Comparison of green bio-based cerium/alginate vs. copper/alginate beads: a study of vibrational and thermal properties using experimental and theoretical methods

Mohammed Elhoudi1 · Rachid Oukhrib2 · Christian A. Celaya3 · Daniel G. Araiza3 · Youness Abdellaoui4 · Issam Barra5 · Younes Brahmi6 · Hassan Bourzi2 · Miguel Reina3 · Abdallah Albourine1 · Hicham Abou Oualid7,8,9

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Abstract
Herein, bio-based alginates (Alg) containing metallic beads (Ce and Cu) were synthesized via an alginate cross-linking method, and their properties were studied using experimental techniques combined with theoretical simulations. Materials were characterized through Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and scanning electron microscope (SEM) images, to determine the cross-linking structural features, thermal stability, and surface morphology of alginates. Besides, density functional theory (DFT) methods were employed to calculate global reactivity parameters such as HOMO–LUMO gap energies ($\Delta E_{H-L}$), electronegativity ($\chi$), hardness ($\eta$), and electrophilic and nucleophilic indicators, using both gas and aqueous media for the study of the complexation process. Among other features, characterization of the thermal properties showed that Alg@Ce and Alg@Cu alginate beads behave differently as a function of the temperature. This behavior was also predicted by the conformation energy differences between Alg@Ce and Alg@Cu, which were found out theoretically and explained with the combined study of the vibrational modes between the carboxylate group with either Ce or Cu. Overall, the reactivity of the Alg@Ce alginate bead was higher than that of the Alg@Cu counterpart, results could be used as a cornerstone to employed the materials here studied in a wide range of applications.

Keywords Alginates · Copper · Cerium · Bio-based beads · DFT

Introduction

Alginates (Alg) are a family of unbranched binary co-polymers extracted from marine brown algae, mainly composed of combined residues from mannuronic and guluronic acids which can be inter-connected through the substitution of...
ions coming from consecutive G-unit blocks [57]. Typically when the compound is ionized, the metal adsorption capability is due to carboxylic groups [36]. Due to their high natural abundance and different exciting properties, it has been reported that Alginates can be employed as biopolymers, exhibiting great potential in a wide range of applications [52, 54, 55, 58]. Specifically, these materials have been used in areas such as medical field, food industry, cosmetics, and pharmaceutical [9, 18, 19, 26, 33, 37]. In pharmaceutical and food industries, alginates are often used as gelling agents, specially when these are cross-linked with divalent and trivalent ions like calcium and iron cations [58]. The alginate gels are as well employed for biomedical treatments and as material-based for cell gridlock, because of the great biocompatibility, safety, low-price, and moderate gelation processes [54]. In the medical field, the use of alginates has improved the clearance of thick mucus, helping in the healing respiratory diseases or allergies [9].

The combination of alginates with divalent ions, especially in aqueous media, has resulted in the formation of heavy and stringent organized structures. Besides, the alginic acid combined with divalent cations such as Cu²⁺ and Ba²⁺ forms salt complexes typically not soluble in water [37]. There is a great variety of alginate salts, like the sodium alginate, which has been used in the pharmaceutical industry as drug delivery vector, due to its adequate physicochemical properties [19, 26]. In environmental applications, alginates with trivalent transition metal ions (e.g., Al³⁺, Fe³⁺, Sn⁴⁺), and lanthanide metals (e.g., La³⁺, Nd³⁺, Eu³⁺) have resulted in the formation of paramagnetic ionotropic hydrogels, used as pH colorimetric sensors to remove organic composites from water [59]. In the industrial sector, alginates have been combined with lanthanum and successfully employed as bimetallic catalysts, due to their high basicity and large surface area [42].

On the other hand, the alginate gelation mechanism via metal cations such as copper (Cu) and cerium (Ce) favors the formation of ionic crosslinks between different constituent polymer chains. Therefore, a better understanding of the adsorption of these metal cations by alginates requires a complete study of the process, and specific data, such as the nature of the interaction between the metal and alginate, the degree of stabilization, and binding durability [50]. To the best of our knowledge, only very few studies can be found in the specialized literature regarding the divalent and trivalent cation-alginate complexation, and much less for lanthanide trivalent cations. In this context, the present investigation focuses in the study of metal-containing alginates, such as Alg@Ce and Alg@Cu, prepared via complexation, and characterized using TGA analysis [12], SEM imaging [23], and FTIR spectroscopy [6, 32, 43], as the suggested techniques cited in the literature. Several works have addressed the molecular details involved in the process of adding metal cations into alginates; however, the physical and chemical features of the molecular structure and electronic properties have not been fully studied over these systems.

To complement the experimental findings, DFT calculations have been used to investigate the physical and chemical features of periodic structures [15, 21]; these methods are based on approximations. The DFT methodology has also been used to determine the interactions between different types of molecules and ions; therefore, it was implemented here as an additional technique for studying this metal-alginate complexation process. The optimization of the different metal/cation-alginate complexes can shed light in their molecular structure, and also helps to find the different nature of the metal-alginate correlations [2, 4, 44, 45]. Moreover, these interactions are often found in the biosorption technology, employed in discharge processes to remove, with high efficiency, toxic metal ions, pigments, and other toxic chemicals components from water [3, 7, 16, 27, 39, 41]. Among the most cost-effectiveness routes to improve the alginate biosorption technology, the following stands out: degradation of chemical and biological silts, and regeneration of biosorbsents, and the metal recovery processes [5, 17, 24, 51].

In this frame, the goals of this joint experimental/computational analysis are summarized as follows:

i. Experimental study of some structural properties of Alg@Ce and Alg@Cu alginates complexes, specifically their thermal behavior, particle size, morphology and structural binding.

ii. Describe and compare the experimental data between the two Alg@Ce and Alg@Cu complexes.

iii. Perform DFT calculations and determine the electronic, energetic, and structural features of the neutral, deprotonated, and complex state of metal-alginate composites.

iv. Compare the experimental and theoretical results regarding the complexation process of the bio-based cation-alginate.

**Materials and methods**

**Reagents**

Cu(NO₃)₂·6H₂O and Ce(NH₄)(SO₄)₄ purchased from Aldrich were used as the metal precursors, sodium alginate (C₆H₇NaO₃) purchased from Aldrich was used as the alginate source, in all experiments, deionized water was used as the solvent agent.
Synthesis procedure

In 100 mL of deionized water, 1.0 g of sodium alginate powder was dissolved at room temperature for 3 h, resulting in a viscous transparent gel solution. In the same water volume, 2.95 g of Cu(NO₃)₂·6H₂O were dissolved to obtain a 0.1 M solution; then, the viscous alginate mixture was added dropwise to the copper nitrate solution and mixed for 2 h at standard conditions, with a slow and constant stirring. Green gel beads were immediately formed, and after 6 h of aging, the Alg@Cu beads were separated from the solution and washed several times with distilled water to eliminate the sodium and nitrate ions remnants from the beads surface. Finally, the beads were dried at room temperature for 24 h. The same method was used in the case of Alg@Ce beads, using Ce(NH₄)(SO₄)₄ with a concentration of 0.1 M.

Materials characterization

The thermogravimetric analysis (TGA) was performed under air atmosphere in a TA Instruments Q500 apparatus, using a 10 °C/min heating ramp between 25 and 1000 °C. Fourier transform infrared spectroscopy (FTIR) was performed to the samples in KBr pellets, using a Bruker Vector 22 spectrometer, in the 4000 to 600 cm⁻¹ range, with a resolution of 4 cm⁻¹. The reported spectra take in consideration subtraction of the background that was previously recorded under air with the same measurement conditions. The morphological studies of synthesized materials were carried out in a FEI Quanta 200 field emission scanning electron microscope (SEM).

Computational details

DFT calculations were performed by running the Gaussian (09) code package [25], and outputs were checked by the linked graphical interface GaussView 6.0 [20]. Starting geometries were sketched and derived from Avogadro software [28], and they were fully optimized using a DFT method [10, 11, 30, 34, 53], with the hybrid B3LYP combined functional [8] that was proven to give reliable results compared to experiments [40, 56]. Employing the polarized triple-Z valence basis set def2-TZVP, the pseudopotential generated by this is suitable for heavy atoms. Additionally, the total electronic energy was corrected considering the dispersion interaction by employing the term D3(BJ) [13]. To include the effects of water as a high-permittivity solvent, the SCRF (solvent cavity reaction field) approach with PCM (Polarizable Continuum Model) [14] were implemented using the Gaussian09 code package. B3LYP-D3(BJ)/def2-TZVP calculations were carried out using the following protocol: A first optimization was performed to find the most stable conformation of the metal-alginate complex, proposed by chemical intuition. After that, all arrangements were optimized in the gas phase and in the PCM mode, for all degrees of freedom.

The reactivity of α-L-guluronate saccharides linked with the divalent and trivalent cations was determined by calculating different properties, like χ (the electronegativity), η (the hardness), IP (the ionization potential vertically), and EA (electron affinity vertically), where IP and EA can be associated to the empirical electrophilic and nucleophilic indexes, respectively. Therefore, the local chemical reactivity of the interaction between the M cation with the Alg molecule was analyzed by local chemical descriptors of the compounds (see Table 1). The above was performed with the aim of understanding how the chemical properties are being favored after the formation of the

| Structural parameters | Alg–Gas phase | Alg–Aqueous media |
|-----------------------|---------------|-------------------|
| **bond length (Å)**   |               |                   |
| O5–C4                 | 1.412 Å       | 1.414 Å           |
| C4–C3                 | 1.503 Å       | 1.499 Å           |
| C3–O2                 | 1.256 Å       | 1.256 Å           |
| C3–O1                 | 1.248 Å       | 1.252 Å           |
| **bond angle (º)**    |               |                   |
| O1–C3–O2              | 112.630 º     | 111.588 º         |
| C4–C3–O1              | 123.135 º     | 123.802 º         |
| C4–C3–O2              | 124.230 º     | 124.608 º         |
| **dihedral angle (º)**|               |                   |
| O1–O2–C3–C4           | 179.368 º     | 179.857 º         |
| O2–C3–C4–O5           | 3.971 º       | 0.109 º           |
O–M bonds (O coming from the alginate). The chemical behavior induced by the metallic cation is noticed through the modification of molecule parameters such as \( \eta \) and \( \Delta E_{\text{H-L}} \) (see Table 2). Therefore, due to the favorable coordination of the alginate’s functional groups with the cations described in the DFT calculations, we can elucidate that the electronic charge transfer mechanism from M to Alg is responsible for the formation of these biopolymers (Alg@Cu and Alg@Ce compounds).

The electronegativity (\( \chi \)) is the negative value of the chemical potential (\( \mu \)) [46]; their definition for a \( N \) electron system that presents a total energy \( E \), beneath an external potential \( v(r) \), can be written as:

\[
\chi = - \left( \frac{\partial E}{\partial N} \right)_{v(r)} = -\mu 
\]  

(1)

where \( \mu \) is the Lagrange multiplier associated with the DFT normalization constraint.

The hardness (\( \eta \)) is defined as the analogous second derivative [47].

\[
\eta = \left( \frac{\partial^2 E}{\partial N} \right) = \left( \frac{\partial \mu}{\partial w} \right)_{v(r)} 
\]  

(2)

The adopted equations to calculate the hardness and the electronegativity can be given using a finite difference method [48]:

\[
\chi = - \mu = \left( \frac{(\text{IP} + \text{EA})}{2} \right) \quad \text{(3)} \quad \text{and} \quad \eta = \text{IP} - \text{EA} 
\]  

(3)

This previous equation can be rewritten according to Koopman’s theorem [35], where HOMO is the highest occupied molecular orbital, and LUMO is the lowest unoccupied molecular orbital, respectively:

\[
\eta \approx \left( E_{\text{HOMO}} - E_{\text{LUMO}} \right) / 2 
\]  

(4)

To understand the interaction between the alginate and the M atom (M = Ce or Cu), the binding energies (\( E_b \)) coming from the Gibbs free energies (\( G \)) were computed following the next reaction scheme:

\[
\text{Alg + M} \rightarrow \text{Alg@M} 
\]

\[
E_b = G(\text{Alg@M}) - G(\text{Alg}) - G(M) 
\]  

(5)

where \( G(\text{Alg@M}) \) is the Gibbs free energy for the complexes and \( G(\text{Alg}) \) and \( G(M) \) correspond to the isolated molecular fragments.

Finally, recent works have employed DFT calculations [29, 31] to elucidate the local interaction between metal atoms and functional groups coming from alginates, at atomistic levels [1]. From this background, we choose the \( \alpha \)-L-guluronate anion (see Table 1) as a model system, the other metal-alginate arrangements were simulated by performing, with precision, repetitive procedures; a glance of this is shown in the following section, where the \( \alpha \)-L-guluronate is the monomeric alginate biopolymer entity, extensively adopted in the biosorption process [22].

Results and discussion

Experimental characterization

In this work, we propose a simple synthesis route, at room temperature, to obtain a 1 wt. % of metal Alg@M complex, as described in the experimental section. In the Alg@Cu sample, a white-green bead is formed and after conventional drying, this turned into a dark-green bead. On the other hand, the Alg@Ce sample resulted in a white-yellow bead and after drying, the color changed into dark yellow (see Fig. 1).

Vibrational FTIR spectroscopy

Both FTIR analyses, theoretical and experimental, were carried out to confirm the cross-linking of copper and cerium cations into the alginate complexes, and helped to characterize the main vibrational modes of the functional groups. Also, FTIR results were used to understand each divalent and trivalent cation’s behavior, respectively.

Vibrational IR bands from copper, cerium, and the functional groups such as hydroxyls and carboxyls coming from the alginates were observed. First, Fig. 2 shows the FTIR analysis of the pristine sodium alginate (Alg@Na), before the cation cross-linking with Cu and Ce. Secondly, Fig. 3 presents the experimental spectra of copper alginate (Alg@Cu) and cerium alginate (Alg@Ce). Finally, Fig. 4 presents the theoretical spectra of Alg@Cu and Alg@Ce complexes obtained through DFT calculations.

By comparing spectra shown in Figs. 2, 3, and 4, all present several bands associated with the main functional groups formed in the alginate complexes under investigation; besides, a rough similarity was noticed between the

| Table 2 Ionization potential (IP), electron affinity (EA), chemical potential (\( \mu \)), chemical hardness (\( \eta \)), and HOMO–LUMO gap energy (\( \Delta E_{\text{H-L}} \)) for all alginate complexes in the present study |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | IP (eV) | EA (eV) | \( \eta \) (eV) | \( \mu \) (eV) | \( \Delta E_{\text{H-L}} \) (eV) |
| Gas phase      | Alg@Cu   | 8.71   | 1.19           | 3.75           | -4.95           | 3.62            |
|                | Alg@Ce   | 6.16   | 0.61           | 3.38           | -2.77           | 1.71            |
| Aqueous media  | Alg@Cu   | 6.45   | 2.83           | 1.80           | -4.64           | 4.17            |
|                | Alg@Ce   | 2.57   | 0.12           | 1.34           | -1.22           | 1.65            |
Theoretical and the experimental spectra in both alginate-metal complexes.

The experimental O–H stretching vibrations exhibited by the Alg@Ce complex were slightly shifted, as compared to the theoretical spectra (from 3013 to 3124 cm$^{-1}$), similar behavior was observed for the COO symmetric and C–O stretching vibrations (from 1777 to 1604 cm$^{-1}$, and from 1082 to 1072 cm$^{-1}$, respectively). Thus, by matching both the theoretical and experimental spectra from the Alg@Cu complex, several similarities in the majority of the characteristic bands are observed, e.g., the stretch vibration of the carboxylic group presents a shift towards lower frequencies, around 80 cm$^{-1}$, while the bend vibration of M–O group moves slightly from 555 to 547 cm$^{-1}$. In general, it was noticed that results above mentioned present several agreements with most of the vibrational frequencies obtained by DFT calculations. The disparity observed between the DFT and the experimental spectra resulted from the harmonic treatment of the vibrations and the inaccuracies of solving the Schrödinger equation inherent of the DFT methodology.

The next important issue to be analyzed in the theoretical FTIR spectra of the two complexes is the differences of vibrational modes between the complexes submitted in aqueous media and in gas phase (see Fig. 3). First, it was noticed that spectrum intensity in an aqueous solution was significantly higher than in a vacuum media. The complexes FTIR spectra present broad bands corresponding to C – O and COO stretching modes for the Alg@Cu sample, and

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Fig. 1 Schematic presentation of materials preparation procedure and actual photographs of the Alg@Ce and Alg@Cu beads

Fig. 2 Experimental FTIR spectrum of the Alg@Na powder, before cross-linking with Cu and Ce cations

Fig. 3 Experimental FTIR spectra of the Alg@Ce (black line) and Alg@Cu (red line) powder beads
these are located at 741 and 1583 cm$^{-1}$ in the gas phase and at 1041, and 1549 cm$^{-1}$ in aqueous media. For the Alg@Ce complex, these vibrational bands were observed in the gas phase in the 894 – 1262 cm$^{-1}$ range, while in aqueous media only a single band was barely identified at 1190 cm$^{-1}$.

The interaction of the Alg@Cu complex with the aqueous solution apparently narrows the O–H stretching band modes. Besides, the intensities observed in the gas phase at the 3655 – 3781 cm$^{-1}$ region are also different to that presented in the aqueous media around the same spectral zone (3312 – 3808 cm$^{-1}$) as a reminder, the latter spectrum was calculated using the polarizable continuum model (PCM). Conversely, the Alg@Ce complex in PCM mode presents an important shift towards higher frequencies. By comparing spectra of the Alg@Ce sample in the two different media (gas phase and aqueous media), it may be concluded that in aqueous media the complex prefers to combine through the O–H and C–O–H functional groups, as evidenced by their respective vibrational modes.

**Thermal TGA analysis**

The thermal behavior of the two Alg@Ce and Alg@Cu samples were carried out using TGA analysis. Figures 5 and 6 show the thermogram profiles and their corresponding derivatives, for both samples, respectively. The obtained thermograms show different stages of weight loss within the temperature range (20–950 °C), the major weight decrease of copper alginate is observed in a wide temperature scope (from 120 to 400 °C), afterward, copper alginate goes gradually into degradation at a lower rate. Conversely, in cerium alginate the main degradation occurred within the temperature range of 700–850 °C. The first stage of copper and cerium alginites weight loss was associated with the dehydration of alginate samples (removal of water bounds) from room temperature up to 140 °C. The second weight decrease for copper alginate was the highest, starting around 200 °C, which was attributed to the polymer decomposition via decarboxylation, and continues up to 330 °C, this time associated with the alginate degradation.

Furthermore, copper alginate’s thermal degradation rates were considerably higher than those of cerium alginate in this low-temperature stage (see Fig. 6). That difference might be attributed to the cracking of glycosidic bonds, dehydration, and decarboxylation. Decarboxylation of alginites are more important on the catalytic reaction with the copper ion than with the cerium ion. The third stage for both alginates (from 350 to 530 °C) may be attributed to the oxidization of carbonaceous residues from inner inorganic
solid particles. After this stage, the residual weight loss of Alg@Cu was almost negligible as temperature increased. On the other hand, Alg@Ce presents the main weight loss at around 820 °C, due to alginate’s total degradation [38].

Morphological SEM analysis

Figure 7 shows representative SEM micrographs of Alg@Cu and Alg@Ce beads obtained after cross-linking of sodium alginate with copper and cerium cations. Figure 7a shows Alg@Cu beads, which are composed of collapsed particles, probably due to the hard water evaporation. It is also observed that these beads are clearly folded and cracked. As reported by other works, these cracks were detected in the case of alginate beads cross-linked with divalent cations such as copper and calcium [49], in agreement with our results.

On the other hand, the Alg@Ce bead is morphologically different. Firstly, beads are not cracked (see Fig. 7b) and their folds are very different than those in the Alg@Cu beads. In summary, two conditions are apparently affecting beads morphology, the binding preferences to M and G block, and ion affinities to the alginate.

DFT calculations

Reactivity parameters

Global reactivity parameters were calculated to determine the reactivity of alginate structures and also to elucidate the chain aggregation. Table 2 shows all the results related to the alginate complexes, like the HOMO–LUMO gap energies (ΔE_{H-L}), and the reactivity indices such as electronegativity (μ), hardness (η), electrophilic (IP), and nucleophilic indices (EA), in both gas and aqueous media.

From Table 2, the Alg@Cu complex exhibits the highest hardness (3.75 and 1.80 eV in gas phase and aqueous media, respectively). This molecule hardly undergoes to a rearrangement of its electronic structure, and it presents the weakest reactivity as compared to the Alg@Ce complex (3.38 and 1.34 eV), which indicates that this latter compound can change the number of its electrons easily by chemically reacting, probably leading to the formation of covalent bonds, but still presenting a high value for that type of bond.

On the other side, the compound with the lower chemical potential is considered a more stable compound. According to the results in Table 2, it is noticed that the Alg@Ce complex exhibits the lowest value of the chemical potential, as compared to Alg@Cu; thus, it can be concluded that the Alg@Ce complex is more stable than the Alg@Cu complex. Besides, to identify the charge dispersion and by observing the rearrangement of molecular orbitals, it was found that the atomic orbital of Ce donates more electrons corresponding to 5d and 6d orbitals, and a rearrangement in the 4f orbital according to the natural electron configuration (see Table 3). In the case of Cu, the electronic charge donation is provided by 4s atomic orbital and in a lesser extent by 3d orbitals. The above is in agreement with the distribution map for HOMO and LUMO isosurfaces.

According to the theoretical calculation, the binding energies (E_b) were computed considering that the total energies are those from Gibbs free energies (Eq. 6). In the Table 4, E_b values are reported for each case under study (gas phase and aqueous media).

The probable spin state from the fully examined structures, specifically for the lanthanide metal cation, is doublet spin – state. The most stable structure is that with α-L-guluronate unit-chains of the Alg@Ce complex in aqueous media, according to the binding energy value (−177.89 kcal/

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**Table 3** Charge transfer using Mulliken, Hirshfeld, and natural charge population analysis (NBO method), and electronic configuration for the metal atom (a.u.) of the two complexes in the present study. All values are reported in |e| units

|          | Mulliken | Hirshfeld | NBO | Natural electron configuration |
|----------|----------|-----------|-----|--------------------------------|
| Gas phase|          |           |     |                                |
| Alg@Cu   | 0.42     | 0.94      | 0.77| 4s^0.22 3d^0.95 4p^0.05       |
| Alg@Ce   | 0.40     | 1.60      | 0.73| 6s^0.78 4f^0.02 5d^0.30 6p^0.04|
| Aqueous media|        |           |     |                                |
| Alg@Cu   | 0.55     | 1.07      | 0.83| 4s^0.17 3d^0.96 4p^0.04       |
| Alg@Ce   | 0.88     | 2.85      | 1.12| 6s^0.42 4f^1.131 5d^0.20 6p^0.03|
Table 4 Binding energies ($E_b$) values for alginate complexes in the present study

|                | $E_b$ (eV) | $E_b$ (kcal/mol) |
|----------------|------------|------------------|
| Gas phase      |            |                  |
| Alg@Cu         | $-2.81$    | $-65.02$         |
| Alg@Ce         | $-6.87$    | $-158.55$        |
| Aqueous media  |            |                  |
| Alg@Cu         | $-3.14$    | $-72.42$         |
| Alg@Ce         | $-7.71$    | $-177.89$        |

Table 5 Binding energies ($E_b$) values for the Alg$_2$@Cu and Alg$_2$@Ce complexes

| Complexes      | $E_b$ (eV) | $E_b$ (kcal/mol) |
|----------------|------------|------------------|
| Alg$_2$@Cu     | $-5.38$    | $-124.12$        |
| Alg$_2$@Ce     | $-11.10$   | $-256.15$        |

mol) this result indicates that the tendency of Ce$^{3+}$ cations for the binding stability is preserved in our investigated complexes, regardless the number of saccharides, and this has been proven thoroughly (see Table 5).

**Optimized geometries and ESP maps for the Alg@Cu and Alg@Ce complexes**

In this section, the most stable conformation was investigated by determining the Alg@Cu and Alg@Ce complexes optimized structures. As presented in Tables 6 and 7, these stable states helped to determine the cations ligands distances. Results show that the distance between copper atoms and some active sites of the alginate structure, i.e., the oxygen atoms that have reacted, present values as a minimum between $2.22 \, \text{Å} > d > 2.08 \, \text{Å}$, while as a maximum the distance between cerium atom and the reacted oxygen atoms from alginate reached to $2.57 \, \text{Å} > d > 2.19 \, \text{Å}$. This shows that there are differences in the strength of the alginate bond between Cu and Ce. Besides, through the complexes polarity taken from ESP maps, we have electron-rich zone and electron-deficient areas, indicating the electrophilic and nucleophilic sites. From these results, we proposed that two active sites in alginate can exchange a pair of electrons to form a new covalent bond and be susceptible to forming a stable complex.

In Fig. 8, it can be noticed that electrophilic regions represented by the red or orange color spread out across multiple parts of the alginate, especially around some oxygen atoms as these are active sites. In contrast, it was noticed that the potential decreases in the region represented by blue or green colors; these zones indicate a positive potential that distinguishes the region around the metal ion, which in both cases are Cu and Ce metal ions, respectively.

**Molecular orbitals analysis**

Considering other issues, the HOMO–LUMO calculations can also help to examine the system reactivity in their ground and excited states. These play a critical role in the understanding of the physicochemical behavior of all chemical compounds. Figure 9 shows the HOMO–LUMO isosurfaces corresponding to the two metal-alginate complexes.

**Optimized geometries of the Alg$_2$@Cu and Alg$_2$@Ce complexes**

Based on the results obtained from the interaction between Alg and M atoms, the local effects of the O–M interaction can be scaled in the biopolymer formation. The optimization of the Alg$_2$@M dimer compound was carried out at the B3LYP-D3(BJ)/def2-TZVP level of theory, while the relaxed geometry and structural parameters are described in Tables 8 and 9. The presence of the Alg$_2$@Cu dimer formation generates an elongation of the O–Cu bonds. Results show that this complex presents a high symmetry in its formation, which is represented in their frontier molecular orbitals HOMO–LUMO (see Fig. 9). In the case of the Alg$_2$@Ce dimer, the variations of the structural parameters are not very important. Also, the Alg structures remain anchored by two O atoms. This result correlates well with the Alg@Cu compound previously studied. This characteristic in the formation of the Alg$_2$@Cu bond can be attributed to the shape and direction of the 3$d$ orbitals in the HOMO isosurface (Alg@Cu, see Fig. 9), which favors an efficient overlap with the 2$p$ orbitals of the hanging oxygen atoms for the Alg fragment. In the case of Alg$_2$@Ce, the 4$f$ orbitals in the HOMO isosurface (Alg@Ce, see Fig. 9) are delocalized, causing distortion of the Alg$_2$@Ce complex. Therefore, the absence of this dimer’s symmetry may be due to the delocalization of 4$f$ orbitals from the Ce atom. Likewise, both isomers formation are exothermic, according to the binding energies ($E_b$) values (see Table 5); this same trend is observed with the Alg@Cu and Alg@Ce complexes. Therefore, the Alg and the M atoms’ structural and energetic analysis are adequately replicated with the dimers formed (Alg$_2$@M).

**Conclusions and perspectives**

The bio-based Alg@Ce and Alg@Cu beads, prepared by the alginate cross-linking method, have been characterized experimentally and studied by DFT calculations. In the first part of this paper, characterization was achieved by FTIR, TGA, and SEM techniques. SEM images indicated
morphological differences between the cross-linking of alginate with copper and cerium cations in the form of the beads. Therefore, this analysis showed that the Alg@Cu beads are morphologically different from the stronger, non-cracked Alg@Ce beads. The FTIR analysis showed the modification of the main functional groups attached to the M-alginate complexes with the presence of several peaks corresponding to specific chemical bonds. The TGA showed the thermal behavior of each of the Alg@Cu and Alg@Ce beads. These results highlighted that the Alg@Cu beads are degradable in a wide temperature range (from 120 to 420 °C), while Alg@Ce beads are degradable at only high temperatures (700–850 °C). The above demonstrated that Alg@Ce can be used in specific conditions, e.g., as catalysts operating at high temperatures, compared to the Alg@Cu sample.

In the second part, for a better understanding of the whole complexation mechanism, DFT theoretical calculations were carried out using the B3LYP-D3(BJ)/def2-TZVP level of theory. Considering the complexes global and local reactivity parameters, results proved that the Alg@Ce sample is the most reactive, as compared to Alg@Cu. This finding reinforces the cerium reactive selectivity with the different functional groups of alginate, in comparison with that of Cu. Similar findings were obtained by a region selectivity investigation that indicated the nucleophilic attacks to either the carboxylic groups or cations. Subsequently, the HOMO

| Structural parameters | Alg@Cu –Gas phase | Alg@Cu –Aqueous media |
|-----------------------|------------------|-----------------------|
| bond length (Å)       |                  |                       |
| Cu6–O2                | 2.090 Å          | 2.083 Å               |
| Cu6–O1                | 2.194 Å          | 2.222 Å               |
| O5–C4                 | 1.418 Å          | 1.424 Å               |
| C4–C3                 | 1.523 Å          | 1.522 Å               |
| C3–O2                 | 1.257 Å          | 1.257 Å               |
| C3–O1                 | 1.271 Å          | 1.257 Å               |
| bond angle (°)        |                  |                       |
| O2–Cu6–O1             | 63.581 °         | 61.774 °              |
| C3–O2–Cu6             | 87.761 °         | 90.688 °              |
| O1–C3–O2              | 121.806 °        | 122.928 °             |
| C4–C3–O1              | 118.459 °        | 116.888 °             |
| C4–C3–O2              | 119.726 °        | 120.167 °             |
| dihedral angle (°)    |                  |                       |
| O1–O2–C3–C4           | 178.99 °         | 178.487 °             |
| O2–C3–C4–O5           | 115.953 °        | 12.473 °              |
| Cu6–O2–C3–O1          | 2.325 °          | 0.170 °               |

Table 6 Optimized molecular geometry and structural parameters of the Alg®Cu complex. The structural parameters are reported in gas phase and in aqueous media.
Table 7  Optimized molecular geometry and structural parameters of the Alg@Ce complex. The structural parameters are reported in gas phase and in aqueous media.

| Structural parameters | Alg@Ce–Gas phase | Alg@Ce–Aqueous media |
|----------------------|-----------------|----------------------|
| **bond length (Å)**  |                 |                      |
| Ce6–O2               | 2.196 Å         | 2.537 Å              |
| Ce6–O5               | 2.480 Å         | 2.573 Å              |
| O5–C4                | 1.451 Å         | 1.443 Å              |
| C4–C3                | 1.534 Å         | 1.534 Å              |
| C3–O2                | 1.309 Å         | 1.282 Å              |
| C3–O1                | 1.205 Å         | 1.228 Å              |
| **bond angle (°)**   |                 |                      |
| O2–Ce6–O5            | 66.346 °        | 63.686 °             |
| C3–O2–Ce6            | 131.615 °       | 127.169 °            |
| O1–C3–O2             | 127.004 °       | 126.133 °            |
| C4–C3–O1             | 114.271 °       | 117.184 °            |
| C3–C4–O5             | 109.664 °       | 109.285 °            |
| **dihedral angle (°)** |                 |                      |
| O5–O2–C3–C4          | 2.933 °         | 6.426 °              |
| C4–C3–O2–Ce6         | 1.560 °         | 12.713 °             |
| Ce6–O2–O5–C4         | 175.752 °       | 156.116 °            |

Fig. 8  Molecular electrostatic potential surface (MEPS) for a Alg, b Alg@Cu, and c Alg@Ce complexes in the aqueous media (The isosurface was plotted with an electron density of 0.004 a.u.)
and LUMO studies explained this behavior and agreed with the reactivity study.

Hence, this work highlights important experimental and theoretical results that indicate that the prepared polymer structure could be adapted to different applications shortly. Finally, the results here presented could be considered a starting point for the lanthanide alginate system employed in polysaccharide composites.
Table 8 Optimized molecular geometry and structural parameters of the Alg₅@Cu complex

| Structural parameters | Alg–Cu–Alg fragments |
|-----------------------|----------------------|
| **bond length (Å)**   |                      |
| Cu4–O1                | 1.998 Å              |
| Cu4–O2                | 1.997 Å              |
| Cu4–O5                | 1.996 Å              |
| Cu4–O6                | 1.999 Å              |
| C3–O1                 | 1.273 Å              |
| C3–O2                 | 1.264 Å              |
| C7–O5                 | 1.273 Å              |
| C7–O6                 | 1.264 Å              |
| **bond angle (º)**    |                      |
| O1–C3–O2              | 117.637 º            |
| O5–C7–O6              | 117.708 º            |
| **dihedral angle (º)**|                      |
| O1–O2–C5–C6           | 179.555 º            |
| O1–O2–Cu4–O5          | 85.651 º             |
| O5–O6–Cu4–O1          | 85.587 º             |
Table 9  Optimized molecular geometry and structural parameters of the Alg@Ce complex

| Bond length (Å) | Alg–Ce–Alg fragments |
|----------------|----------------------|
| Ce3–O1         | 2.245 Å              |
| Ce3–O2         | 2.504 Å              |
| Ce3–O4         | 2.601 Å              |
| Ce3–O5         | 2.310 Å              |
| Bond angle (º) |                      |
| O1–Ce3–O2      | 65.866 º             |
| O4–Ce3–O5      | 64.154 º             |
| Dihedral angle (º) |                |
| O1–O2–Ce3–O5   | 179.621 º            |
| O5–O4–Ce3–O1   | 79.592 º             |

Author contribution  Conceptualization: formulation and evolution of overarching research goals an aims: Mohammed Elhoudi, Rachid Oukhrib, Christian A. Celaya, Youness Abdellaoui, and Hicham Abou Oualid.

Data curation: produce data, including software code use: Mohammed Elhoudi, Rachid Oukhrib, Christian A. Celaya, Miguel Reina.

Investigation: performing the experiments: Youness Abdellaoui, Issam Barra, Younes Brahmi, Hassan Bourzi.

Formal analysis: analyze study data: Mohammed Elhoudi, Rachid Oukhrib, Christian A. Celaya, Youness Abdellaoui, Issam Barra, Younes Brahmi, Hassan Bourzi.

Project administration: management and coordination responsibility for the research activity planning and execution: Youness Abdellaoui, Abdallah Albourine, Hicham Abou Oualid.

Resources: provision of study materials, reagents, laboratory simples, instrumentation computing resources; other analysis tools: Christian A. Celaya, Youness Abdellaoui, Issam Barra, Younes Brahmi, Hassan Bourzi.

Software: implementation of the computer code and supporting algorithms: Mohammed Elhoudi, Rachid Oukhrib, Christian A. Celaya.

Supervision: oversight and leadership responsibility for the research activity planning and execution, including mentorship external to the core team: Youness Abdellaoui, Abdallah Albourine, Hicham Abou Oualid.

Validation: verification, whether as a part of the activity or separate, of the overall replication or reproducibility of results/experiments and other research outputs: Daniel G. Araiza, Youness Abdellaoui, Miguel Reina, Hicham Abou Oualid.

Visualization: preparation, creation and/or presentation of the published work, specifically visualization/data presentation: Mohammed Elhoudi, Rachid Oukhrib, Christian A. Celaya, Youness Abdellaoui, Hicham Abou Oualid.

Writing-original draft: preparation, creation and/or presentation of the published work, specifically writing the initial draft: Mohammed Elhoudi, Rachid Oukhrib, Christian A. Celaya, Daniel G. Araiza.

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Data availability  The authors confirm that the data supporting the findings of this study are available within the article.

Code availability  All data underlying the results are available as part of the article and no additional source data are required. Software code and availability from https://gaussian.com/.

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