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Research Article

Keywords: DFT, FMO, QTAIM, NCI, MEP, Cellulose acetate, chitosan, metal ions.

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Physical and Chemical Aspects of the interaction of Chitosan and Cellulose acetate with ions Ca^{2+} and K^+ using DFT methods

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Abstract

Motivated by the use of chitosan (Ch), and cellulose acetate (AC) as organic matrices in several therapeutic drugs, a theoretical study has been elaborated through the density functional theory method (DFT) to investigate the interaction mechanism between two essential ions for the human body Ca^{2+} , K^+ and two organic matrices chitosan (Ch), and cellulose acetate (AC). Many physical and chemical aspects have been carried out after the achievement of structural optimization. This involves structural parameters, molecular electrostatic potential (MEPs), interaction energy, reactivity indexes, frontier molecular orbitals (FMOs), quantum theory atoms in molecules (QTAIM) analysis and non-covalent interaction (NCI) analysis. The results of FMOs, MEPs and reactivity index studies have revealed that the site of interaction can be predicted. The calculation of electron interaction energies shows that those ions interact with the matrix of AC and Ch. Concretely, the Ca^{2+} ion interacted efficiently with the AC matrix. The structural analysis results show that the interaction of Ch and ions appear spontaneously ($\Delta G < 0$) while the interaction of AC and ions ($\Delta G > 0$), requires more energy to occur. Finally, the QTAIM analysis data indicates that the interactions of AC -ions and Ch-ions are non-covalent presenting an electrostatic character.

Keywords: DFT, FMO, QTAIM, NCI, MEP, Cellulose acetate, chitosan, metal ions.

1. Introduction

Cellulose acetate (AC) is an organic compound results from the acetylating of cellulose (extract from wood or paper) and acetyl acid. It has been used (as organic matrix) in different drugs system due to their bio-compatibility and affinity with the human body, being also a bio-degradable and it has a high surface area which facilitates the fixation and the transport of ions metals[1-2]. It is worth noting that chitosan (Ch) is an organic compound that results from deacyteletion of chitin extracted from shells of shrimp and other crustaceans with an alkaline substance and it is a biomedical compound used as antibacterial in several fields of agriculture and medicine. Moreover, it has been exploited as a drug transporter through the human skin[3-4].

The metal ions play a primordial role in the human body. Indeed, ions such as calcium and potassium are indispensable for life. Concretely, they are required for bone development,

and muscle contraction. In addition, they play a relevant role in the heart function and the formation of different enzymes [5].

In fact, the Potassium or K^+ is found in the plasma with a percent of 98% for an adult body which means that the quantity range between 3.5 to 5.0 meq/l and it plays a key role in the NaK-ATPase pump and leakage of potassium through potassium channels [6-7]. The two relevant functions of potassium are the maintenance of the resting membrane potential of the cells, and the intracellular osmolarity[8]. The existence of the ions of calcium (Ca^{2+}) is critical for human health; about 1 kg of calcium exists in the human body including the bones. It has an important function on muscle contraction, neuronal activity, enzyme activation, programmed cell death, immune response, and cell differentiation[9]. These two metal ions are involved in a large amount of physiological and formation reactions in the human body which make them critical substances owing to the important role that they play in several organs[10]. Actually, the quantity of these two metal ions must be maintained through a balance nutritional system. The deficiency of these two vital elements can cause several diseases and weaknesses of the human body organs[11].The difference between the Ch and the acetate of cellulose is in the constituents and the geometry which affects the sites of interaction and the specific area. Figure 1 represents the structures of the two matrices used as drug delivery.

An experimental study evaluated the impact of cross-linking of Ca^{2+} bridges on the pervaporation and structure of cellulose/alginate blend membranes[12].The intense interaction of hydrogen bonding between cellulose and alginate occurs in the membranes of the cellulose/alginate blend and maintain the function of the alginate membrane. Moreover, they have greater tensile strength, like Ca^{2+} cross-linked bridge. Compared to uncross-linked membrane, the blend membranes including the Ca^{2+} cross-linked bridge have dense architectural structure, great crystallinity, good separation factor and great permeation flux. In addition, the studies have demonstrated that the Ch interact with calcium phosphates[13].It has been reported that according to the phosphorylation mechanism, precipitation of dicalcium phosphate dihydrate and amorphous calcium phosphate from solutions containing Ch is followed by the reactions of phosphate ions with the radicals extracted from Ch molecules, leading in a reduction in the particle size of phosphate.

Recently, intensive efforts have been devoted to study physical and chemical properties of periodic structures using DFT methods. Such methods, which explored to deal with electronic, magnetic and optical properties, are based on certain approximations. Many materials have been approached including graphene and other non-trivial ones. Alternatively, DFT has been used to identify interactions between different types of molecules and ions[14-17].The interactions between Cu^{2+} , the glucosamine and N-acetyl glucosamine have been studied[14].The study of this complex has reported that there was no coordination of N-acetylglucosamine with Cu^{2+} . However, a concerted fixation of Cu^{2+} ions has been observed in the case of glucosamine[14].The interaction mechanism of Cd^{2+} , Cr^{3+} and Cu^{2+} metal ions in cellulose and acetate cellulose have been investigated [15].The Cr^{3+} ion is efficiently interacted with the matrix of cellulose and acetate cellulose compared to the other ions. The

cellulose-Cu²⁺ and AC-Cr³⁺ interactions were electrostatic and the other interactions were partly covalent[15].

The aim of this study is to contribute to these activities by investigating the interaction between the chitosan (Ch), cellulose acetate (AC), and Ca²⁺, K⁺ ions. In particular, we determine the interacting one. Then, we found the type of bonds being created during the interaction. Moreover, Ch and AC are remained biocompatible, biodegradable, and possess good solubility in aqueous systems which gain great interest in the fields of bioorganic chemistry or pharmacology. In addition, the formation of these complexes can be exploited in drugs for patients having an ion deficiency. The study has been performed by using DFT methods, with the topological properties of QTAIM and NCI analysis[18]. In particular, we explore the different geometry, the electronics, and the frequency parameters of the different complexes. The obtained results provide insights for an experimental approach of such interactions. These can find places in the pharmaceutical industry.

2. Methods and computational details

To understand the interaction, the stability, the reactivity, and electronic structure properties between the matrices and ions as well as the optimization of the complex geometry, a theoretical study has been elaborated at their energy minima. The effect of water was considered in the computation by using the polarizable continuum model (PCM) with the integral equation formalism variant (IEFPCM). The hybrid function (B3LYP)linked with 6-31G(d,p) basis set based on the DFT methods has been used through the Gaussian software 09 [19] . After that, a second analysis of the topological properties of QTAIM and NCI have been done with the use of Multiwfn package [20]. The structures have been visualized using the Gauss View 5.09 program and VMD program [21-22].

3. Results and discussions

3.1. Structural and vibration analysis

In order to study the complexation and the nature of the interaction between the ions and two polymers used as matrices, a DFT/B3LYP/6-31G(d,p) method included in the Gaussian software have been exploited to explore the map of MEP, the FMOs, reactivity indices, electrophilicity (ω),hardness (η),chemical potential(μ) and softness (S)[15].

According to Koopman's theorem[23], it is recalled that the lowest unoccupied molecular orbital (LUMO), highest occupied molecular orbital(HOMO)or the FMOs are two parameters indicating the electronic behavior and the mechanism of interactions of the different compounds. Such parameters will be approached in the present study. In fact, the HOMO is the ability of the molecules to give electrons to the ions being charged positively and LUMO is the ability to accept the electrons. Figure 2 reveals the contour plots of matrices and ions which will be dealt with in the present study. It is possible that Ca²⁺ and K⁺ can interact with the nitrogen and the oxygen of the terminal groups of the two AC and Ch matrices located at the obtained HOMO and LUMO positions. For AC, it is clear that HOMO or the electrons are localized in the oxygen parts, while for the Ch, HOMO recovers the part of the oxygen and the nitrogen, and this is due to the electronegativity of these two elements.

The electrostatic potential represented in Fig. 3 shows that the monomer of AC having only a single site of interaction. The red color indicates the negative moiety rich of electrons while the blue one indicates the positive charge of the compounds. The MEPs of ions are totally blue and they are not represented in the figure because they have only the positive charge. The MEP of the dimer of Ch reveals that the electrons or the negatives charges are localized in two parts of the matrices and hence the Ch has two sites of interaction. The first one is the oxygen site and the second one is the nitrogen site. Due to the electronegativity of this part of the matrices, the red part represents the active sites where the interaction will occur with the metal ions.

3.2.Reactivity indices and thermo chemistry of the complexes

The insight of the mechanism of the interaction between the polymers and metal ions cannot be completed without the calculation of several parameters such as the η and S , the gap energy, and the energy of interaction. Table 1 regroups all the calculated parameters of the reactivity indices.

Usually, the soft elements interact with the soft one and the hard elements interact with the hard one. From the reactivity indexes, it is possible to conclude which of the ions is the most suitable for interaction in both polymers. The following equations have been used to calculate the values of η and S of the compounds under study:

$$\eta = -\frac{(E_{HOMO} - E_{LUMO})}{2} \quad (1)$$

$$S = \frac{1}{2\eta} \quad (2)$$

It follows from Table 1 that the matrices show similar softness values. Moreover, the AC is significantly smaller than Ch. In addition, the ions Ca^{2+} and K^+ have large values of the reactivity indices. Then, the interactions between the two organics matrices Ch and AC with metal ions could take place.

According to the values found for HOMO and LUMO, three other parameters can be calculated in order to explain the possibilities of interactions between the matrices and the metal ions. They are the gap energy (Gap), μ and ω , which are calculated by applying the following equations:

$$\text{Gap} = \text{HOMO} - \text{LUMO} \quad (3)$$

$$\mu = \frac{(E_{HOMO} + E_{LUMO})}{2} \quad (4)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (5)$$

As we can see in Table 1, the electro-negativity of the matrices are -55.650 (kcal/mol) for Ch and -86.583 (kcal/mol) for AC. The high values of the electro-negativity are due to the existence of oxygen and nitrogen in the composition of these two matrices, and represent active sites of interactions. For the metal ions charged positively, the electrophilicity is more important which verified that the interaction can occur.

To study the nature of the formation of the matrices and metal ions interaction, the thermo-chemistry can provide the reaction occurring spontaneously associated with an external energy. The sign of the free energy (ΔG) calculated via the relation (6) can define the nature of interaction. The ΔG of the Ch-ions is negative which indicates that the interaction has been done spontaneously; the two sites of Ch have the same values of ΔG . For the AC however, it has been remarkable that the interaction does not occur spontaneously under the standards conditions. Then, the interaction between AC and the ions need more energy.

$$\Delta G = \sum GP - \sum GR \quad (6)$$

The interaction capacity increases with the values of the interaction energy. The greater value of this energy is associated with the reaction efficiency. The interaction energy (E_{int}) is calculated with the equation (7)

$$E_{int} = E_{complex} - (E_{molecule} + E_{ion}) \quad (7)$$

According to the data found in the Table 2, the interaction energy indicates that the capacity of the interaction of Ca^{2+} is more efficient than the K^+ .

Table 3 represents the different interactions occurred on the actives sites. For the Ch site (b), the nitrogen interacts easily with the metal ions and the distances between Ch and ions are 4.575(A°) for the Ca^{2+} and 3.449 A° for the K^+ , while in site (a) the distances are about 7.986(A°) for Ca^{2+} and 6.609 (A°) for K^+ . The AC has only one site of interaction in the carbonyl part. Furthermore, the distances between the oxygen of the AC and ions Ca^{2+} and K^+ are shorter than the distances between Ch and metal ions, the values of the distances are 3.0640 (A°) for Ca^{2+} and 3.0064 (A°) for K^+ . The matrixes frequencies before the interaction for (C-O), (C-N) and (C=O) are: 1531.32(cm^{-1}), 1695.00 (cm^{-1}) and 1797.33 (cm^{-1}) for Ch (a), Ch (b) and AC, respectively. The effect of Ca^{2+} and K^+ ions on the (-C=O), (-C-N) and (-C-O) bonds is remarkable. The frequency of the bonds of all complexes decreases with the addition of ions which indicates that the interactions have been done.

3.3.QTAIM analysis

Regarding the type of interactions occurred between the matrices Ch and AC with the actives substances Ca^{2+} and K^+ , a QTAIM analysis has been performed through the Multiwfn package. Figure 4 shows the geometry of the Ch and the AC after interaction with the ions Ca^{2+} and K^+ .

To investigate the topological parameters as for instance the Laplacian of the electron density ($\nabla^2\rho(r)$), potential energy ($V(r)$), electron density ($\rho(r)$), kinetic energy (G

(r)), electron localization function (ELF) and localized orbital locator (LOL) , a BP path bond has been created between the atoms of the active sites of matrices and the metal ions. This path has formed a density gradient originated from one point between two atoms and it called (BCP) the critical bond point. The analysis of this critical point BCP discovers the type and the nature of the interaction between the matrices from their active sites and the metal ions.

It is recalled that the sum of $G(r)$ and $V(r)$ is the total electronic energy ($H(r)$) being calculated from the BCP using

$$H(r) = G(r) + V(r) \quad (8)$$

In order to determine the type of interactions, the sign of $\nabla^2\rho(r)$ values has been observed. If the values of $\nabla^2\rho(r)$ are negatives then a covalent bond has been formed between the two elements. However, if the values of $\nabla^2\rho(r)$ are positives in this case an intermolecular interaction has been formed. The interaction energy can be calculated according to the equation given by

$$E_{int} = \frac{V(r)}{2} \quad (9)$$

The higher values of $\rho(r)$ of the BCP indicate that the interaction has great intensity. If the values of $\nabla^2\rho(r)$ and $H(r)$ are positive, the nature of the interaction is electrostatic. However, if $\nabla^2\rho(r)$ is positive and $H(r)$ is negative, the interactions, in this case, are partially covalent.

Table 4 depicts the parameters of the QTAIM analysis. All interactions have $\nabla^2\rho(r) > 0$ which confirms that the interactions are non-covalent. This means that one has intermolecular interactions. The values of the $\nabla^2\rho(r)$ and $H(r)$ are positive for all complexes hence the interactions are electrostatic.

The values of the electron density $\rho(r)$ represent the intensities of interactions between the matrixes and the ions. The values of $\rho(r)$ are 0.024 (u.a), 0.015 (u.a), 0.024 (u.a), 0.015(u.a), 0.027 (u.a) and 0.016 (u.a) for CA-Ca²⁺, CA-K⁺, Ch (a)-Ca²⁺, Ch(a)-K⁺, Ch (b)-Ca²⁺ and Ch(b)-K⁺, respectively. Therefore, the values of $\rho(r)$ indicate that the Ca²⁺ interacts more than K⁺ with the active site of the two matrixes. In addition, the interaction on the site (b) is more efficient and intensive because of the high values of $\rho(r)$.

The blue regions depicted in Fig. 5 represent a decrease of the electron localization function ELF. It is remarked a small blue region between the ions and the active sites which exhibit the formation of the complexes. The localization of the electrons is decreased in the regions of intermolecular interaction, which can be linked to the overlap of the "full" orbitals between the two reactive. These results in a repulsive force called the Pauli repulsion effect.

Figure 6 represents the electric field character. The red arrows indicate the magnitude and the start of the electric field. It is remarkable that the electric field starts from the nucleus of each atom. The regions far to the sources of the arrows behave differently; the direction of the electric field vectors is from the ions Ca²⁺ and K⁺ to the O for the AC. Moreover, for the

Ch site (b). The vectors of the arrows are from Ca^{2+} and K^+ to the N for the Ch site (a). This is due to the electro-negativity of the oxygen and the nitrogen.

Small circular shapes are found in the middle of the maps representing the small magnitude of electric fields. In fact, these regions have the negative values of ESP and all the arrows are surrounding these regions to indicate the end of molecular electric fields.

3.4. NCI analysis

The non-covalent interaction (NCI) method, also called the reduced density gradient (RDG) method is one of the popular methods used to study weak interaction. According to [22], the RDG function is calculated via the relation :

$$RDG = \frac{1}{2(3\pi^2)^{1/3}} \times \left(\frac{|\nabla\rho(r)|}{\rho(r)^{4/3}} \right) \quad (10)$$

The different colors showed in the RDG isosurface of Fig. 7 indicate the type of interactions. The blue colors are for the h-bond. The strong attraction of this bond has a decrease of the electronic density $\rho(r)$ while the repulsion part has an increase of $\rho(r)$. The green color represents the Van der Waals interaction for this type of bonds. The electronic density is null, and the red color is for the steric effect.

In the scatter maps of the Fig. 7, the X-axis corresponds to sign $(1/2)r$ and Y-axis is associated with RDG functions. In such a figure, every point matches with a grid point in 3D space. An isosurface is around 0.5 and the color range is from -0.035 to 0.02. At this level, we would give certain comments.

-For the AC, the band between the oxygen and the Ca^{2+} is an H bond type while for the K^+ is a Van der Waals bond.

-For the Ch site (a) and site (b), the nitrogen and the oxygen interact with the Ca^{2+} and the relevant bonds are the H bonds types, while for the K^+ the types of bonds are a van der Waals one

4. Conclusion

In this work, we have presented a theoretical study based on the DFT/B3LYP methods linked with a 6-31G (d,p) basis set and the QTAIM analysis. In particular, we have found that the interaction between ions Ca^{2+} and K^+ with two organic matrices AC and Ch can occur. Moreover, it has been shown that Ca^{2+} and K^+ have an interesting reactivity. The hardness of these two ions could facilitate the interaction with the two organics soft matrices. The free energy of the Ch ions has been found to be negative. It has been revealed that the reaction occurs spontaneously while for the interaction of AC with the ions Ca^{2+} and K^+ needs more energy to occur. Also, the interactions energies obtained by the DFT methods are the same values as the energies calculated by the equation 9 with $(\nabla^2\rho(r)) > 0$, $(H(r)) > 0$. It has been confirmed that the interactions are non-covalent and have an electrostatic field behavior for all complexes.

This work comes up with certain open questions. A natural one concerns the investigation of an experimental approach of such interactions. This could be addressed in forthcoming works.

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Declarations

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Conflicts of interest/Competing interests The authors declare that they have no conflict of interest and no competing interests exist.

Ethics approval The manuscript is prepared in compliance with the Ethics in Publishing Policy as described in the Guide for Authors.

Consent to participate The manuscript is approved by all authors for publication.

Consent for publication The consent for publication was obtained from all participants.

Availability of data and material All data generated or analyzed during this study are included in this published article.

Code availability The calculations were performed using: Gaussian 09W, GaussView 5.0 provided by Gaussian, Inc and Multiwfn package version 3.7 provided by sobereva and VMD program version 1.9.1 provided by www.Ks.uiuc.edu/Research/vmd/.

Authors' contributions Hajar Atmani, Abdelkhalk Aboulouard and Fatima Ezzahra Bakkardouch: Article writing; Latifa Laallam, Ahmed Jouaiti, and Mohammed El idrissi: Directing. Discussion; Abdelkhalk Aboulouard and Mohammed El idrissi: Final review and editing.

References

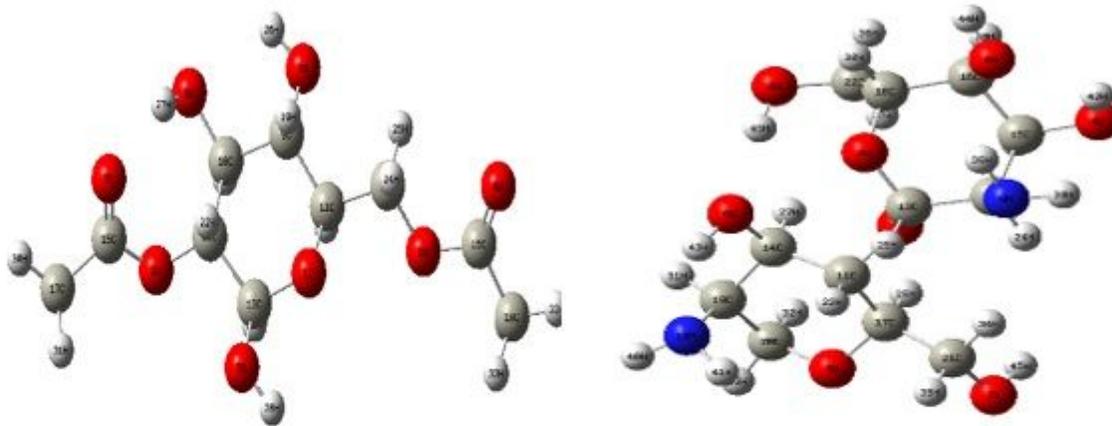
- [1] K. J. Edgar, (2007) "Cellulose esters in drug delivery," *Cellulose*, vol. 14, no. 1, pp. 49–64, doi: 10.1007/s10570-006-9087-7.
- [2] S. Hu, Z. Qin, M. Cheng, Y. Chen, and J. Liu, (2018), "Improved properties and drug delivery behaviors of electrospun cellulose acetate nanofibrous membranes by introducing carboxylated cellulose nanocrystals," *Cellulose*, doi: 10.1007/s10570-018-1662-1.
- [3] S. E. Elsaka and A. M. Elnaghy, (2012) "Antibacterial activity of calcium hydroxide combined with chitosan solutions and the outcomes on the bond strength of RealSeal sealer to radicular dentin," *J. Biomed. Res.*, vol. 26, no. 3, pp. 193–199, doi: 10.7555/JBR.26.20110136.
- [4] N. Farhadian, M. Godiny, S. Moradi, and A. Hemati, (2018) "Materials Science & Engineering C Chitosan / gelatin as a new nano-carrier system for calcium hydroxide

- delivery in endodontic applications : Development , characterization and process optimization,” *Mater. Sci. Eng. C*, vol. 92, no. July, pp. 540–546, doi: 10.1016/j.msec.2018.07.002.
- [5] A. Sigel, H. Sigel, and R. K. O. Sigel, (2013), *Interrelations between essential metal ions and human diseases*, vol. 13,doi: 10.22607/IJACS.53003.
- [6] R. C. Greer *et al.*, 2020, “Potassium-Enriched Salt Substitutes as a Means to Lower Blood Pressure Benefits and Risks,” pp. 1–9, doi:10.1161/HYPERTENSIONAHA.119.13241.
- [7] B. F. Palmer and D. J. Clegg, (2016) “Achieving the Benefits of a High-Potassium, Paleolithic Diet, Without the Toxicity,” *Mayo Clin. Proc.*, pp. 1–13,doi: 10.1016/j.mayocp.2016.01.012.
- [8] B. Honrath, I. E. Krabbendam, C. Culmsee, and A. M. Dolga, , (2017), “Small conductance Ca²⁺-activated K⁺ channels in the plasma membrane, mitochondria and the ER: Pharmacology and implications in neuronal diseases,” *Neurochem. Int.*, vol. 109, pp. 13–23, doi: 10.1016/j.neuint.2017.05.005.
- [9] D. Li, G. Liu, Y. Guo, R. Zhou, and H. Deng, (2018), “The good , the bad , and the ugly of calcium supplementation : a review of calcium intake on human health,”13, pp. 2443–2452, doi: 10.2147/CIA.S157523
- [10] A. S. Kshatri, A. Gonzalez-hernandez, and T. Giraldez, , (2018), “Physiological Roles and Therapeutic Potential of Ca²⁺ + Activated Potassium Channels in the Nervous System,” vol. 11, no. July, pp. 1–18, doi: 10.3389/fnmol.2018.00258.
- [11] V. Yildirim, S. Vadrevu, B. Thompson, L. S. Satin, and R. Bertram, (2017), “Upregulation of an inward rectifying K⁺channel can rescue slow Ca²⁺oscillations in K(ATP) channel deficient pancreatic islets,” *PLoS Comput. Biol.*, vol. 13, no. 7, pp. 1–23, doi: 10.1371/journal.pcbi.1005686.
- [12] G. Yang, L. Zhang, T. Peng, and W. Zhong, (2000), “Effects of Ca²⁺ bridge cross-linking on structure and pervaporation of cellulose/alginate blend membranes,” *J. Memb. Sci.*, vol. 175, no. 1, pp. 53–60, doi: 10.1016/S0376-7388(00)00407-5.
- [13] I. V. Fadeeva, S. M. Barinov, A. Y. Fedotov, and V. S. Komlev, (2011), “Interactions of calcium phosphates with chitosan,” *Dokl. Chem.*, vol. 441, no. 2, pp. 387–390, doi: 10.1134/S0012500811120044.
- [14] R. Terreux, M. Domard, C. Viton, and A. Domard, (2011), “Interactions study between the copper II ion and constitutive elements of chitosan structure by DFT calculation,” *Biomacromolecules*, vol. 7, no. 1, pp. 31–37, doi: 10.1021/bm0504126.
- [15] D. T. Reis, I. H. S. Ribeiro, and D. H. Pereira, (2020), “DFT study of the application of polymers cellulose and cellulose acetate for adsorption of metal ions (Cd²⁺, Cu²⁺ and Cr³⁺) potentially toxic,” *Polym. Bull.*, vol. 77, no. 7, pp. 3443–3456, doi: 10.1007/s00289-019-02926-5.
- [16] A. Attar, L. Cubillana-Aguilera, I. Naranjo-Rodríguez, J. L. H. H. de Cisneros, J. M. Palacios-Santander, and A. Amine, (2015), “Amperometric inhibition biosensors based on horseradish peroxidase and gold sononanoparticles immobilized onto different electrodes for cyanide measurements,” *Bioelectrochemistry*, vol. 101, pp. 84–91, doi:

10.1016/j.bioelechem.2014.08.003.

- [17] A. Mohamed, A. M. Fahim, and M. A. Ibrahim, (2020), “Theoretical investigation on hydrogen bond interaction between adrenaline and hydrogen sulfide,” *J. Mol. Model.*, vol. 26, no. 12, doi: 10.1007/s00894-020-04602-2.
- [18] D. T. Reis, S. Q. de Aguiar Filho, C. G. L. Grotto, M. F. R. Bihain, and D. H. Pereira, (2020), “Carboxymethylcellulose and cellulose xanthate matrices as potential adsorbent material for potentially toxic Cr³⁺, Cu²⁺ and Cd²⁺ metal ions: a theoretical study,” *Theor. Chem. Acc.*, vol. 139, no. 6, pp. 1–8, doi: 10.1007/s00214-020-02610-2.
- [19] M. Frisch *et al.*, (2009), “gaussian 09, Revision d. 01, Gaussian,” *Inc., Wallingford CT*, vol. 201.
- [20] T. Lu and F. Chen, (2011), “Multiwfn : A Multifunctional Wavefunction Analyzer,” doi: 10.1002/jcc.22885.
- [21] T. A. Keith and M. J. Frisch, (2011), “Subshell Fitting of Relativistic Atomic Core Electron Densities for Use in QTAIM Analyses of ECP-Based Wave Functions,” pp. 12879–12894, doi.org/10.1021/jp2040086.
- [22] A. M. W. Analyzer and T. Lu, 2019, “Multiwfn,” vol. 7.
- [23] T. Tsuneda, J. W. Song, S. Suzuki, and K. Hirao, (2010), “On Koopmans’ theorem in density functional theory,” *J. Chem. Phys.*, vol. 133, no. 17, pp. 1–9, doi: 10.1063/1.3491272.

Figures



Cellulose Acetate (CA)

Chitosan (Ch)

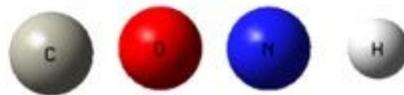


Figure 1

Chemical Structure of cellulose acetate (CA) and chitosan (Ch).

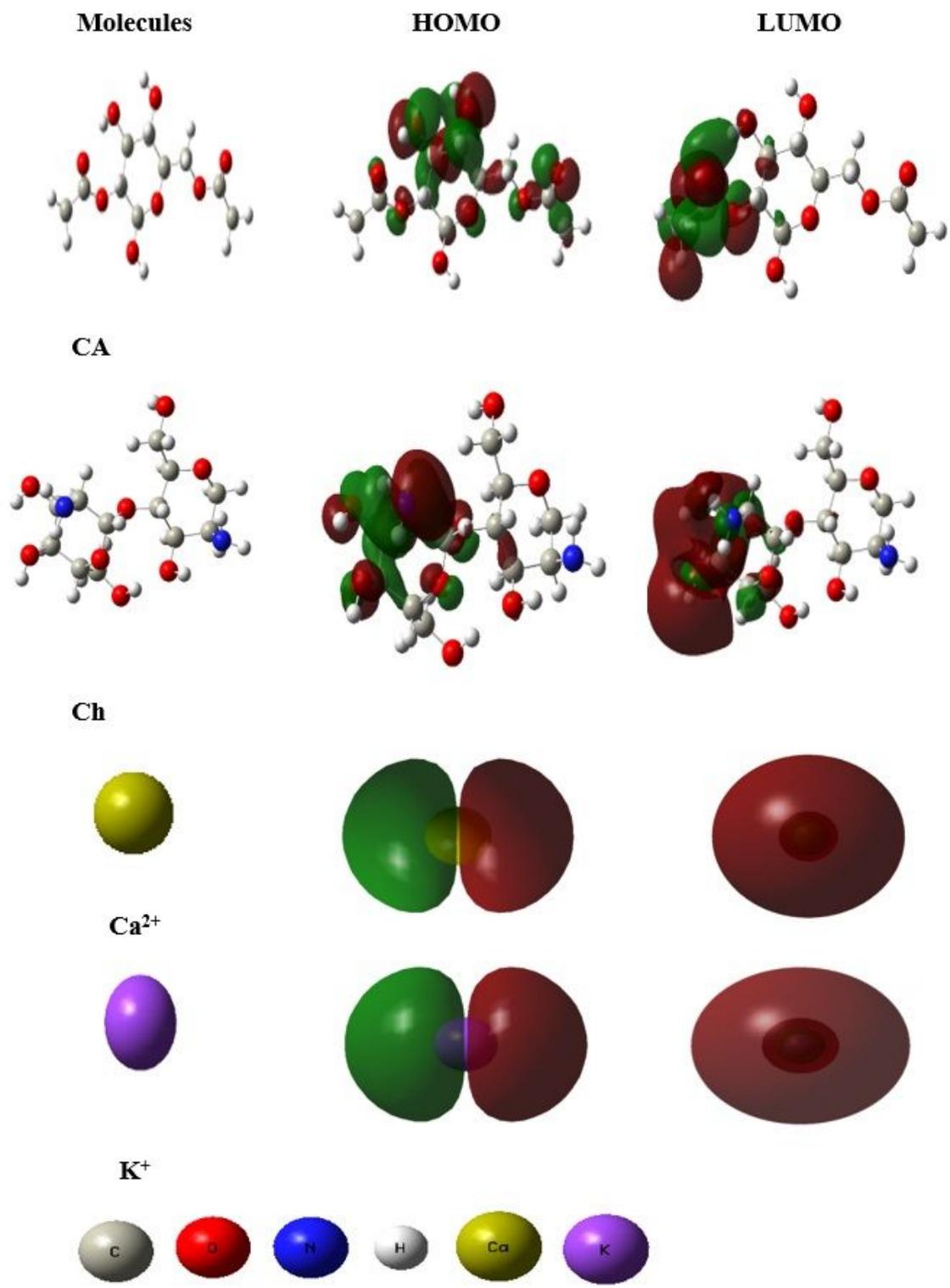


Figure 2

The contour plots of HOMO and LUMO orbitals of the studied compounds.

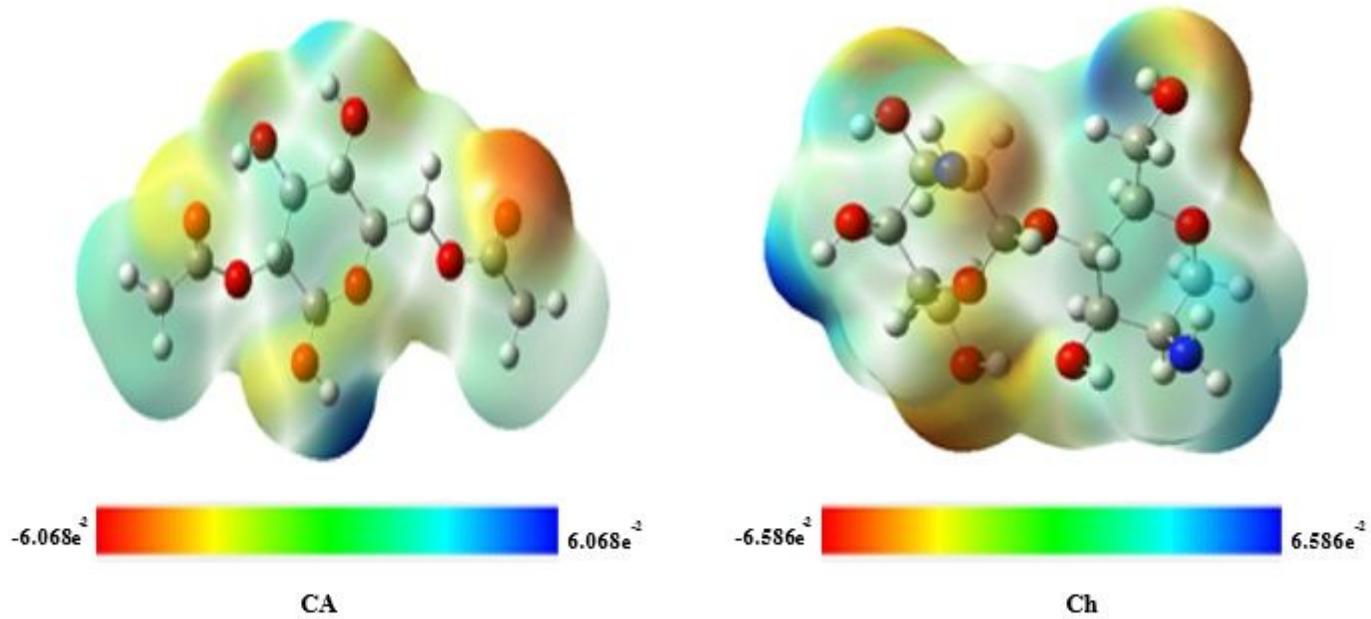


Figure 3

Maps of electrostatic potential (MEP) of cellulose acetate (CA) and chitosan (Ch).

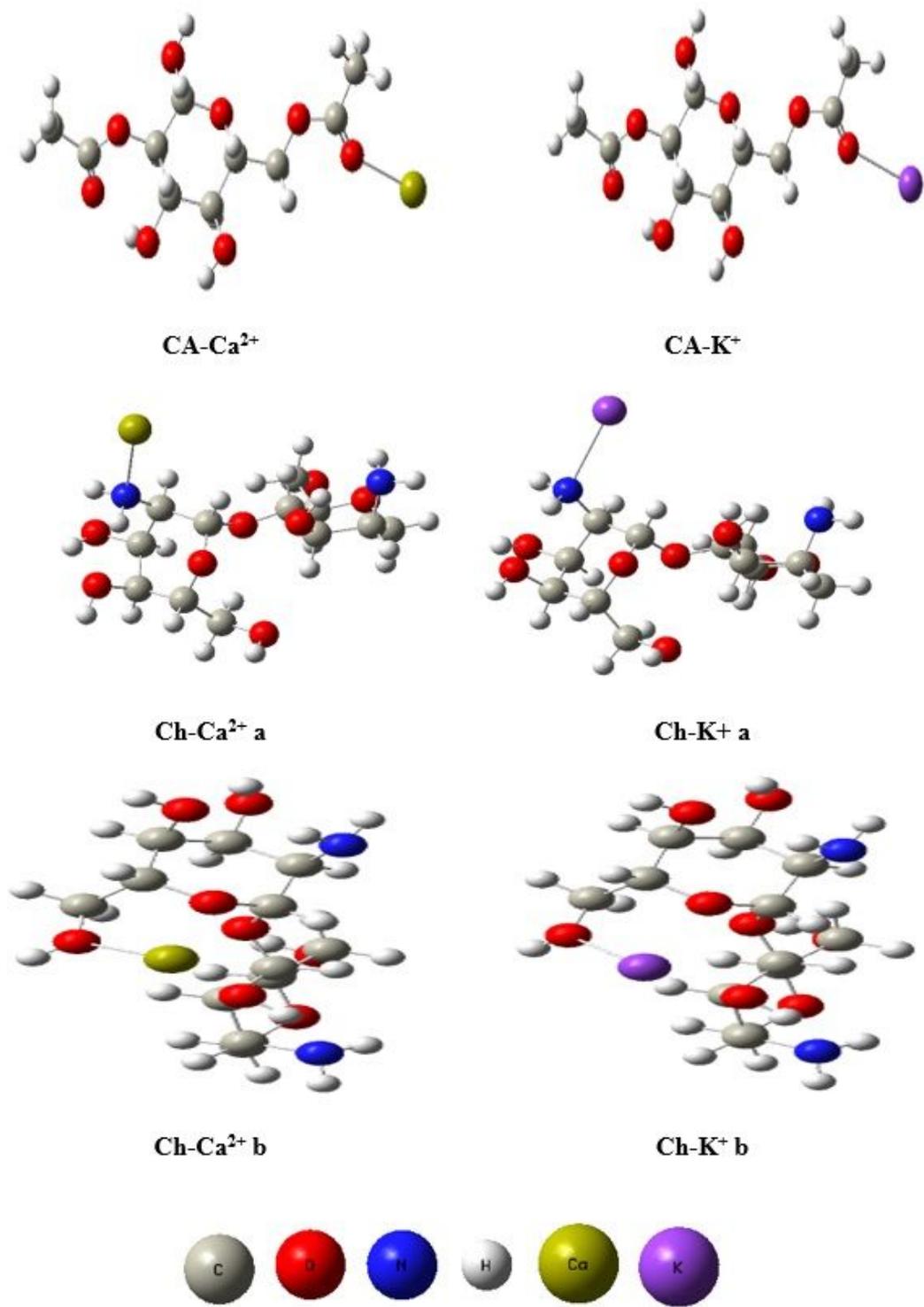


Figure 4

Optimized structures of cellulose acetate and chitosan interacting with ions Ca²⁺ and K⁺.

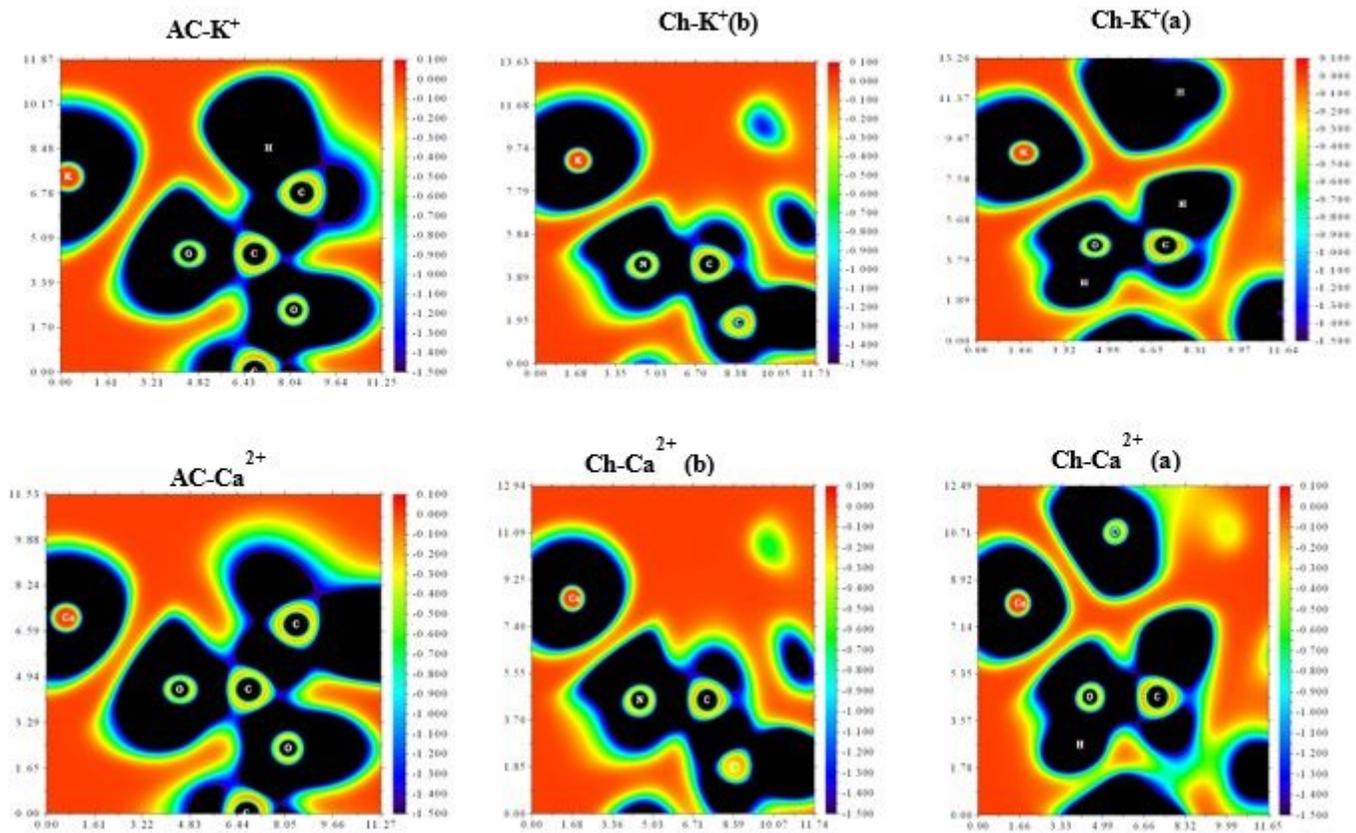


Figure 5

Shaded surface map with projection effect of electron localization function (ELF).

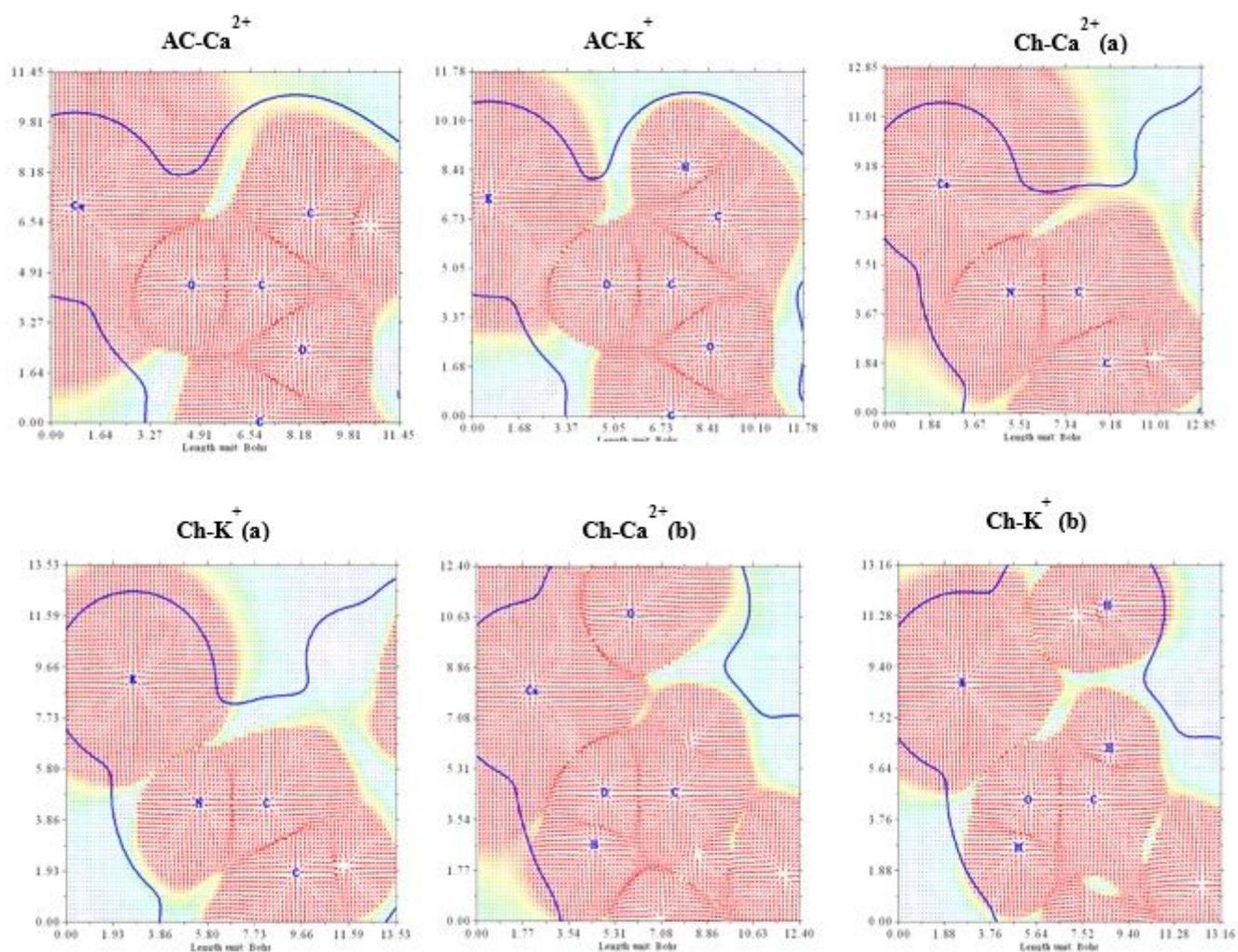


Figure 6

Vector field map to display electric field character of cellulose acetate-ions and chitosan-ions.

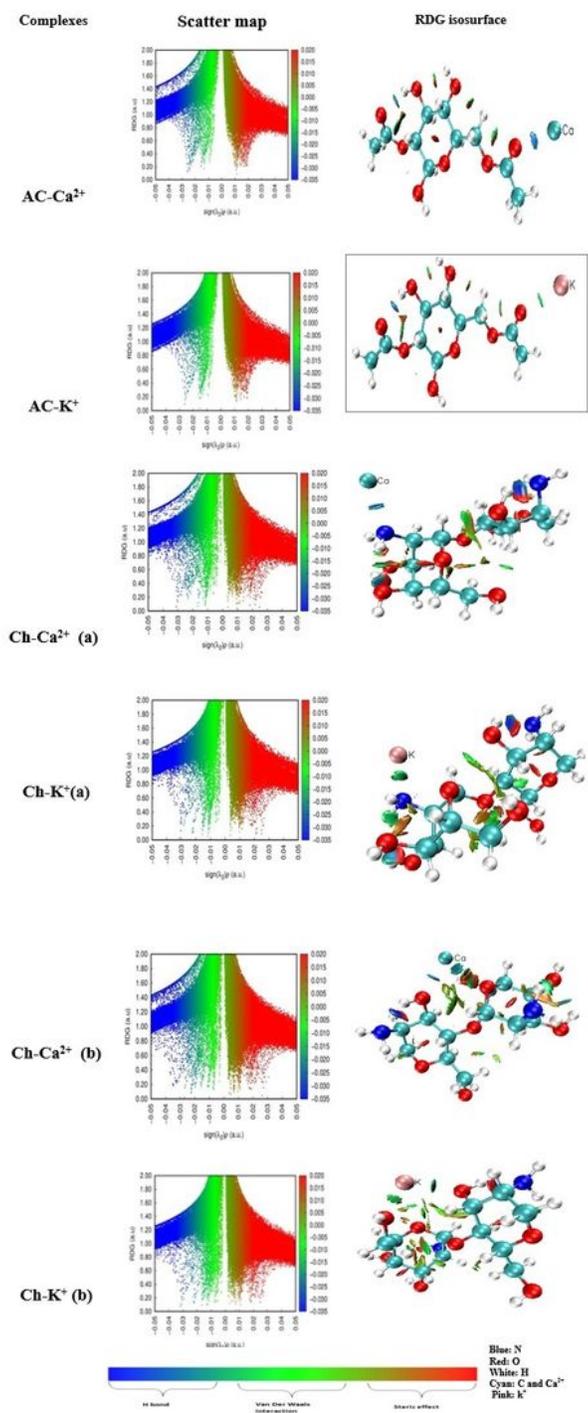


Figure 7

The NCI results using the Multiwfn program, and the VMD program.