

Article

Calcium Alginate/Laponite Nanocomposite Hydrogels: Synthesis, Swelling, and Sorption Properties

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Abstract: This study presents the synthesis, characterization, and evaluation of hybrid hydrogels based on calcium alginate (Ca-Alg) and synthetic nanoclay LaponiteRD (Lap), with an emphasis on their swelling and sorption properties. The motivation behind the development of these hybrid hydrogels stems from the need for sustainable materials with enhanced mechanical strength, swelling properties, and sorption capacity for environmental remediation and controlled-release applications. Synthesis methods for the ionotropically cross-linked Ca-Alg hydrogel and Alg–Lap composite hydrogels, based on Alg and Lap in the form of granules and fibres, have been developed. The Fourier-transform infrared spectroscopy (FTIR), Energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD) analyses of composite hydrogels confirmed the successful incorporation of Lap into the Ca-Alg matrix, indicating strong interactions between the polymer and clay, which enhanced the structural integrity of the hydrogels. The morphology of the surface and pore structure of nanocomposites were studied using Scanning Electron Microscopy (SEM). The swelling behaviour of the nanocomposites was largely dependent on the concentrations of Lap and the cross-linking agent (CaCl₂), with higher concentrations leading to more rigid, less swellable structures due to the increased cross-linking density. The sorption studies, specifically with Fe(II) ions, demonstrated that the hybrid hydrogels possess a large sorption capacity, with Lap contributing to selective sorption at lower Fe(II) ion concentrations and Alg enhancing overall capacity at higher concentrations. This suggests that the synergistic interaction between Alg and Lap not only improves mechanical stability but also tailors the sorption properties of the hydrogels. These findings position the Alg-Lap hydrogels as promising materials for a range of environmental applications, including wastewater treatment, heavy metal ion removal, and the design of advanced filtration systems. The study’s insights into the tunability of these hydrogels pave the way for further research into their use in diverse fields such as biomedicine, agriculture, and industrial water management.

Keywords: hybrid hydrogels; alginates; laponite; swelling degree; diffusion; ionotropic cross-linking; Fe(II) sorption



Citation: Samchenko, Y.; Terpilowski, K.; Samchenko, K.; Golovkova, L.; Oranska, O.; Goncharuk, O. Calcium Alginate/Laponite Nanocomposite Hydrogels: Synthesis, Swelling, and Sorption Properties. *Coatings* **2024**, *14*, 1519. <https://doi.org/10.3390/coatings14121519>

Received: 24 October 2024

Revised: 20 November 2024

Accepted: 27 November 2024

Published: 2 December 2024



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1. Introduction

Hydrogels which are based on polymer cross-linked networks have been proven to have great potential in biomedical and environmental applications [1–4]. Hydrogels composed of natural polymers like polysaccharides and proteins have undeniable advantages

compared to synthetic hydrogels. For instance, alginates (Alg), polysaccharide naturally derived from brown seaweed, and some bacteria (e.g., *Pseudomonas* and *Azotobacter*) [5] are well-known for their biocompatibility, biodegradability, non-toxicity, and ability to form hydrogels [6,7]. The polymer chains are composed of β -D-mannuronic acid (M-blocks) and α -L-guluronic Alg acid (G-blocks) connected by (1 $\rightarrow$ 4) glycosidic bonds [8]. One of the simplest and most common methods for synthesizing Alg hydrogels is ionotropic cross-linking. In this case, Algs form three-dimensional hydrogels through the interactions of their carboxylate groups (primarily from the G-blocks) with multivalent cations like calcium (Ca^{2+}). This process follows the “egg-box” model, where calcium ions fit into the cavities formed by the guluronic acid residues, creating a stable three-dimensional network. The exchange of Na^+ ions in sodium alginate (Na-Alg) for Ca^{2+} ions occurs when an aqueous solution of Na-Alg mixes with a solution containing Ca^{2+} ions [9]. Polymerization and cross-linking take place when Ca^{2+} ions bind to two carboxyl groups located in different polymer chains, resulting in a gel-like structure. The properties of Alg hydrogels depend on several factors, including the molecular weight of Alg, the content of G-blocks vs. M-blocks, the concentration of Ca^{2+} ions, and the ionic environment. Algs with a larger G-block content form stronger hydrogels, while those with more M-blocks form weaker gels. Additionally, the kinetics of the ionic cross-linking process, including the gelation time and the cross-linking density, can be controlled by varying the concentration of the cross-linking agent and adjusting the pH of the solution [9,10].

Alg is one of the most environmentally friendly materials for the design of hydrogels applied in various fields of science and technology. Due to their structural similarity to the extracellular matrices in tissues, Alg hydrogels are particularly attractive for wound healing, drug delivery, and tissue engineering [11]. In addition to their applications in biomedicine, Algs have also shown significant potential in environmental applications, namely in soil treatment and remediation for agriculture [5]. These low-cost and abundant materials are eco-friendly and contribute to sustainable agricultural practises by reducing the need for synthetic additives and promoting soil health [12]. In addition, Algs form ionotropic cross-linked beads that are easily convenient for practical applications, have good acid stability, have the ability to mimic natural soil moisture dynamics, and have excellent adsorption properties for metal ions, which is justified by their interactions with the carboxyl groups present on the surface of the Alg beads. This makes Algs a desirable component of polymer nanocomposites for agricultural practises [13]. Furthermore, they can be engineered to have tunable mechanical properties, making them more adaptable to different environmental conditions than traditional synthetic polymer hydrogels. One of their key roles is enhancing the water-holding capacity of soil, which is crucial in the regions prone to drought or where water conservation is critical [4,14]. Hydrogels swell upon exposure to water and slowly release moisture, maintaining a consistent hydration level in the soil, which can prevent plant stress during dry periods. This function is essential in arid and semi-arid regions, where water scarcity is a major challenge. Alg beads can provide sustained nutrient availability by encapsulating nutrients within the hydrogel network, reducing the need for frequent fertilization and promoting more efficient nutrient uptake by plants [15,16]. This slow-release system helps to reduce nutrient leaching into the groundwater and minimizes environmental pollution. When applied to soils, Alg-based hydrogels can help to retain moisture and prolong the release of nutrients, thus enhancing plant growth and reducing water usage. In addition, the adjustable swelling properties of hydrogels [17] can contribute to the prolonged release of nutrients into the soil for plant nutrition.

Clay minerals can be used as functional fillers in hydrogels to modify their mechanical properties, swelling degree, and sorption capacity. They are promising natural sorbents for heavy metal removal due to their large surface area and strong ionic interactions [13,17,18]. Non-toxic, inexpensive, and widely available minerals like sepiolite, bentonite, and zeolite are effective at adsorbing pollutants, particularly heavy metals and dyes, making them valuable in water and soil treatment [19]. Owing to the good compatibility of clays and

Algs, they are also used in water and soil purification, as part of hydrogel nanocomposites. It should be noted that polymeric nanocomposites are used in various fields, such as mechanical engineering, agriculture, ceramic and surface coatings, catalysis, etc. The most promising combinations are polysaccharides (primarily Algs) and clay minerals (natural or synthetic), which can form biocompatible and biodegradable systems and are also effective for the production of adsorption-focused systems, particularly for the encapsulation and controlled release of active ingredients such as drugs and fertilizers [20]. These hybrid hydrogels demonstrate enhanced mechanical properties, increased water retention, and improved pollutant sorption, making them ideal for applications in sustainable agriculture and soil remediation.

Furthermore, the features of the structure of hydrogels and/or incorporated inorganic fillers can enhance their sorption properties in relation to some environmental pollutants, such as heavy metal ions. For example, carboxyl and hydroxyl groups present in Alg and other natural polymers can form complexes with metal ions, allowing for the removal of heavy metals like lead (Pb^{2+}), cadmium (Cd^{2+}), mercury (Hg^{2+}), and strontium (Sr^{2+}) [11,21] from contaminated soils. On the other hand, the large surface area and charge distribution of fillers like clays can enhance hydrogel's ability to bind and immobilize pollutants, preventing them from entering the food chain or water systems.

The use of hydrogel nanocomposites based on synthetic (instead of natural) clay minerals for the sorption of heavy metals from water and agricultural soils can be seen as promising. They are characterized by their high homogeneity, and the products made from them are characterized by improved reproducibility. For instance, LaponiteRD (Lap) is a white synthetic smectite clay, a layered hydrous magnesium silicate that forms transparent colloidal dispersions in water [22]. Lap nanoparticles are discs with a diameter of about 25–30 nm and a thickness of about 1 nm [23], with a structure similar to that of natural hectorite and with the empirical ratio $\text{Na}_{0.7}(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4$. They are composed of silicic acid salts with a very heterogeneous charge distribution and volatile interactions between platelets [24]. The complex action of hybrid composites based on calcium Alg and Lap can be expected to have a synergistic effect in the remediation of contaminated fields.

Thus, the purpose of this study was the development of Alg-Lap hydride hydrogels, the determination of the features of structure formation during ionotropic cross-linking and its effect on the main properties of the hydrogels, namely their swelling and sorption features in relation to heavy metal ions, with the further prospect of their use as soil conditioners.

2. Materials and Methods

2.1. Materials

Alginic acid sodium salt (Na-Alg, viscosity 450–550 cP (1% in H_2O), Glentham Life Science, Corsham, UK), LAPONITE^{®RD} (Lap, Rockwood Additives Ltd., Widnes, UK), and calcium chloride (CaCl_2 , 97%, Sigma-Aldrich, St. Louis, MI, USA), were used as obtained without further purification. Distilled water was used as a solvent in all experiments.

2.2. Synthesis of Ca-Alg–Lap Hydrogels

Calcium-alginate (Ca-Alg) gels, particularly those filled with nanoclays, were synthesized using two different methods. The first one involved the extrusion of sodium alginate (Na-Alg) by continuous flow into a solution of the crosslinking agent— CaCl_2 . The gels were synthesized in the form of fibres and then subjected to repeated mechanical grinding and sieving to form a powder with a particle size of about 1 mm. An alternative method involved extruding Na-Alg into the crosslinking agent solution in a dropwise manner, using a pipette, a syringe, or a peristaltic pump. The size of the resulting beads could be controlled by varying the diameter of the nozzle.

Firstly, a solution of Na-Alg ($C = 2$ wt%) in distilled water was mixed using periodic heating and stirring until a homogeneous mixture was obtained (≈ 3 h). Subsequently, clay was added to the gel ($C = 0.5$ – 5 wt%), and the mixture was stirred in the same manner until homogeneity was achieved (approximately 2 h). Next, the gel was injected into a CaCl_2 solution ($C = 0.25$ – 2 wt%) using the two methods described above and left to crosslink for 15 min with stirring, followed by an additional 45 min without stirring. Afterward, the gel was washed twice for 15 min with ample water and then dried in a thermostat at 40°C for one day. The synthesis was carried out at a temperature of $20 \pm 2^\circ\text{C}$. In the dried xerogels, the concentrations of the components were as follows: 100 wt% of Alg; 80 wt% of Alg and 20% of Lap; 66.7 wt% of Alg and 33.3% of Lap; and 50 wt% of Alg and 50 wt% of Lap.

2.3. Methods

2.3.1. Infrared (IR)

Analysis was conducted using a Fourier-transform infrared spectrometer (Shimadzu IRAffinity-1S, Shimadzu, Kyoto, Japan) with an attenuated total reflection detector (Specac Quest ATR, Shimadzu, Kyoto, Japan) in the range of 4000 cm^{-1} to 400 cm^{-1} , with an accumulation of 25–40 scans and a resolution of 4 cm^{-1} . The data were processed using the LabSolutions IR Ver. 2.26 data processing software.

2.3.2. Scanning Electron Microscopy (SEM)

Information about the morphology and pore structure of the samples was obtained from the microphotographs taken using the scanning electron microscope (Tescan Mira LMU, Tescan, Brno, Czech Republic) equipped with an energy-dispersive spectrometer (Oxford X-Max 80) and a sample preparation system (PECS Gatan 682, Gatan, Inc. Corporate Headquarters, Pleasanton, CA, USA). The microstructures of the samples were investigated after the lyophilization of swollen samples to an equilibrium water content. The samples were contrasted by sputtering with AuPd. Fragments of the samples were mounted on an adhesive conductive substrate (carbon tape [05081-AB, SPI Supplies] on aluminum pin-type SEM mounts [01506-MB, SPI Supplies]). The mounted samples were coated with a thin (30 nm thick) layer of conductive material (Au/Pd mixture) using the PECS Gatan 682 to avoid local charge accumulation during scanning electron microscopy examination.

2.3.3. X-Ray Powder Diffraction (XRD)

X-ray powder diffractograms (XRDs) of Lap and Alg–Lap nanocomposites were obtained on a universal Empyrean diffractometer (Malvern Panalytical Empyrean, UK) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154\text{ nm}$) over the 2θ range of 10 – 90° .

2.3.4. Swelling Study

The equilibrium swelling degree of hydrogels, Q , was calculated using the following formula:

$$Q = \frac{m_s - m_d}{m_d} \quad (1)$$

where m_s is the mass of the swollen hydrogel in the equilibrium state after 24 h of swelling and m_d is the mass of the dried gel (xerogel).

Hydrogel samples were incubated in a thermostat (TC-1/80 SPN, MICROmed, Shanghai Sanshen Medical Instrument Co., Shanghai, China) and weighed with an accuracy of 10^{-4} g on an analytical scale (AXIS). The data are presented as the mean value $\pm$ standard deviation of three to five independent experiments. ANOVA was used for the statistical data analysis, with $p < 0.05$ considered statistically significant.

2.3.5. Fe(II) Sorption

To evaluate the sorption properties of the synthesized hybrid hydrogels, Fe(II) ions were selected as a model of doubly charged cations. While Fe(II) ions themselves can not be considered highly toxic, their presence in water and soil environments where the hydrogels are intended to be applied is relevant. Additionally, studying Fe(II) ions helps to determine baseline sorption characteristics that can model future research of various divalent cations, including toxic Cd(II) and Pb(II), which pose great environmental risks.

The adsorption of Fe(II) ions was studied based on the difference in their concentration in the examined solution before and after the adsorption process. The concentration of iron in the solution was determined using the spectrophotometric method. A method using 1,10-phenanthroline was employed for the Fe(II) spectrophotometric determination. This method is based on the property of iron(II) ions to form an orange-red-coloured complex with 1,10-phenanthroline in water. The colour intensity of the solution is directly proportional to the iron concentration and does not depend on the pH values of the solutions in the range of 2–5. The preparation of ferric chloride solution in water and the construction of a calibration line were carried out as follows: 1 mL of a standard iron solution with a concentration from 0.0005 M to 0.005 M was added to 25 mL volumetric flasks, then 1 mL of a 10% solution of hydroxylamine hydrochloride was added to each flask. A total of 2.5 mL of a 10% solution of sodium citrate and 2.5 mL of a 0.25% solution of 1,10-phenanthroline in 0.1 M HCL were added and the volumes were brought up to 25 mL. After 10 min, the optical density of the obtained solutions was measured at a wavelength of 511 nm (reference solution—water) on a Specord M-40 spectrometer (Carl Zeiss, Jena, Germany). According to the obtained results, a calibration direct dependence of the concentration of iron C_0 on the optical density of the solutions was constructed. A separate calibration graph was made for each series of solutions. Later, these straight lines were used to calculate the concentration of iron in the studied solutions after adsorption.

The Langmuir (2) [25] and Freundlich (3) [26] models were used to process experimental data through the appropriate linearization procedures.

$$\frac{C}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C \quad (2)$$

$$\lg q_e = \lg K_F + \frac{1}{n} \lg C \quad (3)$$

where q_e is the equilibrium adsorption value ($\mu\text{mol/g}$); C is the equilibrium concentration (mol/L); K_L is the constant of the Langmuir equation; and K_F and $1/n$ are the constants of the Freundlich equation.

3. Results

3.1. Characterization of the Structure of Hybrid Hydrogels Using the FTIR and XRD

Figure 1 shows the FTIR spectra of Lap, Na-Alg, Ca-Alg, and hybrid gels, based on Ca-Alg with incorporated Lap. The FTIR spectrum of the nanocomposites based on Ca-Alg and Lap shows a combination of absorption bands characteristic of these individual components.

For the initial Lap, the broad band $950\text{--}1010\text{ cm}^{-1}$, with the maximum at $\approx 970\text{ cm}^{-1}$, corresponds to the asymmetric stretching vibrations of the Si-OH bond in different environments in layered silicates [27]. The absorption bands around 470 cm^{-1} are caused by in-plane and out-of-plane vibrations of the -Si-O-Si- and -Si-O- bonds of the crystal lattice of the mineral nanodisks, and the peak at 650 cm^{-1} corresponds to the bending vibrations of the Si-O-M bonds (where $M = \text{Mg}$ or Li) [28]. The slight shift in the band at 970 cm^{-1} to lower wavenumbers in the FTIR spectrum of Lap, when incorporated into the Alg-Lap composites, indicates changes in the local environment of the Si-OH groups in the Lap structure. Specifically, the formation of hydrogen bonds or ionic interactions between the hydroxyl groups of Lap and the carboxyl groups of Alg can alter slightly the vibrational

energy of the Si-OH bonds, leading to the observed shift. The shift to lower wavenumbers typically indicates a weakening of bond strength due to the interaction between the Lap and Alg in the composite, which is consistent with the idea that the Alg is intercalating between the Lap layers or interacting with its surface groups. This phenomenon often suggests the enhanced dispersion of Lap within the Alg matrix, improving the composite's overall structure and properties.

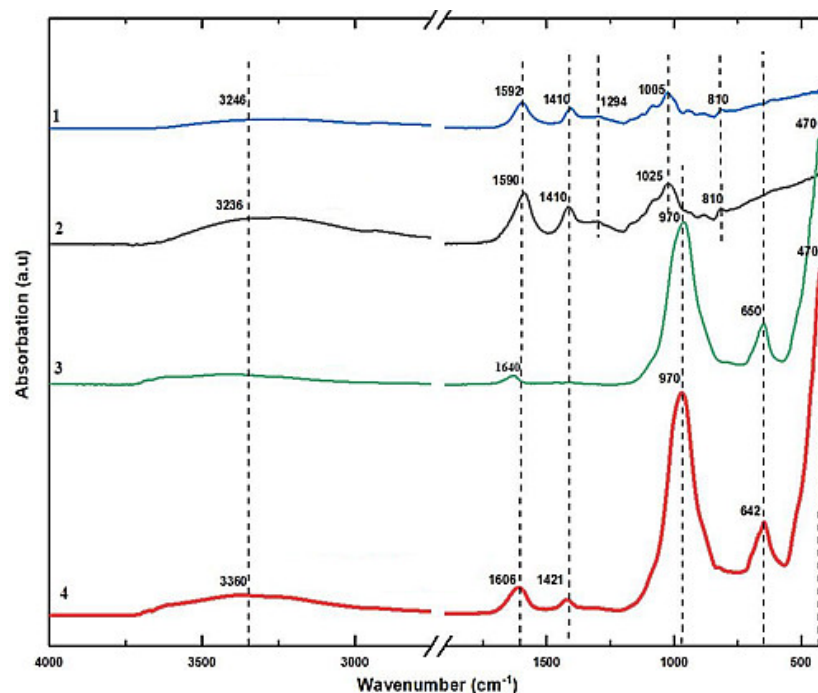


Figure 1. FTIR spectra of Na- (curve 1) and Ca-Alg (curve 2), Lap (curve 3), and Alg-Lap composite based on them (curve 4).

The FTIR spectra of Na-Alg and ionically cross-linked Ca-Alg are characterized by symmetric stretching vibrations of -C-O- bonds in the rings of guluronic and mannuronic acids, which are overlapped with the 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} , corresponding to the carboxyl group, is crucial for understanding the ionic interactions between Ca^{2+} ions and Alg during the formation of the Ca-Alg gel. For Na-Alg, this band reflects the symmetric stretching of the carboxylate groups, which are not fully involved in ionic bonding with the metal ions. In contrast, for Ca-Alg, the same band typically shows a shift due to the ionic cross-linking between the carboxylate groups of Alg and Ca^{2+} ions. This shift, although often slight (from 1590 cm^{-1} to a slightly lower wavenumber, for example, ~1580–1590 cm^{-1}), indicates stronger bonding and the formation of a denser gel structure. Therefore, a slight shift in the band at 1590 cm^{-1} can be observed between Na-Alg and Ca-Alg in the FTIR spectra, reflecting the structural changes due to the ionic cross-linking.

The bending vibrations of the C-H bonds of the carbon skeleton of Alg cause absorption at 1410 cm^{-1} , and wagging vibrations of these bonds appear at 1294 cm^{-1} . The absorption bands associated with the hydroxyl group of Na-Alg appear at 3246 cm^{-1} and 810 cm^{-1} , which correspond to the valence and strain vibrations of O-H bonds. The ionic crosslinking of Na-Alg by Ca^{2+} enhances the intensity of the vibrations of its functional groups, probably due to an increase in the dipole moment of the hydrogel macromolecule [29].

Therefore, the FTIR spectra analysis confirms the successful incorporation of Lap into the Ca-Alg matrix, evidenced by characteristic shifts in the absorption bands associated with Si-OH and carboxylate groups, indicating interactions between the components, the improved dispersion of Lap, and enhanced ionic cross-linking, leading to a denser, more structured composite gel.

The XRD patterns of Lap and Alg-Lap hybrid hydrogels are presented in Figure 2.

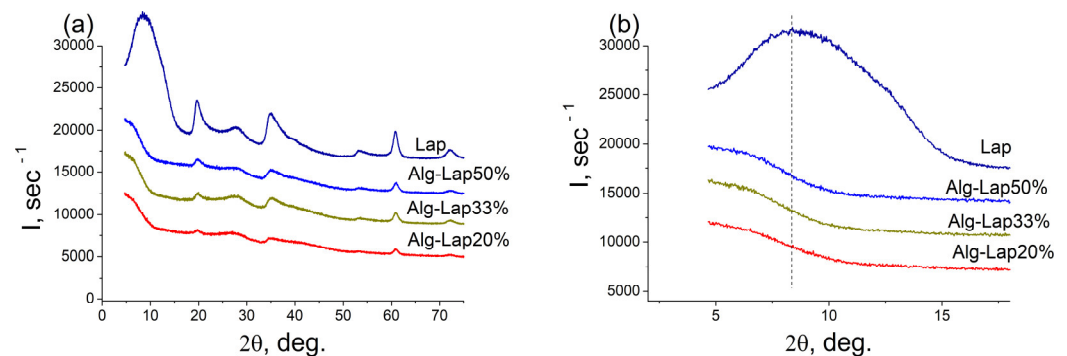


Figure 2. XRD patterns for the LaponiteRD and the Alg-Lap composite hydrogels with different component ratios: (a) full $2\theta^\circ$ range and (b) the first peak from 5 to 20 of $2\theta^\circ$.

On the diffractogram of the initial Lap, the reflections are observed at the following diffraction angles $2\theta^\circ$: 8.52, 19.76, 27.89, 35.05, 53.16, and 60.78. The corresponding inter-plane distances have values of 10.25, 4.50, 3.19, 2.56, 1.72, 1.52, and 1.31, respectively, which were determined using the following Wolff–Bragg diffraction equation:

$$2 \cdot d \cdot \sin \theta = \lambda \quad (4)$$

where d is the lattice interplanar spacing, θ is the X-ray incidence angle (Bragg angle), and λ is the wavelength for the characteristic X-rays (for Cu $K\alpha$ radiation, it is 1.5418 Å).

The type of diffraction pattern and the positions of the reflections (or interplane distances) are typical for layered silicates from the smectic group. The observed reflexes can be distinguished with the help of Miller indices (hkl), characterizing the reflecting planes in the Lap structure, such as (001), (110), and (020), (004), (130), and (220), (150) and (240) and (310), (060), and (330), respectively, according to [30,31].

The most prominent reflection often occurs around 6.5–7 Å of the first basal reflex (001) with an interplane distance $d(001)$, which corresponds to the period of the layered structure in the direction of the c axis of the elementary cell of Lap [32,33].

For Lap in the hydrated state, depending on the degree of hydration, the basal reflex (001) occurs typically at around $2\theta^\circ = 6.6$ –7, indicating that the interplane distance $d(001)$ is 12–13.5 Å; under dry conditions, the d -spacing can reduce to around 9.6–10 Å, due to the collapse of the interlayer spacing.

For the initial Lap, a strong reflection corresponding to the (001) basal plane at $2\theta \approx 8.4^\circ$ (Figure 2b) is observed. This corresponds to the d -spacing of approximately 10.5 Å, which is close to the thickness of a single silicate layer, namely 9.6 Å. The diffractograms of the composites show the reflections characteristic of the initial Lap. Their intensity changes symbiotically with changes in the Lap content. For the Alg-Lap composite dried gels, the reflection corresponding to the (001) basal plane shifts to $2\theta \approx 5^\circ$, which confirms a d -spacing of around 17.7 Å. Taking into account the thickness of a single silicate layer, the space between the silicate layers increases to ~8 Å. This increase in the interlayer spacing indicates that the Alg macromolecules are intercalated between the Lap layers, expanding the basal spacing due to the interactions between the Alg and silicate layers of Lap [34].

The diffraction patterns of the Alg-Lap composites contain the reflections corresponding to the initial Lap. Their intensity changes symbiotically with the change in the Lap content. The analysis of the reflected Lap in the composition of the Alg-Lap composites revealed differences in the position, intensity, and width of the peaks at $2\theta \approx 8.4^\circ$ and $2\theta \approx 53.2^\circ$. For the Alg-Lap composite dried gels, the reflection corresponding to the (001) basal plane shifts to $2\theta \approx 5^\circ$, which confirms a d -spacing of around 17.7 Å. This increase in the interlayer spacing suggests that the Alg macromolecules are intercalated between the Lap layers, expanding the basal spacing due to the interactions between the Alg and Lap silicate layers [34–36]. It is known that the peak at $2\theta \approx 53.2$ in the initial Lap corresponds to the in-plane reflections such as the (060) or (061) planes, which can be reduced or disappear in the composite due to structural disruption caused by Alg intercalation. Alg, as a biopolymer, can intercalate between the layers of Lap, altering the arrangement of ions (such as Mg^{2+} and Li^+) within the octahedral sheet.

The XRD analysis shows that incorporating Lap into the Alg matrix leads to structural changes, such as increased interlayer spacing. These changes suggest that Lap is well-dispersed and intercalated within the Alg matrix, and the structural modifications observed in the XRD data provide a solid basis for understanding how Lap incorporation can improve the functional properties of such hydrogels.

The combined FTIR and XRD analyses confirm the successful incorporation of Lap into the Ca-Alg matrix, demonstrating significant structural interactions between the components. The FTIR data reveal shifts in characteristic absorption bands, indicating hydrogen bonding and ionic interactions between the Alg and Lap. The XRD results show an increased interlayer spacing in the composite, confirming the intercalation of Alg molecules between Lap layers. Thus, these findings indicate that the formation of hybrid hydrogels leads to the enhanced dispersion of Lap and structural modifications that improve the overall properties of the composite.

3.2. Morphology of Hybrid Hydrogels (SEM)

The microstructure of Ca-Alg granules and nanocomposites based on them, in particular the pore size and interconnection between them, are of great importance for medical and agricultural applications, determining their diffusion properties concerning pharmaceuticals and plant protection products [33,34]. Electron microscopy allows us to evaluate surface topography and pore morphologies. We analyzed the surface morphology and the internal structure of Alg beads, as well as those of Alg-Lap composite hydrogel ($C_{\text{Alg}} = 2 \text{ wt\%}$, $C_{\text{Lap}} = 1.25 \text{ wt\%}$, $C_{\text{CaCl}_2} = 0.5 \text{ wt\%}$ in reaction solution). Before the SEM examination, the samples were dried by freeze-drying. The freeze-drying of wetted materials conserves their three-dimensional structure using rapidly freezing water and the sublimation of formed ice under vacuum, which avoids substantial deformation caused by water evaporation.

Figure 3 shows the surface morphology of freeze-dried beads of Alg gel and the Alg-Lap composite. It should be noted that the sizes of the granules are approximately the same (about 4 mm in diameter), and they share the rough, wrinkled surface inherent to them. Native Alg possesses greater sphericity than the Alg-Lap composite. The loss of sphericity in the composite is probably due to the increase in the viscosity of the Alg solution when Lap is added, which leads to the deformation of the droplets when they are embedded in the cross-linker solution during the ionotropic crosslinking process. The surfaces of the beads of alginate and Alg-Lap composite show some wrinkles. This effect is due to the low density of cross-linked polymer links in the 2 wt% gel. After drying, the beads shrink, essentially, causing the polymer matrices at the surface to fold and stack.

Figure 4 illustrates the inner structure of Alg-Lap composite beads, which looks like a sponge with a cellular organization of numerous quite homogeneous pores (dark areas) between the Ca-Alg matrices. The pores are formed as a consequence of the removal of water between the cross-linked polymer matrices during the freeze-drying procedure.

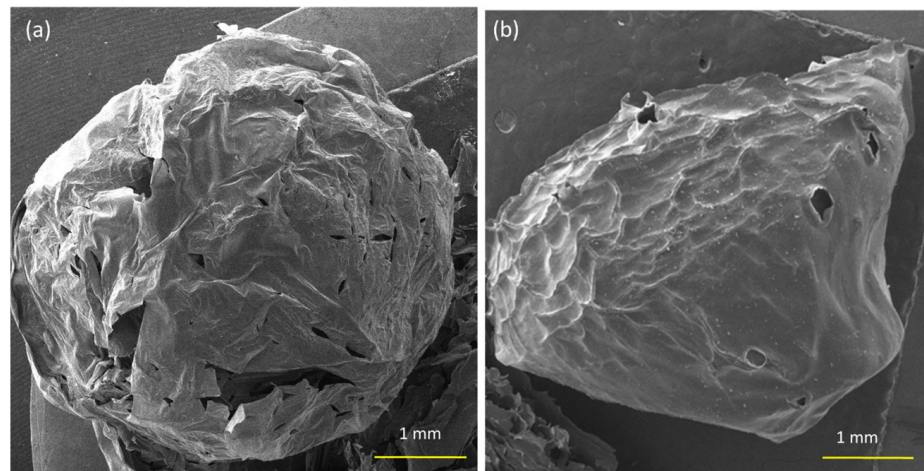


Figure 3. SEM micrographs of alginate gel ($C_{\text{Alg}} = 2 \text{ wt\%}$ in reaction solution) (a) and Alg-Lap composite hydrogel (b) ($C_{\text{Alg}} = 2 \text{ wt\%}$, $C_{\text{Lap}} = 1.25 \text{ wt\%}$, $C_{\text{CaCl}_2} = 0.5 \text{ wt\%}$ in reaction solution) (zoom $37\times$ (a) and $39\times$ (b)).

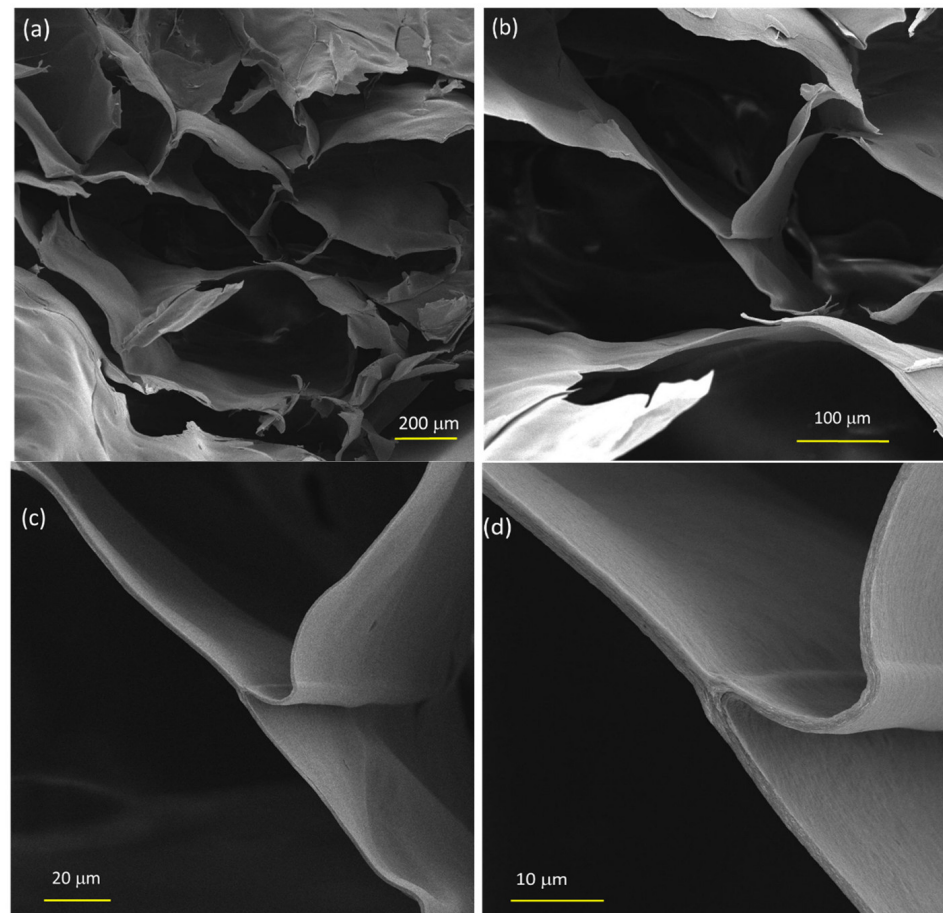


Figure 4. Cross-section of Alg-Lap ($C_{\text{Alg}} = 2 \text{ wt\%}$, $C_{\text{Lap}} = 1.25 \text{ wt\%}$, $C_{\text{CaCl}_2} = 0.5 \text{ wt\%}$ in reaction solution) composite (zoom $126\times$ (a), $379\times$ (b), $1260\times$ (c), and $12,600\times$ (d)).

The pore size is approximately $150\text{--}300 \mu\text{m}$ (Figure 4a,b). The thickness of the walls forming the pores is about $1\text{--}2 \mu\text{m}$ (Figure 4c,d). With great magnification, it can be seen that the surface of the pore walls of the composite has a fluffy structure, which is absent in the Alg gel without a filler (Figure 4d). The Alg gel surface is also much smoother than that of the composite gel, with a much flatter surface in between the folds and flatter topography

with very few distinguishable features compared to the composite (Figure 5). The looser spongy structure of the composite in comparison with the original Alg gel is illustrated in Figure 6.

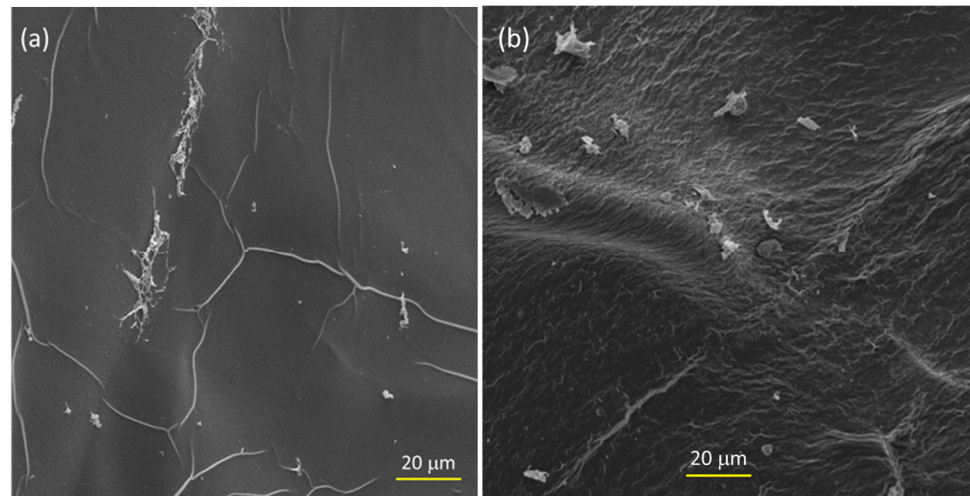


Figure 5. Surface of alginate gel (a) and Alg-Lap ($C_{\text{Alg}} = 2 \text{ wt\%}$, $C_{\text{Lap}} = 1.25 \text{ wt\%}$, $C_{\text{CaCl}_2} = 0.5 \text{ wt\%}$ in reaction solution) composite (b). Zoom 1260 $\times$.

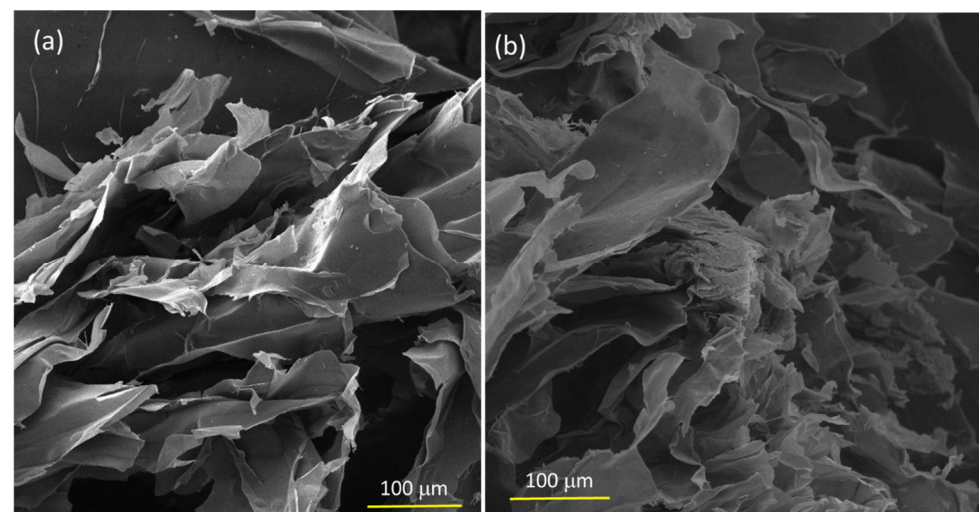


Figure 6. Comparison of cross-section of alginate gel (a) and Alg-Lap ($C_{\text{Alg}} = 2 \text{ wt\%}$, $C_{\text{Lap}} = 1.25 \text{ wt\%}$, $C_{\text{CaCl}_2} = 0.5 \text{ wt\%}$ in reaction solution) composite (b). Zoom 379 $\times$.

According to the results of EDX analysis (Figure 7a), the Lap nanoparticles are quite homogeneously distributed throughout the composite. They are presented in the form of aggregates with a size of about 50–100 μm, the appearance of which is caused by the formation of a dense house-of-cards structure inherent in Lap [37].

The comparative elemental analysis of the samples of Ca-Alg gel and Alg-Lap composite revealed that the carbon content in the composites decreased from an average of 50 to 36%, and the oxygen content increased from an average of 38 to 46%, while Si, Mg, and Na appeared in significant amounts (Figure 7c,d). The above confirms the successful incorporation of Lap into the Alg matrix.

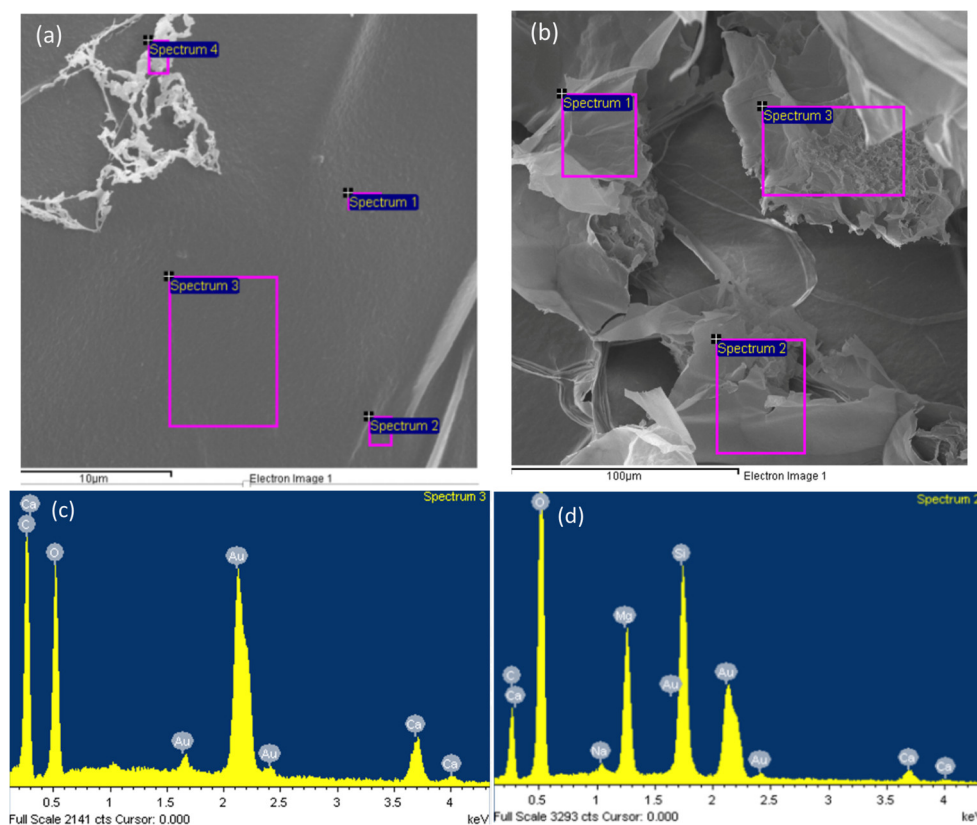


Figure 7. Area of Ca-Alg (a) and Alg-Lap composite (b) selected for EDX analysis and comparison of EDX-spectra of Ca-Alg (c) and Alg-Lap composite (d).

3.3. Swelling Behaviour of Alg-Lap Hydrogels

This experimental study of the swelling properties of hybrid hydrogels is crucial for understanding their potential applications in various fields, including biotechnology and environmental remediation. Swelling behaviour reflects the ability of hydrogels to absorb water and expand, which is influenced by the cross-linking density, polymer composition, and interactions between the components of the composite.

The swelling of Alg gels has been described in detail in numerous papers, e.g., in [38,39]. The influence on the equilibrium degree of swelling of such diverse factors as pH, ionic strength, temperature, type and concentration of crosslinker, etc., has been analyzed [40].

At the same time, less research has been devoted to the swelling of hydrogel nanocomposites, which concerned mainly synthetic hydrogels [41] as well as composites based on Lap and chitosan [22]. The very few studies on Alg-Lap nanocomposites are mainly devoted to the description of synthesis and drug release studies [42] with a very brief description of swelling during the first 2–3 h [43]. This directed our detailed study of swelling and its kinetics in relation to Ca-Alg-Lap hydrogels, analyzing the effects of different cross-linker and clay concentrations as well as their inherent diffusion mechanism and water uptake capacity.

The swelling of the Ca-Alg-Lap nanocomposites is described by standard saturation curves, with the maximum equilibrium swelling degree achieved in about 24 h (Figure 8). The swelling degree of nanocomposites based on Alg gels and clay nanoparticles depends largely on the crosslinking density of gel networks, which is determined by the concentration of CaCl_2 . At Na-Alg concentrations lower than 0.5 wt% in the reaction solution, even if a gel is formed, it is very heterogeneous and possesses poor mechanical properties, which is probably due to the insufficient G-blocks content. At low CaCl_2 concentrations, the hydrogels exhibit initially rapid swelling, followed by a plateau, indicating equilibrium (Figure 8). The growth of the crosslinking agent concentration resulted in the predictable

transition of the hydrogel to a denser conformation. Moreover, the swelling is more restricted (Figure 8), probably due to stronger ionic cross-linking between Alg and Ca^{2+} ions, which limits the water uptake.

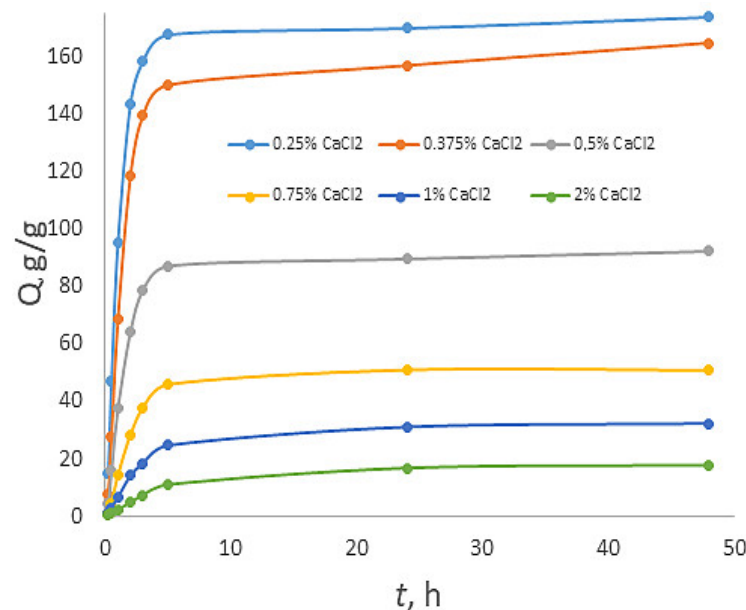


Figure 8. Swelling kinetics of nanocomposites based on Ca-Alg and Lap at low and high CaCl_2 concentrations ($C_{\text{Alg}} = 2 \text{ wt\%}$; $C_{\text{Lap}} = 1 \text{ wt\%}$ in reaction solution).

The appearance of Alg-Lap composite granules at different stages of synthesis and visualization of their initial swelling stage are shown in Figures 9 and 10. Figure 9 highlights the changes in the size of hydrogel beads during processing. The beads expand significantly after swelling and shrink back after drying, demonstrating their capacity for reversible size changes. This indicates the potential of hydrogels for applications where repeated swelling and drying cycles are needed.

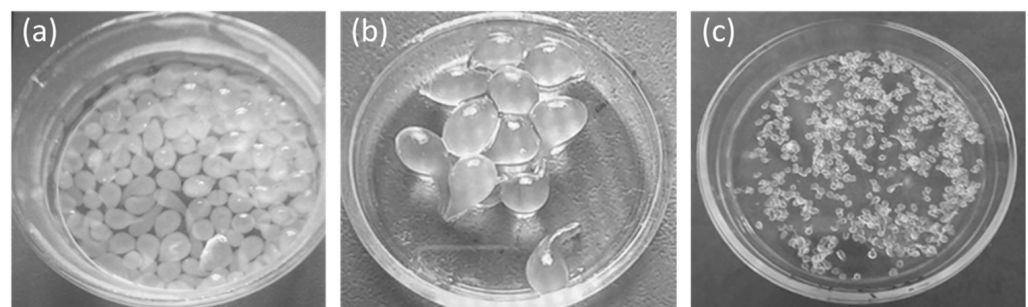


Figure 9. Changes in the size of hydrogel beads based on Ca-Alg and Lap ($C_{\text{Alg}} = 2 \text{ wt\%}$, $C_{\text{Lap}} = 0.5 \text{ wt\%}$, $C_{\text{CaCl}_2} = 0.5 \text{ wt\%}$ in the reaction solution) during processing: (a) after synthesis; (b) after swelling; (c) after drying.

Figure 10 visualizes the swelling of dry Alg-Lap beads during the first three hours. The rapid initial swelling reflects the ability of the hydrogels to absorb large amounts of water within a short period, which could be advantageous for applications in drug delivery or water absorption.

When a glassy dry gel 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. The swelling of a hydrogel involves more extensive segmental movements, which ultimately leads to an increase in the distance between the hydrogel chains [44]. The main regularities of the kinetics of this

process were described by Peppas and Ritger [45] and they introduced a simple exponential. Equation (5) represents the diffusion mechanism of the polymeric system [45], as follows:

$$\frac{M_t}{M_\infty} = kt^n \quad (5)$$

where M_t and M_∞ denote the amount of solvent diffused into the gel at time t and infinity (at equilibrium), respectively; k is the constant related to the structure of the network; and the exponent n is the number used to determine the type of diffusion [46].

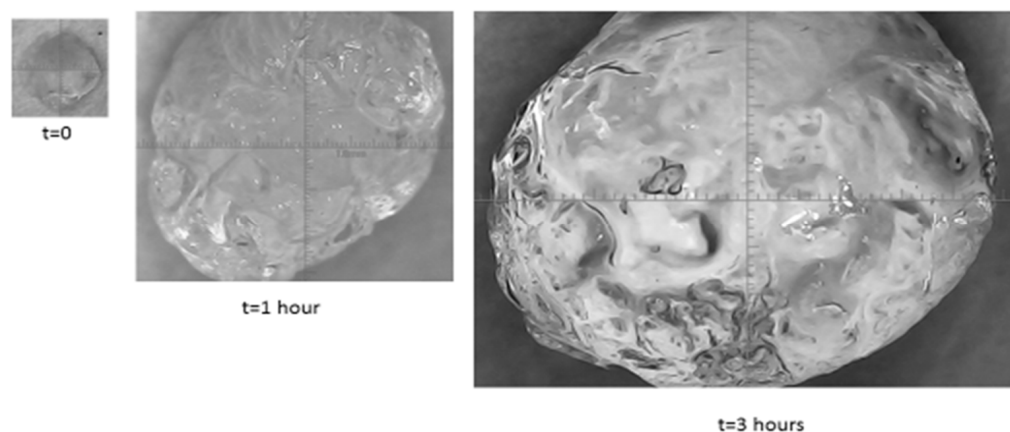


Figure 10. Visualization of dry Alg-Lap bead ($C_{\text{Lap}} = 1$ wt%; $C_{\text{Alg}} = 2$ wt%; $C_{\text{CaCl}_2} = 0.25$ wt% in the reaction solution) swelling during the first three hours.

The 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 swelling has not reached the equilibrium, but where only 60% of the water mass has entered the structure of gels and where F is the fraction of the solvent absorbed by the gel or polymer matrix over time. The 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 the Fickian diffusion, whereas $0.50 < n < 1.0$ indicates that diffusion is non-Fickian (DNF) [47]. 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 one [45]. The values of n greater than one reflect the so-called Super Case II transport [37], whereas the case with n in the range from 0 to 0.45 corresponds to the so-called hindered Fickian diffusion [48]. Some of the kinetic curves of swelling of the synthesized nanocomposites after logarithmization are shown in Figure 11.

Based on the slopes and intercepts of straight lines obtained after the logarithmization of the swelling kinetic curves (M_t versus t), it becomes possible to establish the diffusional exponent n and the coefficient k , as well as the statistical indicator R^2 (Tables 1 and 2). The diffusion exponent (n) values decrease with increasing Lap concentration, indicating a transition from the Fickian diffusion ($n \approx 0.5$) to the non-Fickian diffusion ($n < 0.5$) as more Lap is incorporated. This suggests that a higher Lap content hinders the diffusion of water, probably due to the increased structural rigidity of the hydrogel network. And so, it can be concluded that, when the Lap content in the composite increases, the value of the coefficient n tends to decrease with the transition from the anomalous non-Fickian diffusion to the true-Fickian and pseudo-Fickian diffusion (Table 1).

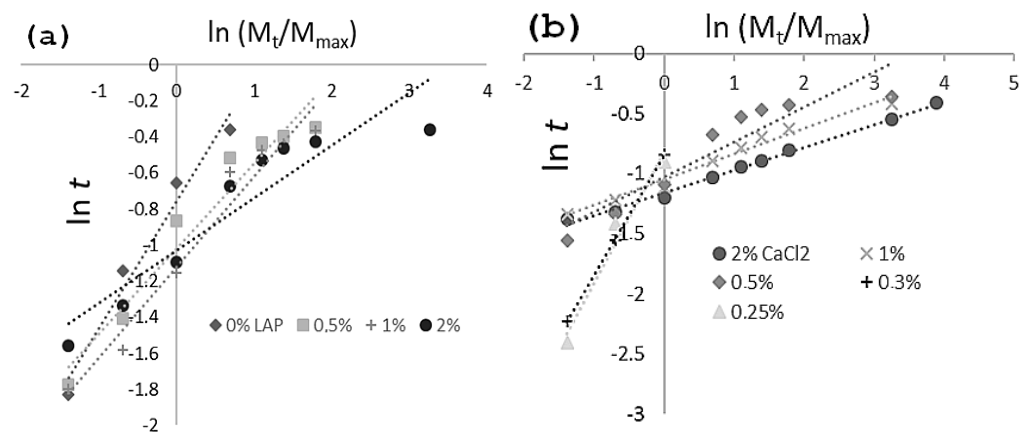


Figure 11. Dependencies according to the Peppas and Ritger equation for determining the type of diffusion in the Alg gel and the Alg-Lap composites: (a) $C_{\text{Alg}} = 2 \text{ wt\%}$, $C_{\text{CaCl}_2} = 0.5 \text{ wt\%}$; (b) $C_{\text{Alg}} = 2 \text{ wt\%}$, $C_{\text{Lap}} = 2 \text{ wt\%}$, in reaction solution.

Table 1. Effect of LaponiteRD concentration on the diffusion parameters.

C_{Lap} , %	n	k	R^2
0	0.7063	−0.7539	0.9694
0.5	0.4731	−1.0166	0.9451
1	0.5032	−1.1236	0.9638
2	0.291	−1.0295	0.8656

Table 2. Effect of CaCl_2 concentration on the diffusion parameters.

C_{CaCl_2} , %	n	k	R^2
0.3	0.9958	−0.853	0.999
0.5	0.291	−1.030	0.866
1	0.2118	−1.049	0.979
2	0.1897	−1.158	0.994

At the same time, when the cross-linking agent (CaCl_2) concentration increases, the transition from Super Case II transport to zero-order diffusion and, subsequently, to pseudo-Fickian diffusion is observed (Table 2). The above transition is explained by the fact that, in the case of highly cross-linked hydrogel, the rate of water penetration is much smaller than the relaxation rate of the polymer chain [49]. Larger CaCl_2 concentrations lead to lower diffusion exponent values, suggesting a tighter, more cross-linked network that restricts water movement. At lower CaCl_2 concentrations, the gels are less cross-linked, resulting in greater swelling due to easier water penetration.

Thus, the swelling behaviour of the Alg-Lap hybrid hydrogels is largely dependent on the concentrations of both Lap and CaCl_2 . The larger Lap content and the increased CaCl_2 concentration lead to more rigid and less swellable structures, due to enhanced cross-linking. This tunable swelling property makes these hybrid hydrogels suitable for controlled release applications, where the balance between swelling and structural integrity is crucial.

3.4. Sorption Properties of the Synthesized Hydrogels in Relation to Fe(II)

The sorption isotherms of Fe(II) ions on the initial Lap and Alg hydrogels without a filler and on those filled with Lap are shown in Figure 12a. From the individual isotherms of Fe(II) adsorption on Lap and Alg hydrogel without a filler and the constants calculated from them, it can be seen (Table 3) that the affinity of Fe(II) ions for Lap is greater than that for Alg.

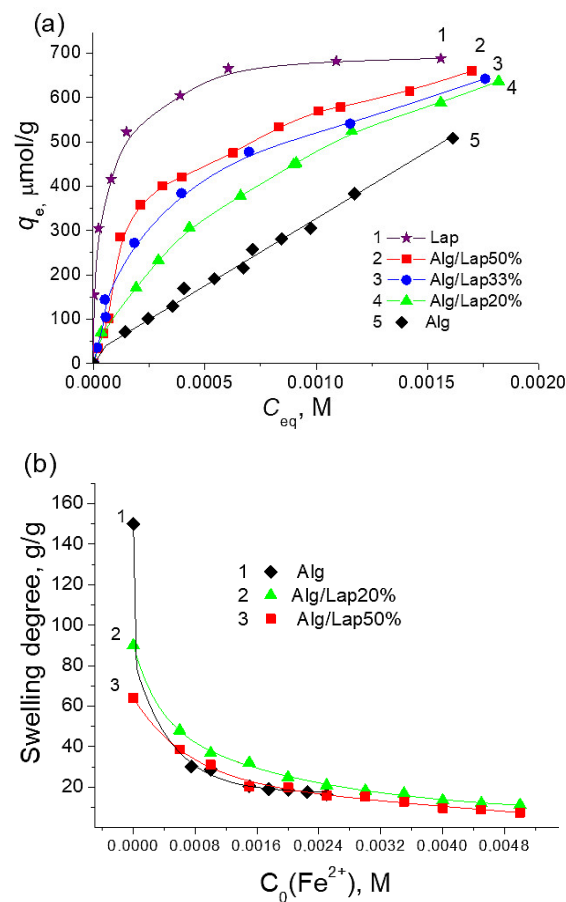


Figure 12. Adsorption isotherms of Fe(II) on the Alg-based composites filled with Lap (a) and the effect of Fe(II) sorption on the degree of swelling (b) of hybrid hydrogels.

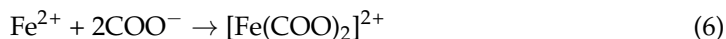
Table 3. Isotherm parameters for the adsorption of Fe(II) ions on the hybrid hydrogel samples (cross-linked with CaCl_2 0.3%wt), calculated using the Langmuir and Freundlich models.

Sorbate	Sorbent Sample	Langmuir			Freundlich		
		q_m , $\mu\text{mol/g}$	K_L , $\text{L}/\mu\text{mol}$	R^2	$1/n$	K_F , $\mu\text{mol/g}$ ($\mu\text{mol/L}$) $^{-1/nF}$	R^2
Isotherm Parameters for Fe(II)	Lap	704	27,313	0.999	0.212	167.41	0.968
	Alg	1394	314	0.644	0.807	1.232	0.989
	Alg50%/Lap50%	719	3926	0.987	0.336	55.512	0.974
	Alg67%/Lap33%	735	3083	0.994	0.589	9.834	0.944
	Alg80%/Lap20%	869	1302	0.956	0.606	7.213	0.993

The analysis of Fe(II) ion sorption behaviour for pure Ca-Alg hydrogel and Alg-Lap composites reveals noticeable differences in their sorption capacities and the mechanisms. Understanding these differences is critical for optimizing their applications in the environmental remediation, particularly in wastewater treatment and soil conditioning.

The sorption mechanisms of unmodified Ca-Alg gel are based on the fact that Alg is a polyanionic biopolymer characterized by a large density of carboxylate ($-\text{COO}^-$) groups, primarily derived from its guluronic acid blocks. These carboxylate groups are primarily responsible for the ion exchange and chelation processes during the metal ions sorption. When cross-linked with Ca^{2+} ions, the Alg matrix forms a network capable of exchanging cations, because, at the applied CaCl_2 concentrations, most of the carboxyl groups in the

structure of the Alg gel are not involved in the interactions with Ca^{2+} ions and that can interact with Fe(II) ions (5), forming chelate structures [50–52], as follows:

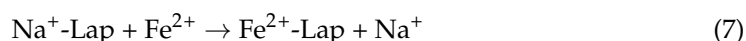


This mechanism contributes to the overall higher sorption capacity at elevated concentrations, due to the abundance of active sites available for ion exchange.

A sharp decrease in the degree of swelling of the Alg hydrogel (Figure 12b) indicates additional cross-linking of the hydrogel structure in the formation of the mentioned above chelate complex.

The ability of pure Alg to reach a large maximum sorption capacity ($\geq 1394 \mu\text{mol/g}$) can be attributed to the extensive distribution of carboxylate groups throughout the polymer matrix, enabling formation of stable complexes with Fe(II) ions. However, the affinity for Fe(II) in pure Alg is relatively small, according to the Langmuir constant $K_L = 314 \text{ L}/\mu\text{mol}$ (Table 3), which indicates a less selective binding process at small ion concentrations.

The sorption mechanism of initial Lap is determined by its structural features: Lap is a synthetic layered silicate clay, which contains negatively charged silicate sheets that are neutralized by the interlayer cations, such as Na^+ ions. The primary sorption mechanisms for Fe(II) ions on Lap include ion exchange and surface adsorption. The presence of negatively charged silicate sheets facilitates ion exchange, where Fe(II) ions replace Na^+ ions in the interlayer spaces (6).



Additionally, surface adsorption occurs through electrostatic interactions with hydroxyl (OH^-) groups located at the edges of the Lap sheets, forming surface complexes [53,54].

The Lap sorption behaviour is shown by its larger affinity for Fe(II) at low concentrations, as indicated by a significant Langmuir constant $K_L = 27,313 \text{ L}/\mu\text{mol}$ (Table 3). This great selectivity results in the efficient binding of Fe(II) ions in dilute solutions. However, its overall sorption capacity ($704 \mu\text{mol/g}$) is smaller than that of pure Alg, reflecting a limitation in the number of accessible active sites. The value of the Freundlich equation parameter $1/n$ for Lap is much smaller (0.212) than that for the Alg gel (0.807), which indicates a more specific and uniform adsorption process on the Lap surface.

Combined sorption characteristics in Alg-Lap composites are manifested in the fact that both materials contribute synergistically to the sorption process. For hybrid hydrogels, the sorption constants depend on the ratio of components. An increased proportion of Lap in the hybrid hydrogels enhances the affinity for Fe(II), as reflected by the growing values of K_L and K_F (Table 3). At small concentrations of Fe(II), the composite benefits from the high selectivity of Lap, leading to efficient ion exchange facilitated due to its layered structure and surface properties. As the Fe(II) concentration increases, the Alg component becomes the dominant contributor to sorption, leveraging its extensive network of carboxylate groups to enhance the overall adsorption capacity. The maximum sorption capacity, calculated from the Langmuir equation for the hybrid hydrogels, aligns with the average between the individual components (Lap and Alg) and increases with the Alg content in the composite.

4. Conclusions

The methods for synthesizing ionotropically cross-linked calcium alginate gels, in the form of granules and fibres, as well as hydrogel composites based on the alginate and synthetic clay mineral LaponiteRD, have been successfully developed. The synthesized materials were characterized using FTIR spectroscopy, XRD, and scanning electron microscopy (SEM) to examine their surface and pore structure. The EDX analysis confirmed the homogeneous distribution of Lap nanoparticles within the composite, typically forming aggregates $50\text{--}100 \mu\text{m}$ in size. These aggregates contribute to a dense “house of cards” structure characteristic of Lap. The FTIR and XRD analyses confirmed strong interactions

between Alg and Lap, with characteristic shifts in the absorption bands indicating hydrogen bonding and ionic interactions. The XRD data also indicated that Alg molecules intercalated between Lap layers, increasing the interlayer spacing and contributing to the overall stability and enhanced properties of the hybrid hydrogels.

The swelling behaviour of the synthesized gels and composites was investigated using the Peppas–Ritter equation. The determining factor in the swelling mechanism of Alg composites with the addition of Lap should take into consideration the concentration of the crosslinking agent CaCl_2 , which ensures the appropriate degree of crosslinking. Thus, at a high concentration of the cross-linking agent (0.5–2 wt%), true-Fickian and pseudo-Fickian diffusion is observed when the diffusion rate is much lower than the relaxation rate. A rare cross-linked gel absorbs water by the mechanism of anomalous non-Fickian diffusion to the transport mechanism of Case II or by the mechanism of the so-called super-diffusion. In these cases, diffusion occurs very quickly compared to the process of polymer relaxation. Thus, as the CaCl_2 concentration increased, the hydrogels shifted towards more restricted diffusion behaviour, reflecting the influence of cross-linking density on the mobility of water molecules within the hydrogel matrix. The incorporation of Lap further reduced the swelling due to the increased structural rigidity and enhanced cross-linking. The analysis of the swelling kinetics using the Peppas and Ritger model indicated a transition from the anomalous non-Fickian diffusion ($n > 0.5$) to the true-Fickian and the pseudo-Fickian diffusion ($n \leq 0.5$), when the Lap concentration in the composite increased. This transition suggests that larger Lap content hinders water diffusion, probably due to the formation of a denser hydrogel network. These results indicate that the swelling properties of Alg-Lap hydrogels can be finely controlled by adjusting the composition, making them adaptable to various practical applications requiring specific hydration levels. The hybrid hydrogels demonstrated a significant sorption capacity for divalent ions such as Fe(II) , with Lap contributing to selective sorption at low ion concentrations through ion exchange mechanisms, and Alg enhancing overall sorption capacity at higher concentrations. The dual mechanisms of the composite—Lap-driven selectivity at low concentrations and Alg-driven capacity at higher concentrations—enable a versatile response to varying metal ion concentrations. Alg-Lap composite material is not only effective at low Fe(II) concentrations due to the great affinity of Lap but also sustains greater sorption at higher concentrations due to the larger number of active binding sites of Alg. The observed peculiarities of the swelling and sorption behaviour of composite hydrogels enable the purposeful regulation of the water retention properties of the developed materials and the prediction of the sorption capacity, not only for iron ions, but also for divalent ions of other metals, depending on the ratio of components and the degree of crosslinking.

Author Contributions: Conceptualization, Y.S. and O.G.; methodology, K.T., Y.S. and O.O.; validation, O.G., K.T. and Y.S.; formal analysis, Y.S., O.G. and O.O.; investigation, K.T., K.S., O.O. and L.G.; resources, K.T. and O.G.; data curation, O.G. and Y.S.; writing—original draft preparation, K.S., Y.S., L.G. and O.O.; writing—review and editing, O.G. and K.T.; visualization, K.S. and Y.S.; supervision, O.G.; project administration, O.G. and Y.S.; funding acquisition, O.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Polish Academy of Sciences and U.S. National Academy of Sciences (Agreement No. PAN.BFB.S.BWZ.331.022.2023 ‘Biocompatible hybrid hydrogels with functional inorganic fillers for strengthening of plant vegetation’).

Institutional Review Board Statement: The study did not require ethical approval.

Informed Consent Statement: Not applicable.

Data Availability Statement: Dataset is available on request from the authors. The raw data supporting the conclusions of this article will be made available by the authors on request.

Conflicts of Interest: The authors declare no conflicts of interest.

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