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Research Article

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Molecular Dynamics Simulation Study on the Adsorption of Various Biopolymers on Iron Oxide Nanosurface

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Abstract

Biopolymers are widely used in surface modification of magnetic nanoparticles for biomedical applications. To improve the functionality of nanoparticles, it is of great significance to study the interaction mechanisms between these nanoparticles and biopolymers at the atomic level. Hence, in this study, the adsorption process of three different biopolymers (Gum Tragacanth, pectin and carrageenan) on Fe₃O₄ nanosurface was investigated through molecular dynamics (MD) simulations. In this regard, the adsorption process was first simulated under NVT (constant number of molecules, volume and temperature) condition. Then, the details of the interaction mechanisms between the biopolymers and Fe₃O₄ were comprehensively studied based on the interaction energies, concentration profiles and radial distribution functions. The obtained results indicated that all of the biopolymers were well adsorbed on the Fe₃O₄ surface, as a result of the interaction between Fe₃O₄ and the active atoms of the polymer chains. These interactions were mainly caused by hydrogen bonds formation and van der Waals forces. According to the obtained results, the strongest binding belongs to Fe₃O₄/carrageenan, followed by Fe₃O₄/Gum Tragacanth and Fe₃O₄/pectin, respectively.

Keywords: Adsorption; Molecular dynamics simulation; Biopolymers; Interaction mechanisms

1. Introduction

Magnetic nanoparticles are widely used in various biomedical applications such as MR contrast reagents, hyperthermia, drug delivery, biosensors, etc [1,2]. However, surface modification is usually required to improve the functionality of these nanoparticles. Nowadays, biopolymers have received significant attention owing to their exclusive properties such as biocompatibility, safety to body tissues and biodegradability [3,4]. In this regard, it is of great importance to understand the interaction mechanisms between biopolymers and magnetic nanoparticles at the

atomic level. Khmara et al. [5] studied the stabilization of Fe_3O_4 nanoparticles by a chitosan coating. The super paramagnetic performance of chitosan-stabilized nanoparticles was confirmed by experimentally measured magnetization curves. The modified nanoparticles demonstrated negative contrast magnetic resonance imaging (MRI) properties, making them useful for biomedical applications. Similar experimental study was performed by Arsalani et al. [6] on the coating of Fe_3O_4 nanoparticles by natural rubber latex, for the purpose of early cancer diagnosis. The obtained results demonstrated that the latex coating reduced the nanoparticles nuclear relaxivity ratio, and increased their magnetization. Hence, it was concluded that Fe_3O_4 nanoparticles modified by rubber latex could effectively be used as contrast agent for MRI. Doustkhah et al. [7] synthesized Fe_3O_4 nanoparticles encapsulated by apple pectin. The prepared magnetic nanoparticles were applied for immobilization of copper ions, leading to the fabrication of a recyclable nanocatalyst used in organic click reactions. The carboxylate groups of pectin acted as a chelating agent to Fe_3O_4 nanoparticles and consequently lead to the enhanced copper ions supporting. Duman et al. [8] synthesized oxidized multi-walled carbon nanotube (OMWCNT)/carrageenan/ Fe_3O_4 nanocomposites for the purpose of Methylene Blue removal from aqueous solutions. The obtained experimental results revealed that OMWCNT was effectively modified by carrageenan, making it a suitable adsorbent for removing the cationic dyes from waste waters. Yue et al. [9] used molecular dynamics simulation to study the adsorption behavior of gold (Au) nanoparticles on Fe_3O_4 surface. It was shown that an intermediate layer like a polymer, surfactant or silica could effectively enhance the adsorption of Au nanoparticles, due to the strong non-bonding interactions among the functional groups of the intermediate layer with both Fe_3O_4 surface and Au nanoparticles. Also, the adsorption behavior of amino acids on Au/PEI/ Fe_3O_4 nanocomposite was investigated by MD simulation. The obtained results indicated the effective role of the intermediate layer on the adsorption of amino acids, which improves the nanocomposite functionality for biomedical applications. Jihong et al. [10] studied the adsorption of graphene and graphene oxide onto Fe_3O_4 (111) surface through MD modeling. The adsorption analysis demonstrated that the interaction between Fe_3O_4 /graphene oxide is stronger than that of Fe_3O_4 /graphene due to the strong interactions between the iron atoms of Fe_3O_4 and the carboxyl groups of GO edges. Because of the soft sheet structures of graphene and graphene oxide, folded structures were created on Fe_3O_4 surface, which improved superficial area of nanoparticles, making them ideal material for drug carrier applications. Qiang et al. [11] studied the interaction mechanisms between chitosan and different Fe_3O_4 crystallographic planes using MD simulation. The results obtained by concentration profiles and the interaction energies revealed that the strongest

interaction occurred between chitosan and Fe₃O₄ (1 1 1) surface compared to the (1 1 0) and (0 0 1) surfaces. Similar MD simulation was carried out by Qiang et al. [12] to study the interaction mechanisms between Fe₃O₄ (1 1 1) surface and various biopolymers (i.e. polysaccharides and polyesters). Based on the radial distribution function analysis, it was shown that the strongest interaction was formed between Fe₃O₄ and polysaccharides, as a result of hydrogen bond creation between the oxygen atoms of Fe₃O₄ and functional groups of polysaccharides. Also, the flexibility of a polymer chain was reported to be the most significant parameter influencing the morphology of a polymer on Fe₃O₄ surface.

According to the above-mentioned literature, there hasn't been any study toward adsorption analysis of Gum Tragacanth (GT), pectin and carrageenan on Fe₃O₄ surface, by MD simulation. MD is a promising numerical technique for analyzing the interaction mechanisms between various materials at the atomic level [13]. In addition, the interaction details can't be easily captured by experimental tests, especially at the atomic scale. Hence, the main purpose of the present research is to study the adsorption behavior of the above-mentioned biopolymers on Fe₃O₄ surface by MD simulations. For this purpose, the adsorption process was first simulated under NVT (constant number of molecules, volume and temperature) condition. Then, the details of the interaction mechanisms between the biopolymers and Fe₃O₄ were studied based on the interaction energies, concentration profiles and radial distribution functions.

2. Molecular dynamics modeling

Molecular dynamics (MD) is a powerful numerical method for studying the interactions and movements of atoms and molecules of a system. In MD simulations, the trajectories of system constituents are estimated using Newton's equations of motion. In this respect, the potential energies and the particles forces are calculated based on the molecular mechanics force fields or interatomic potentials [14]. It should be mentioned that all of the MD simulations were carried out through the COMPASS force field, in which, the total potential is composed of three main components, including bond energy terms, cross energy terms and non-bond energy terms, as expressed by Equations (1)-(4) [15,16]:

$$E_{potential} = E_{bond} + E_{non-bond} + E_{cross} \quad (1)$$

$$E_{bond} = E_b + E_\theta + E_\varphi + E_{inv} \quad (2)$$

$$E_{non-bond} = E_{vdW} + E_{elec} \quad (3)$$

$$E_{cross} = E_{b,b'} + E_{\theta,\theta'} + E_{b,\varphi} + E_{b,\theta} + E_{\theta,\varphi} + E_{\theta,\theta',\varphi} \quad (4)$$

As shown, the bond energy term (E_{bond}) includes bond stretching (E_b), angle bending (E_θ), torsion energy (E_ϕ) and out of plane inversion energy (E_{inv}). $E_{non-bond}$ is composed of van der Waals (E_{vdW}) energy and Coulombic electrostatic energy (E_{elec}); and E_{cross} consists of coupling energies (i.e. the interaction between bend-bend ($E_{\theta,\theta'}$), stretch-stretch ($E_{b,b'}$), bend-torsion ($E_{\theta,\phi}$), stretch-torsion ($E_{b,\phi}$), stretch-bend ($E_{b,\theta}$), and bend-bend-torsion ($E_{\theta,\theta',\phi}$) items).

The adsorption process of the biopolymers was simulated through dynamics runs under NVT (constant number of molecules, volume and temperature) ensemble at 298 K. In this regard, a 1000 ps NVT dynamics run was carried out to simulate the system. The first step of MD simulations is modeling the molecular structures of the system constituents (i.e. biopolymers and Fe_3O_4 nanoparticles). The biopolymers used in this study are Gum Tragacanth (GT), pectin and carrageenan; which, are types of polysaccharides. The molecular structure of these biopolymers is depicted in Fig. 1. Since, the most stable surface of Fe_3O_4 is (1 1 1), this surface was chosen for the interaction analysis of Fe_3O_4 with the aforementioned biopolymers [11,12]. For this purpose, the crystal model of Fe_3O_4 was created based on the magnetite structure (as shown in Fig. 2), and then the interaction surface was built by cleaving the magnetite crystal along the (1 1 1) plane. The primary dimensions of the surface were $a=b=5.935 \text{ \AA}$ and $c=14.539 \text{ \AA}$; and the angles were $\alpha=\beta=90$ and $\gamma=120$. The thickness of the surface was chosen to be a little more than the non-bond cutoff distance. In order to represent more realistic surface area, a supercell was created from the (1 1 1) surface, with dimensions of: $a=b=71.22 \text{ \AA}$. After initial modelling - considering available crystallographic data in the literature [11,12]- whole magnetite structure was structurally optimized to reach its generically favorable state, then solely undergoes canonical ensemble, i.e. NVT, to reach its final equilibrium state at the desired temperature. Finally, the optimized structure is employed for further adsorption analysis. To this end, a vacuum slab with the height of 150 \AA was built. Due to the periodic boundary conditions, the adsorbate (i.e. biopolymers molecules) can potentially interact with both sides of the Fe_3O_4 surface; hence, the height of the vacuum slab was set to be large enough to ensure that the adsorbate interacts only with one side of the surface. In the following, the molecular models of GT, pectin and carrageenan were built. As the main objective of the study is to explore the adsorption of various biopolymers on magnetite, the length of polymer in the main simulations is selected small enough to obtain short simulation time as according to the previous simulations, it was believed that geometrical parameters do not have a noticeable effect on the adsorption process. Hence, the chain length of ten was selected for MD simulations.

After the initial relaxation and optimization process, the optimized biopolymer structures are placed in cut off range of (1 1 1) surface in the vacuum slab. Then, the final simulation regarding the adsorption of biopolymer on the magnetite surface was performed and analyzed. Finally, the interaction energy was calculated to evaluate the binding strength and the interfacial compatibility between Fe₃O₄ and biopolymers, as described by Eq. (5):

$$E_{int} = E_{total} - (E_{poly} + E_{surf}) \quad (5)$$

where, E_{int} and E_{total} are the interaction energy and the energy of the whole system, respectively. E_{poly} is the energy of polymer without Fe₃O₄ surface and E_{surf} denotes the energy of the surface without polymer. Positive value of E_{int} indicates repulsion between two components; while, negative value indicates attraction. The more negative is the E_{int} , the stronger is the adhesion.

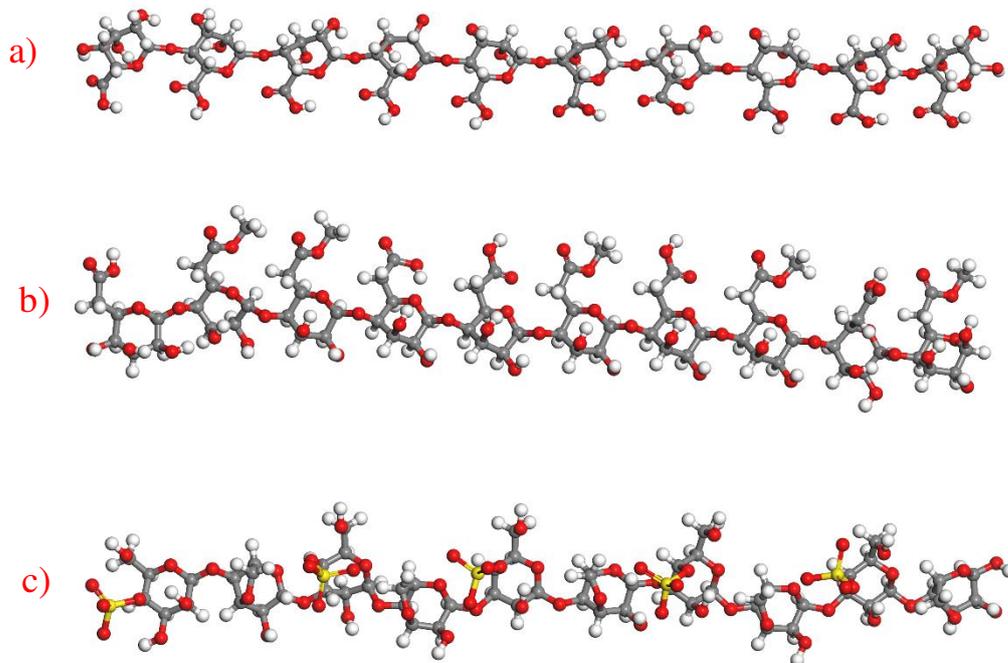


Figure 1. Molecular structure of biopolymers; a) GT, b) Pectin and c) Carrageenan.

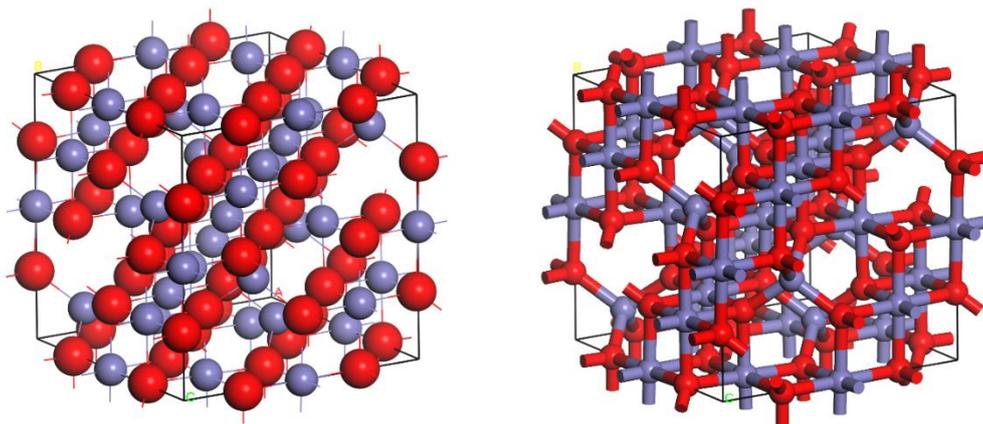


Figure 2. Crystal model of magnetite (Fe_3O_4).

The starting point is one of the important parameters regarding the intrinsic properties of nanostructures considering the fact that each simulation with a different starting point may lead to slightly different results. So, in order to incorporate the effect of starting points, for each model, several simulations with various starting points have been performed then the results have been averaged. Although, in the adsorption process, according to the previous publications, it was observed that the initial configuration does not have a considerable effect on the final configuration. Herein, each simulation has been performed five times, with two configurations, i.e., vertical and horizontal.

3. Results and discussion

At first, in order to study the effect of geometrical parameters, i.e. the length of polymer on the interaction energy, Fig. 3 is revealed. In this regard, various chain lengths (i.e. 5, 10, 15, 20, 25 and 30), are selected. As demonstrated, by increase of the chain length, the absolute value of the binding energy increases, which is due to the monomer structure and the atom types that leads to different level of rigidity of its backbone, and also the values of coefficients of nonbonded interaction for interaction atoms of biopolymer and magnetite surface. However, for all chain lengths, the highest binding energy is related with carrageenan, followed by GT and Pectin, respectively. (Note that the binding energy of carrageenan is depicted in the right axis).

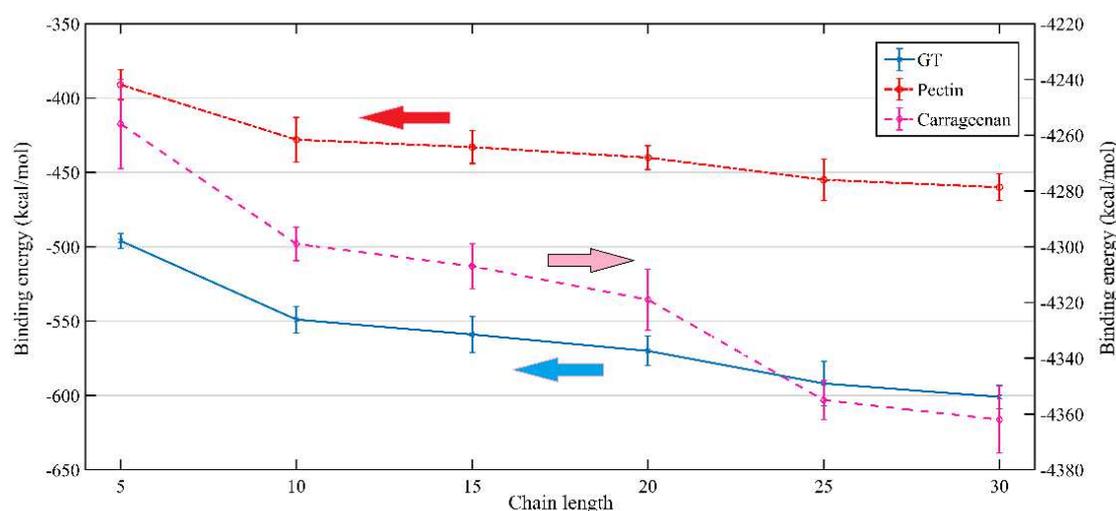


Figure 3. Calculated interaction energies for various chain lengths of biopolymers in horizontal configuration. (The interaction energy of Fe₃O₄/carrageenan is shown in the right axis).

To study the binding strength between the biopolymers with the length of 10 monomers and Fe₃O₄, the interaction energy was calculated for both vertical and horizontal configurations, as depicted in Table 1. The more negative value of the interaction energy reflects stronger adhesion among the components; therefore, the strongest binding relates to Fe₃O₄/carrageenan followed by Fe₃O₄/GT and Fe₃O₄/pectin, respectively. Making a Comparison between the interaction energies of the two vertical and horizontal configurations, demonstrates that GT and Pectin adsorbed on the surface stronger in vertical configuration than that in horizontal configuration. In vertical configuration, the binding energies of GT and Pectin are 46.23% and 59.42% more than that of horizontal configuration, respectively. However, for carrageenan, the binding energy in the case of vertical configuration is 69.73% less than that of horizontal configuration. In spite of the configuration type, the strongest binding is associated with Fe₃O₄/carrageenan followed by Fe₃O₄/GT and Fe₃O₄/pectin, respectively.

Table 1. The interaction energy between biopolymers and Fe₃O₄ surface (for both horizontal and vertical configurations).

Polymer		E _{total} (kcal/mol)	E _{poly} (kcal/mol)	E _{surf} (kcal/mol)	E _{int} (kcal/mol)
GT	Horizontal	-4349705024143.773	589.564	-4349705024183.256	-550.081
	Vertical	58601613640148140204.25	909.596	58601613640148140099.05	-804.396

Pectin	Horizontal	-4349704619420.522	304.025	-4349704619297.084	-427.463
	Vertical	58601613640148099007.82	470.659	58601613640148099218.61	-681.449
Carrageenan	Horizontal	-4349704337976.886	361.617	-4349704334040.127	-4298.376
	Vertical	58601613640148115303.18	1374.323	58601613640148115229.77	-1300.913

In order to explore the interaction mechanisms of Fe_3O_4 and biopolymers, the MD simulations were performed in Materials Studio software, based on the procedure explained in Section 2. The potential energy evolution of the Fe_3O_4 /biopolymers systems during NVT simulations is illustrated in Fig. 4. It is obvious that, the potential energy of all biopolymers has converged to a persistent value with small oscillations at the end of the NVT runs; indicating that all of the systems have reached to the equilibrium condition.

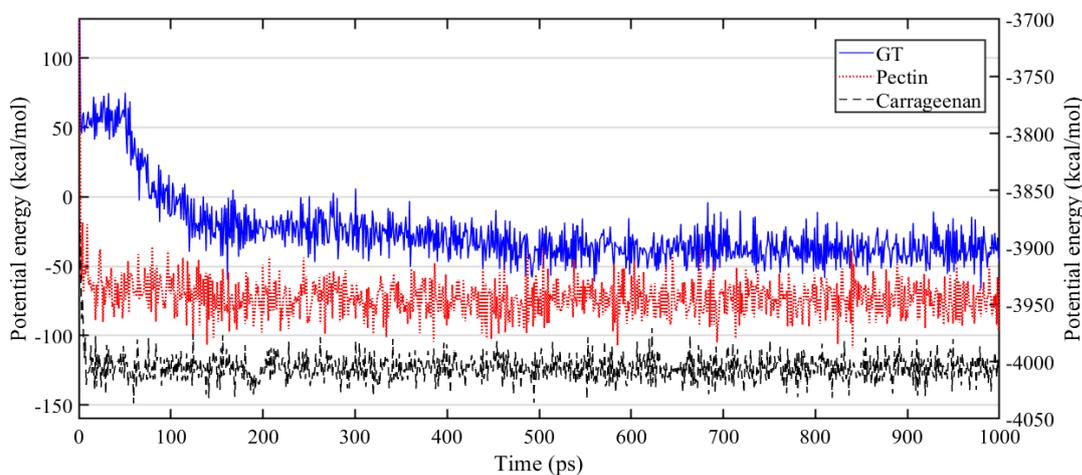


Figure 4. Evolution of potential energy during NVT dynamics run. (The Fe_3O_4 /carrageenan potential energy is shown in the right axis)

The configuration of the biopolymer's chains on Fe_3O_4 surface before and after NVT runs are illustrated in Figs. 5 and 6, for both horizontal and vertical configurations. As illustrated, all of the polymer chains are well adsorbed on the Fe_3O_4 surface and covered the surface; however, carrageenan molecules have been adsorbed in more expanded form than the other biopolymers.

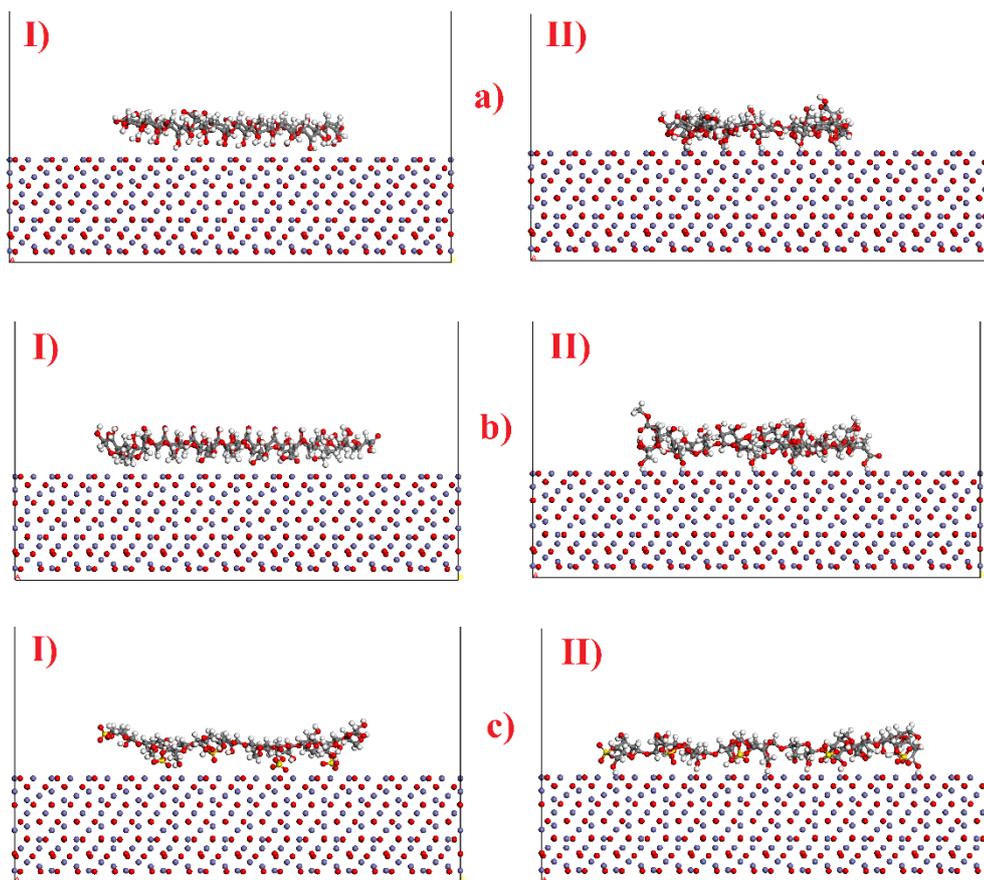
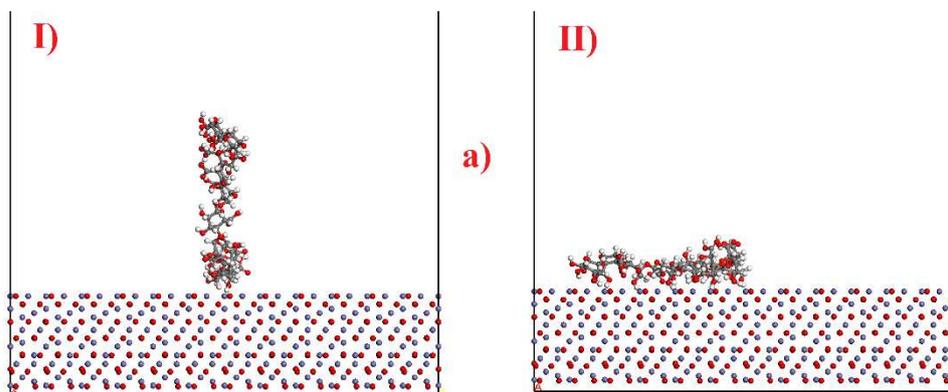


Figure 5. The configuration of biopolymers on Fe_3O_4 surface in *horizontal* configuration; a) GT, b) Pectin and c) Carrageenan. (I: before MD, II: after MD)



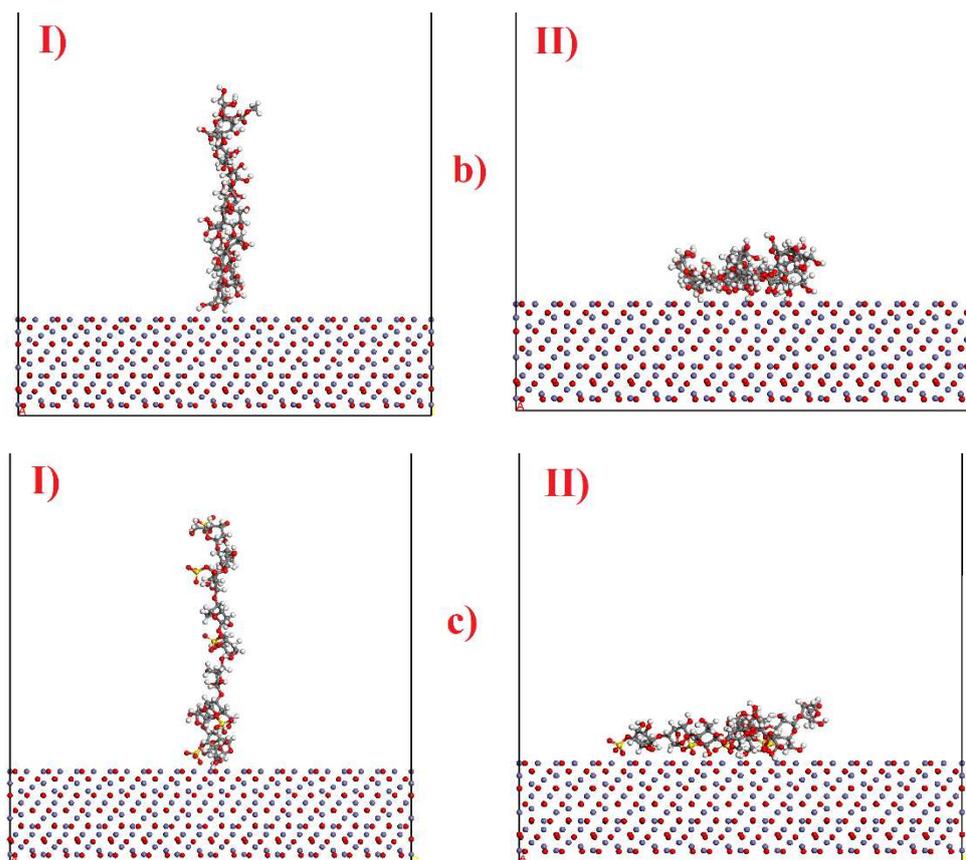
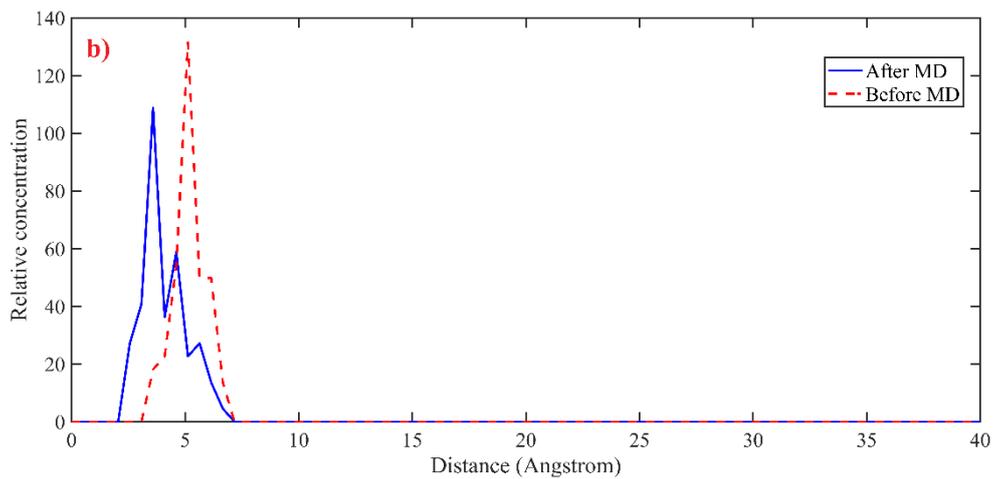
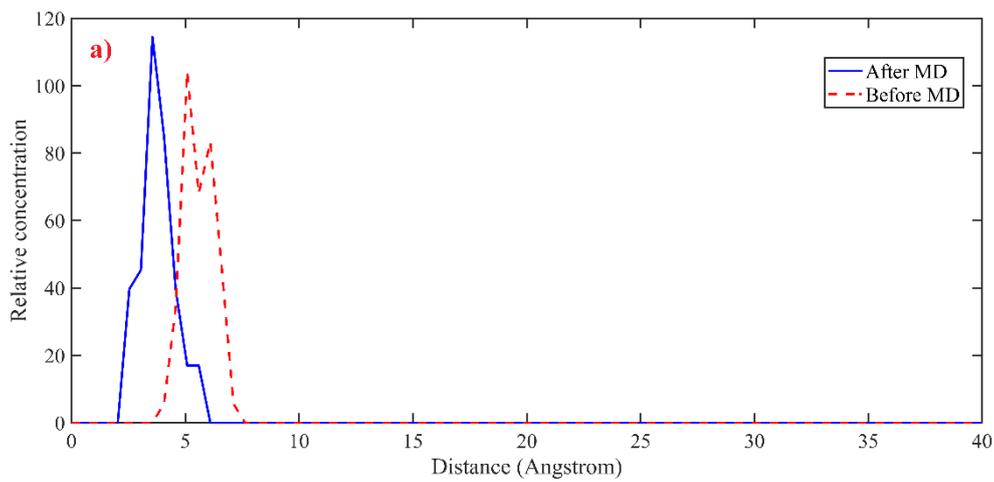


Figure 6. The configuration of biopolymers on Fe_3O_4 surface in *vertical* configuration; a) GT, b) Pectin and c) Carrageenan. (I: before MD, II: after MD)

In order to study the polymers chain morphologies, the concentration profiles were used to analyze the distribution of carbon atoms around the Fe_3O_4 surface as the resemblance of interfacial distances which occurs at the pick of the relative concentration profile. In the following, the concentration profiles of the carbon atoms of the polymer chains were depicted in Figs. 7 and 8 for better illustration of the polymers' adsorption on the Fe_3O_4 surface and understanding the chains morphologies. These profiles illustrate the distribution of carbon atoms (as the representative of the whole polymer) along the axis normal to the Fe_3O_4 surface, before and after MD simulations. As depicted in Fig. 7, after NVT ensemble, the carbon atoms of the polymer chains have been dispersed in a narrower band (2.04-6.11 Å for GT, 2.05-7.17 Å for pectin and 2.02-7.07 Å for carrageenan), in comparison to the state before MD simulation (3.56-8.14 Å for GT, 3.08-7.17 for pectin and 2.53-7.58 Å for carrageenan). The first peak of the concentration profile reflects the nearest distance between the Fe_3O_4 surface and carbon atoms. For horizontal configuration, after dynamics runs, the first peak corresponding to GT, pectin and carrageenan is respectively located in 3.56 Å, 3.59 Å and 3.03 Å; whereas, before

MD simulations it is located in 5.08 Å, 5.13Å and 5.05Å, respectively. For vertical configuration, after dynamics runs, the first peak corresponding to GT, pectin and carrageenan is respectively located in 4.21 Å, 4.60 Å and 3.53 Å; while, before MD simulations it is located in 5.23 Å, 5.63Å and 5.04 Å, respectively. The obtained results show that, in both the horizontal and vertical configurations, all of the polymers have well adsorbed on the Fe₃O₄ surface. The comparison between first peak locations of various polymers indicates that there is a closer contact between Fe₃O₄ surface and carrageenan atoms, followed by GT and pectin, respectively. The closer are the polymer chains to the Fe₃O₄ surface, the stronger is the interaction between them. This conclusion is consisted with the calculated interaction energies, as described earlier.



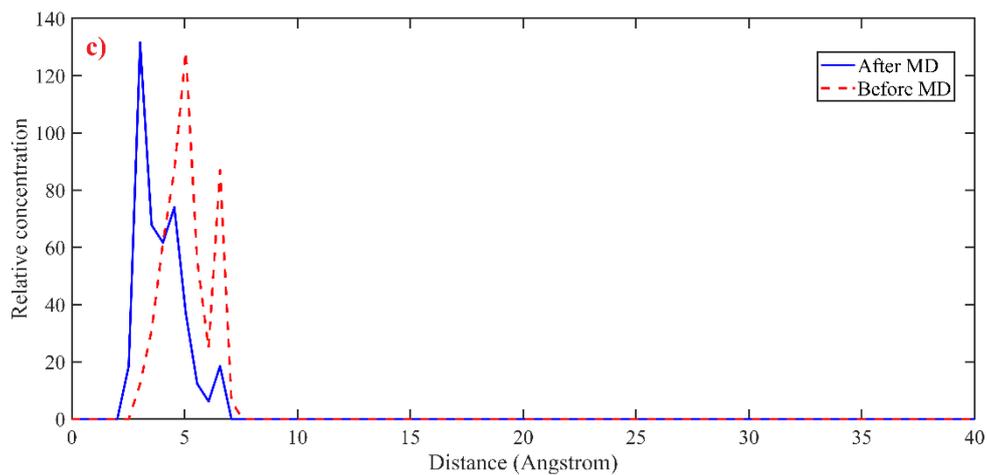
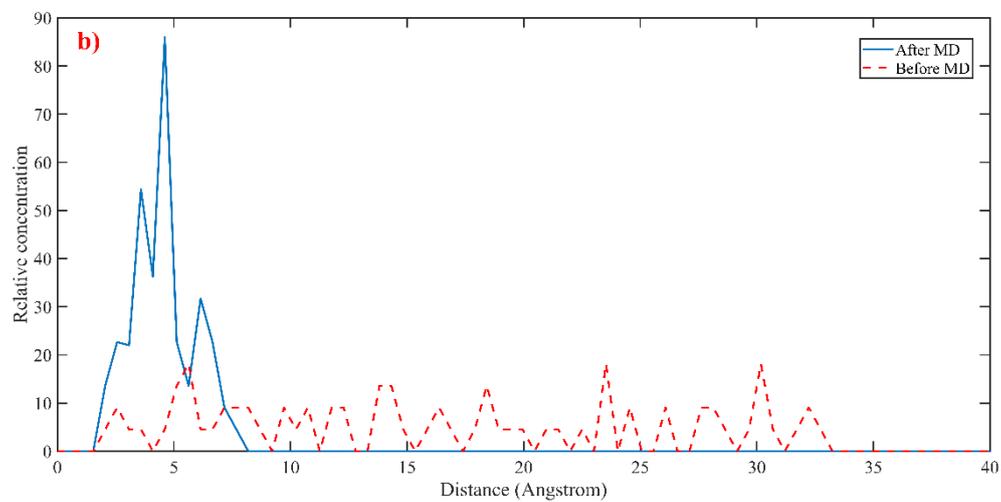
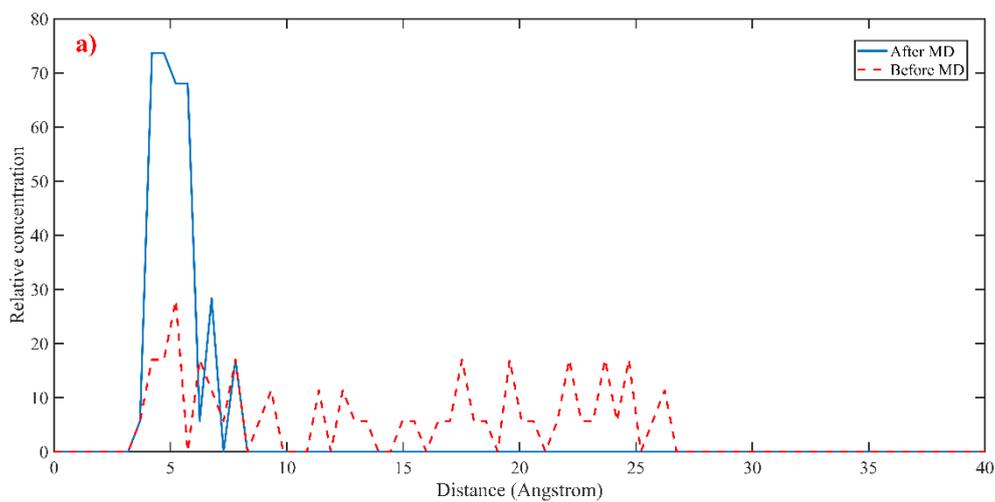


Figure 7. The concentration profiles of the carbon atoms of the polymer chains before and after MD simulations chains for *horizontal* configuration; a) GT, b) Pectin and c) Carrageenan.



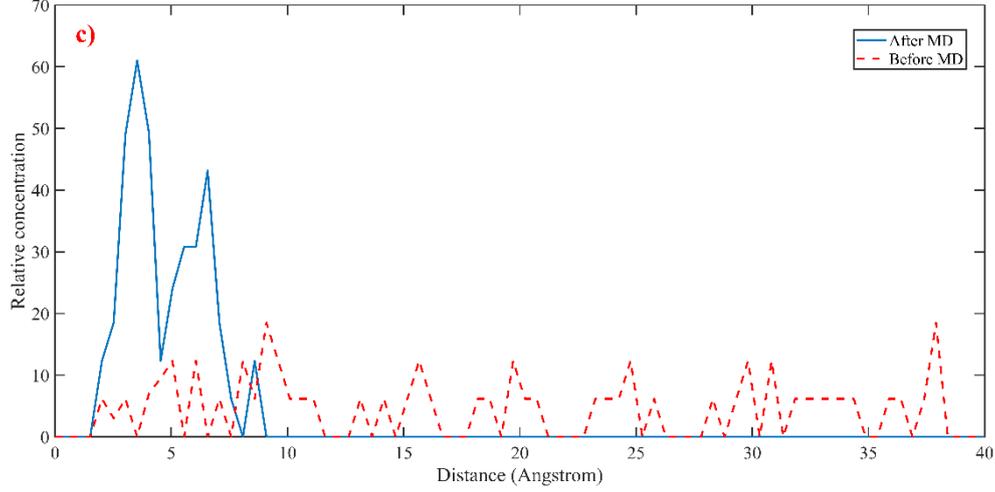


Figure 8. The concentration profiles of the polymer chains for *vertical* configuration, before and after MD simulations; a) GT, b) Pectin and c) Carrageenan.

The radial distribution function (RDF) was applied to analyze the details of Fe₃O₄/biopolymers interactions in the atomistic level. RDF provides an estimation of the possibility of finding another atom at a specified distance from a reference atom, as explained by Eq. (6):

$$g(r)_{A-B} = \frac{\left(\frac{n_B}{4\pi r^2 dr}\right)}{\left(\frac{N_B}{V}\right)} \quad (6)$$

where, $g(r)$ is the radial distribution function, n_B denotes the number of B atoms surrounding A atoms at a distance r , N_B is the total number of B atoms and V is the volume of the system. In order to study the interaction mechanisms of Fe₃O₄/biopolymers at the atomistic level, the radial distribution function (RDF) was employed. The RDF reflects the essence of the intermolecular forces of the interface (such as van der Waals forces, hydrogen bond, etc.), which are principally because of the interaction among the active atoms on polymer chains and Fe₃O₄ surface. Generally, peak values less than 3.5 Å are related to hydrogen bonds or chemical bonds; while, the values more than 3.5 Å are associated with van der Waals forces [17]. The RDF curves between various atoms of the biopolymers and Fe₃O₄ are illustrated in Figs. 9 and 10. The first peak corresponding to oxygen atoms of Fe₃O₄ surface and oxygen atoms of GT, pectin and carrageenan is located in 2.37Å, 2.45 Å and 2.24 Å, respectively. The first peak of oxygen atoms of Fe₃O₄ and hydrogen atoms of GT, pectin and carrageenan is located in 1.65Å, 1.56 Å and 1.25Å, respectively. These distances confirm the formation of hydrogen bonds

between oxygen and hydrogen atoms of biopolymers and oxygen atoms of Fe_3O_4 . In a similar study performed on the adsorption of other polymers (such as chitosan and dextran) on Fe_3O_4 (1 1 1) surface [11,12], the interaction between Fe_3O_4 surface and dextran and chitosan was reported to be due to hydrogen bond formation between oxygen atoms of Fe_3O_4 and the hydroxyl and amino groups of the polymers. According to the RDF analysis, it was revealed that the first peak location of oxygen/nitrogen atoms on chitosan and dextran were at about 2.85 Å, which is very close to the average distance between hydrogen bond acceptor and donor. By comparing the heights of the first peaks, the possibility of hydrogen bond formation can be analyzed for various polymers. As illustrated in Fig. 9, carrageenan has the maximum peak intensity (height), followed by GT and pectin. Hence, it can be concluded that the probability of hydrogen bond formation has the order of: “ $\text{Fe}_3\text{O}_4/\text{carrageenan} > \text{Fe}_3\text{O}_4/\text{GT} > \text{Fe}_3\text{O}_4/\text{pectin}$ ”. Looking back to the RDF curves shown in Fig. 9 reveals that there are some other peaks located in the distance more than 3.5 Å, which indicates the presence of van der Waals forces between oxygen and hydrogen atoms of the polymers and oxygen atoms of Fe_3O_4 .

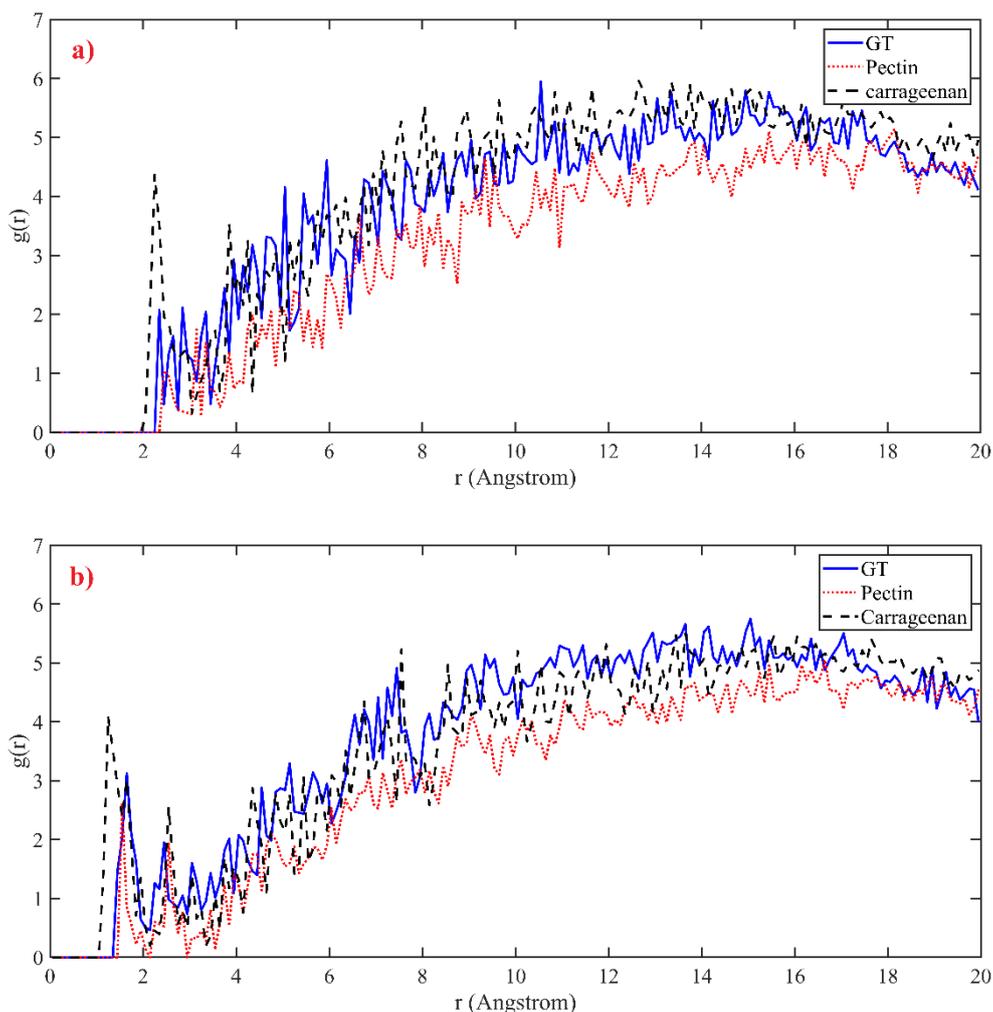


Figure 9. RDF curves between oxygen atoms of Fe_3O_4 with: a) oxygen and b) hydrogen atoms of different biopolymers in horizontal configuration.

In order to explore the possible interactions among the other atoms, the RDF curves between oxygen atoms of the biopolymers and iron atoms of Fe_3O_4 were investigated, as shown in Fig. 10a. The first peak corresponding to iron atoms of Fe_3O_4 surface and oxygen atoms of GT, pectin and carrageenan is located in 2.84 \AA , 2.95 \AA and 2.63 \AA , respectively; which reflects the existence of some interactions between iron atoms of Fe_3O_4 and oxygen atoms of the polymers. Also, the RDF curves between sulfur atoms of carrageenan and iron atoms of Fe_3O_4 surface were depicted. As shown in Fig. 10b, the first peak of the curve is located in 3.35 \AA ; indicating that some hydrogen bonds have been formed between these two atoms, leading to stronger binding between carrageenan and Fe_3O_4 surface.

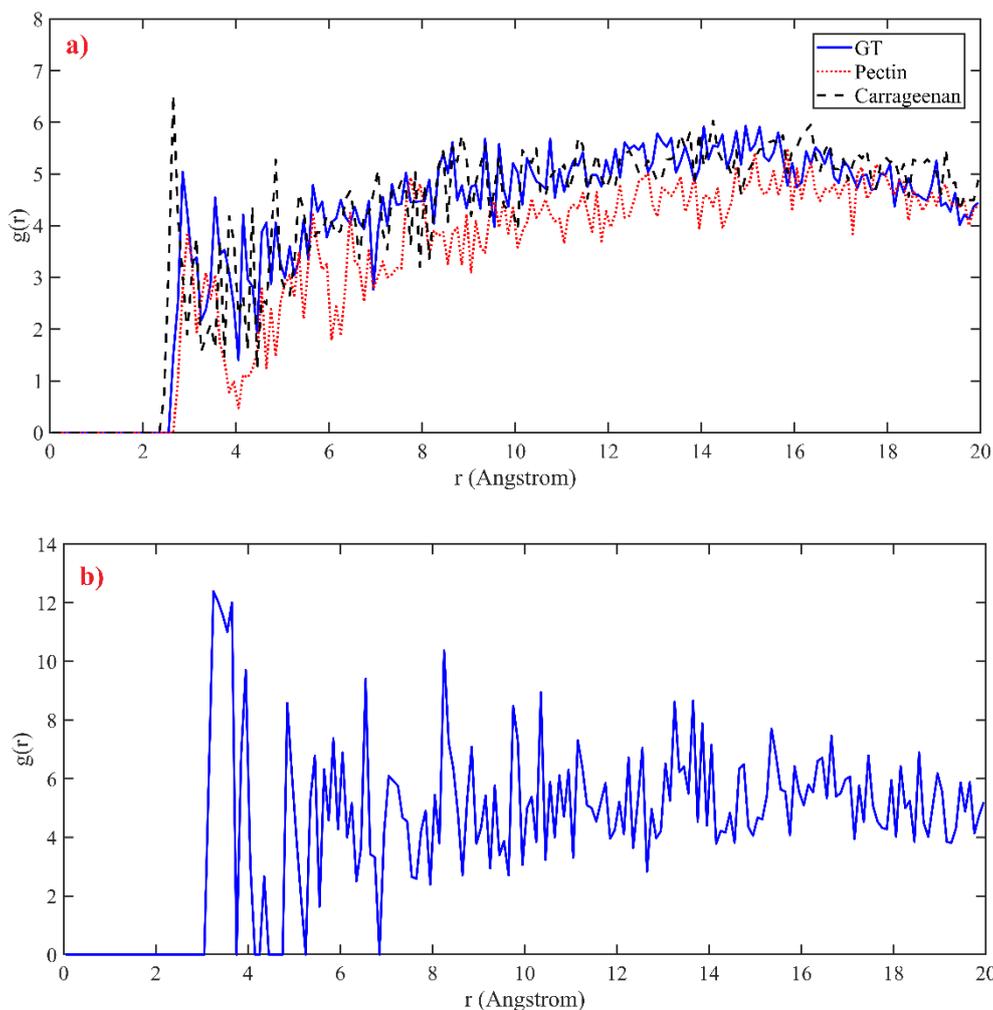
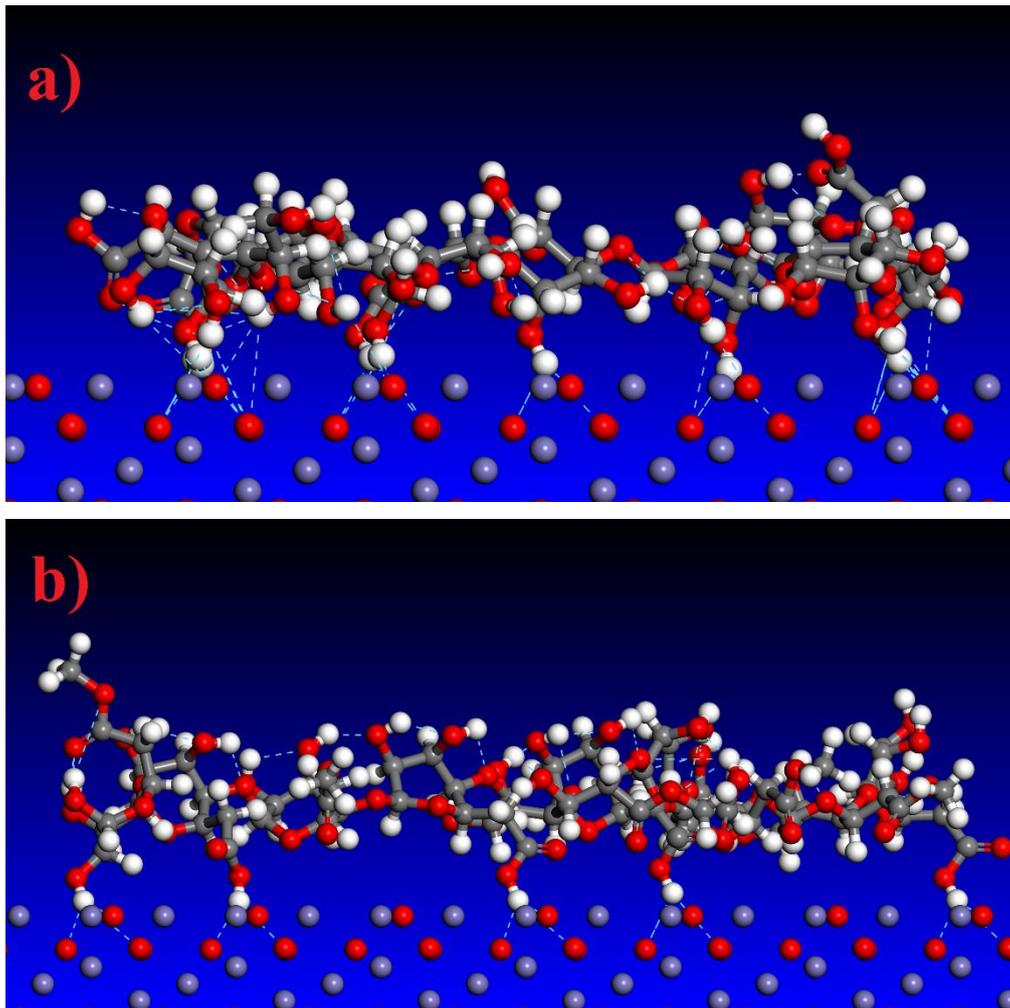


Figure 10. RDF curves between iron atoms of Fe_3O_4 with: a) oxygen atoms of the biopolymers and b) sulfur atoms of carrageenan in horizontal configuration.

All of the above-mentioned observations (i.e., concentration profiles, interaction energies and radial distribution functions) indicate that the biopolymers have been well adsorbed on the Fe_3O_4 surface, as a result of the interaction between the active atoms of the polymer chains and Fe_3O_4 . Generally speaking, depending on the starting points, cut off parameters and coefficients of the selected force fields and simulated atoms, the intermolecular interactions, i.e., Vdw and electrostatic, acts and results in the adsorption of polymer on the surface. Considering the interfacial distance, H bonds may be formed or break between atoms of polymers and magnetite surface. As the simulation continues enough, the attractive and repulsive force in Vdw interaction together with electrostatic interaction between partial charges of atoms and H bonds reaches an equilibrium magnitude and results in the interaction force with equilibrium interfacial distance. Vdw interaction force and electrostatic interaction act over all atoms of polymers and the outer surface of magnetite while some H bonds remain intact as equilibrium interfacial distance is achieved as demonstrated in Fig. 11 which led to the strongest binding of $\text{Fe}_3\text{O}_4/\text{carrageenan}$, followed by $\text{Fe}_3\text{O}_4/\text{Gum Tragacanth}$ and $\text{Fe}_3\text{O}_4/\text{pectin}$, respectively.



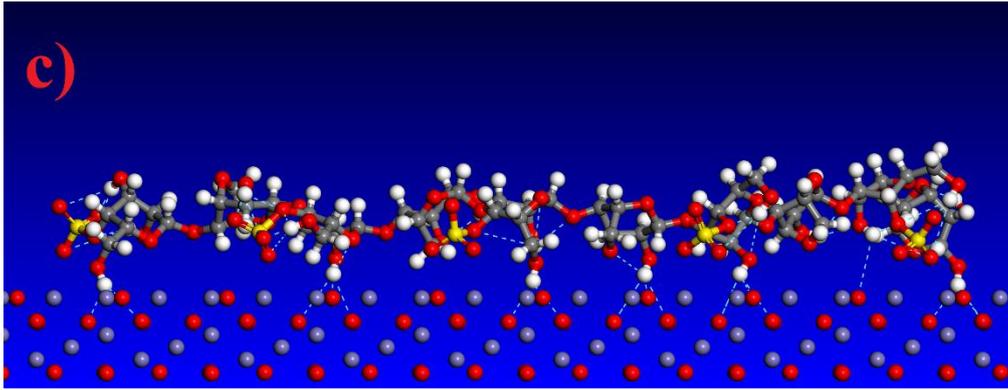


Figure 11. Hydrogen bond formation in horizontal configuration.; a) GT, b) Pectin and c) Carrageenan.

4. Conclusions

The main purpose of this research was to simulate the adsorption process of three different biopolymers (Gum Tragacanth, pectin and carrageenan) on Fe_3O_4 nanoparticles through MD simulations. In this regard, the interaction mechanisms among the biopolymers and Fe_3O_4 were comprehensively investigated based on the interaction energies, concentration profiles and radial distribution functions. In order to incorporate the effect of starting points, for each model, several simulations with various starting points were performed then the results were averaged. The simulation results revealed that the biopolymers were well adsorbed on the Fe_3O_4 surface, as a result of the interaction among the active atoms of the polymer chains and Fe_3O_4 . These interactions were mainly caused by hydrogen bonds formation and van der Waals forces. Based on the calculated binding energies for both horizontal and vertical configurations, it was seen that the strongest binding belongs to Fe_3O_4 /carrageenan followed by Fe_3O_4 /GT and Fe_3O_4 /pectin, respectively. Making a Comparison between the interaction energies of the two vertical and horizontal configurations, demonstrated that GT and Pectin adsorbed on the surface stronger in vertical configuration than that in horizontal configuration. In vertical configuration, the binding energies of GT and Pectin were 46.23% and 59.42% more than that of horizontal configuration, respectively. However, for carrageenan, the binding energy in the case of vertical configuration was 69.73% less than that of horizontal configuration. According to the concentration profiles, after NVT ensemble, the carbon atoms of the polymer chains were dispersed in a narrower band, in comparison to the state before dynamics runs, for both horizontal and vertical configurations. Also, according to the RDF results, the first peak of oxygen atoms of Fe_3O_4 and hydrogen atoms of GT, pectin and carrageenan is located in 1.65Å, 1.56 and 1.25Å, respectively. These distances confirm the formation of hydrogen bonds

between oxygen and hydrogen atoms of biopolymers and oxygen atoms of Fe₃O₄. There were also some other peaks located in the distance more than 3.5 Å, which indicates the presence of van der Waals forces between oxygen and hydrogen atoms of the polymers and oxygen atoms of Fe₃O₄. Vdw interaction force and electrostatic interaction act over all atoms of polymers and the outer surface of magnetite while some H bonds remain intact as equilibrium interfacial distance is achieved, which led to the strongest binding of Fe₃O₄/carrageenan, followed by Fe₃O₄/Gum Tragacanth and Fe₃O₄/pectin, respectively. The first peak locations of RDF curves revealed the existence of some interactions between iron atoms of Fe₃O₄ and oxygen atoms of the polymers. The comparison between the first peak locations of various polymers indicates that there is a closer contact between Fe₃O₄ surface and carrageenan atoms, followed by GT and pectin, respectively. The closer are the polymer chains to the Fe₃O₄ surface, the stronger is the interaction between them.

Declarations

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Data Availability

The datasets generated during the current study are available from the corresponding author on reasonable request.

Authors' Contributions

Conceptualization, Formal Analysis, Methodology and Writing original draft were performed by [Farzad Pashmforoush]; Data curation and supervision were done by [Shahram Ajori].

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