_t and M_∞ denote the amount of solvent diffused into the gel at time t and infinity (at equilibrium) respectively, k is a constant related to the structure of the network, and the exponent n is a number to determine the type of diffusion [11]. Diffusion exponential of n can be estimated from the slope of a line obtained from ln$F$-ln$t$ graph data of the region where the swelling has not reach the equilibrium, but only 60 % of the water mass enters in the structure of gels. Coefficient k can be calculated from the intercepts of the plots of ln$F$ vs ln$t$. For cylindrical shapes, $n = 0.45$-0.50 and corresponds to Fickian diffusion, whereas $0,50 < n < 1,0$ indicates that diffusion is non-Fickian (DNF) [12]. DNF, also called anomalous, arises from the simultaneous and comparable contribution of the diffusion phenomenon of the bioactive agent molecules and the relaxation of the polymer chains. The diffusional exponent obtained when the system presents zero order diffusion (or Case II diffusion) is 1 [10]. Values of n greater than 1 reflects the so-called Super Case II transport [13], whereas the case with n in the range from 0 to 0.45 corresponds to the so-called Hindered Fickian diffusion [14]. Some of the kinetic curves of swelling of the synthesized nanocomposites after logarithmization are shown in Fig. 6.
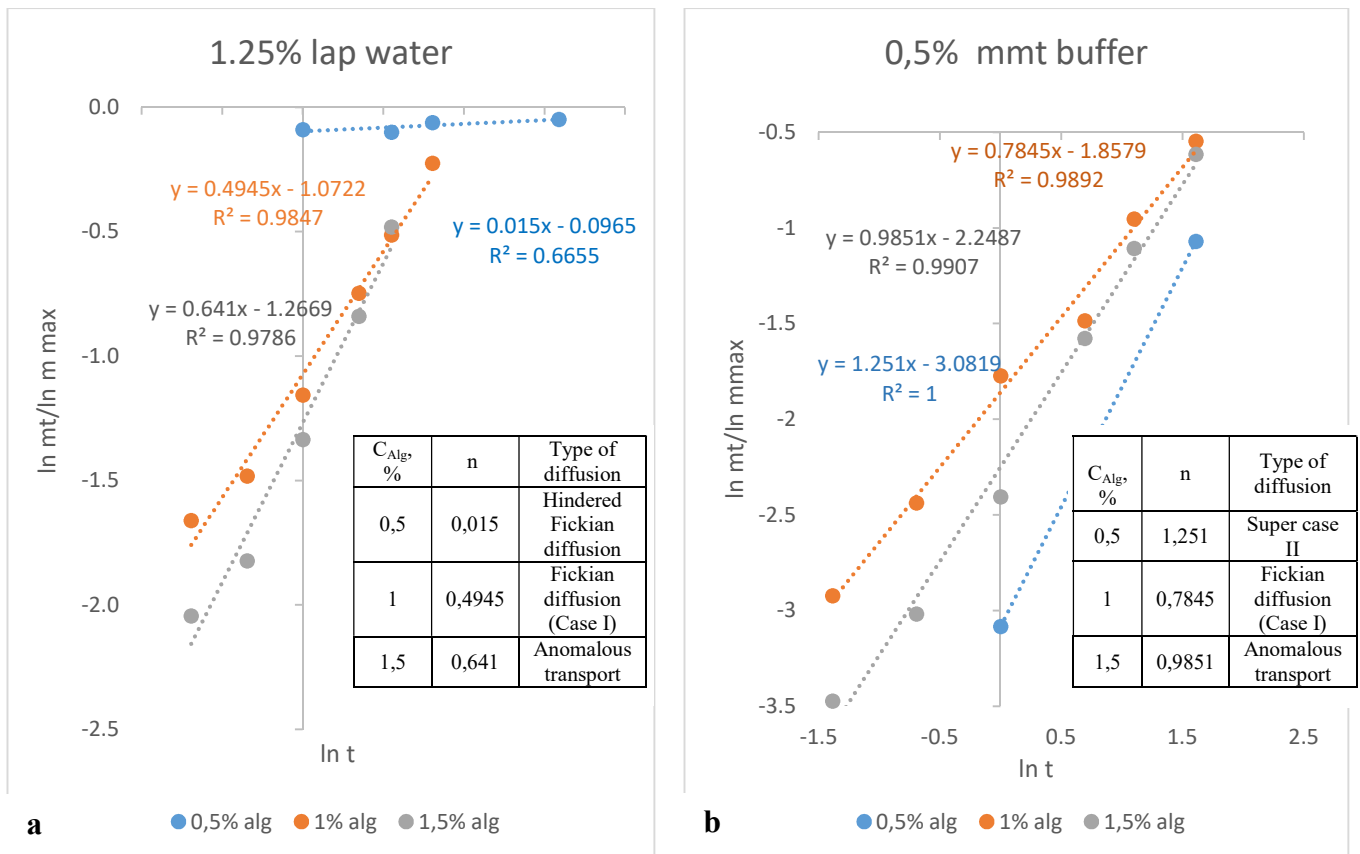
Fig. 6. Plots for the evaluation of the diffusion exponent n on the base of swelling kinetic curves; a - C_{Lap}=1.25 %, in water; b - C_{Lap}=0.5 %, in phosphate buffer

CONCLUSIONS

Thus, the research on the swelling of nanocomposites in solutions of various nature allowed us to establish some kinetic regularities of this process and determine the type of Fick diffusion inherent to them.

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