

BOMD study on the reaction among one amaranth dye molecule and one chitosan repetitive unit

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Abstract: The interaction between the reactants formed by a repeating unit of chitosan (adsorbent) and an amaranth dye molecule (adsorbate) is calculated using Born Oppenheimer Molecular Dynamics (BOMD) to determine possible adsorption. The attack of the adsorbent to the adsorbate is oriented between NH₂ and OH of the functional group of C₁₄H₂₄N₂O₉ chitosan repetitive unit and the functional group of SO₃Na sodium sulfonate dye. The electronic effects in the calculation of the dynamics are useful to determine the way these molecules interact. In the first model, it is observed the breakage of a sodium-oxygen bond and another of sulfur-oxygen, belonging to the dye molecule with a reorganization of hydrogens in the chitosan repetitive unit functional group. This shows that there are changes in the site where dye adsorption is predicted on chitosan assuming that the molecules are at neutral pH. For the second model it is observed that the collision of the dye molecule shows repulsive effects by the chitosan repetitive unit forming a deviation angle less than 90°. For this study, DFT was used with exchange and correlation using DZVP basis set function.

Keywords: Chitosan, amaranth dye molecule, adsorption, Born Oppenheimer Molecular Dynamics, Density Functional Theory.

Introduction

The study of water pollution has been of great interest nowadays due to the difficulties caused by its treatment, especially when its pollutants are azoic dyes that generally come from the manufacture of products from the textile, leather, paper, plastics industries, pigments, etc. Among these is the azoic dye amaranth also known as red dye No.2 E123 and Red 9 in food, it is a synthetic anion dye, widely used in foods and beverages such as wines, confectionery, cereal, salads, sweets, caviar and coffee to make it more appetizing ¹. It is also widely used to color textiles, paper, wood, leather and formaldehyde-phenol resins. During this process, the excess of dye reaches the residual water ^{2,3}. When discharged into the bodies of water without previous treatment, the residual water contained in the dye affects the aesthetics and transparency of the water, which blocks the penetration of sunlight and oxygenation, which is very dangerous for aquatic life ⁴. Another consequence of the use is that it can cause adverse health effects, such as tumors, allergies, respiratory problems, birth defects, mutations and cancer, among

other things ^{1,5,6}. The anionic dye amaranth is highly soluble and stable in water, reason why it is difficult to remove it from the wastewater of industries ⁵.

Conventional treatment methods for the elimination of dyes, such as chemical coagulation, activated sludge, biodegradation, oxidation, membrane separation, adsorption and photodegradation, have been extensively explored ⁷. However, they have not been very effective due to a large number of aromatic rings present in the dye molecules ^{8,9}. Among the physical and chemical methods, adsorption process is an effective and economical method and produces high-quality effluents to decontaminate the water without the formation of harmful substances ⁷, so it is proposed to treat the problem by adsorbing the amaranth azoic dye by chitosan.

Chitosan is an amino polysaccharide obtained from the deacetylation of chitin, which is one of the most abundant polysaccharides in nature after cellulose ¹⁰, it is used as one of the most popular adsorbents that eliminate metal ions and dyes from aqueous solutions ^{7,9}.

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Also, chitosan has been widely used in waste treatment applications. However, the conditions of the solution, about its pH, ionic strength, temperature and the presence of impurities are some of the factors that influence the adsorption on chitosan⁹. As results of researches, the adsorption of pollutants increases temperature because it provides a faster molecule diffusion to be adsorbed adsorbent solution¹¹. Considering that dye adsorption is normally exothermic, the temperature also increases the rate of adsorption in parallel decreases the adsorption capacity^{12,13}. Variations in temperature do not significantly affect the discoloration of pollutants water with the dye¹². Also, adsorption processes are not usually handed at high temperatures due to the increase in operating costs¹⁴. When temperature increases the capacity of adsorption and solubility decreases, becoming only a physical phenomenon and not thermodynamic. So the interaction force between the dye and the solvent for the case of water presents an increase, having a greater difficulty to adsorb material pollutants¹⁴.

On the other hand, the distribution of charge in the hydroxyl groups in the chitosan gives criteria on an attractive interaction on the dye. However, the amino groups of this polymer used as adsorbent are the main active group for the adsorption of dyes¹⁵. The adsorption process can occur through a single functional group or in a combination of the hydroxyl (OH) and amino (NH₂) group that may or may not be protonated in this scheme the reaction on several parameters depending on the contaminant¹⁴. The amino group was the main active group for the adsorption of dyes, although the hydroxyl group (especially positioned at carbon 3) could contribute to the adsorption and intermolecular interaction of the dye molecule^{16,17}.

In this work, energy calculations were performed under the molecular dynamics scheme in the interaction between a chitosan unit and one amarant dye molecule, considering two models for determining both structural and electronic changes and correlate them with the total energy values of the system. The changes in the values of the energy obtained at each instant in the dynamics allow knowing in which moment of the simulation the azoic dye at neutral pH presents adsorption on the chitosan. These energy changes also determine structural changes going out from interaction between molecules generating evaluation criteria when there is attraction or repulsion among nearby neighboring atoms. Given the number of atoms and electrons in molecules, the atomic bond changes occurring are not precisely determined as adsorption energy or activation explicitly due to a poor visualization to identify bond changes at each instant, and by the degrees of associated freedom each time. However, a detailed structural analysis is made on the first model (model i), noticing that there are structural changes in the molecule, which are associated to a chemical

reaction by observing breakdown sodium-oxygen and sulfur-oxygen bonds of the dye molecule, as well as changes of the bonds of hydrogen with nitrogen the functional group of the chitosan unit. In the second model (model ii) observing that the interaction of the dye molecule does not present an attractive interaction, given that when one molecule attacks on the other in order to collide, an angle of deviation is observed, which it is assumed to present a repulsion of the repetitive unit of chitosan (RUC) for this preferential interaction direction. In the molecular dynamics calculations, it is applied the Born-Oppenheimer approximation within the Density Functional Theory using the corresponding exchange and correlation functional.

Models and Methodology

To obtain stable structures, geometry optimization calculations were carried out on the model molecules associated with an ADM and a RUC, using DFT. Optimized molecules were considered to develop dynamics calculations, and to determine structural and electronic properties of the interaction for these models i and ii. Calculations include effects of electronic correlation, in addition to orbital spin corrections at the DFT level. The code implemented in NWChem¹⁸ software reveals accesses to different modules, among them the dynamic one. In the task where DFT is used at input file, gradient correction method is chosen with exchange Becke 88 functional¹⁹, and Lee Yang-Parr (LYP) functional²⁰ is chosen for correlation. These together make up the exchange and correlation Becke88-LYP functional, which is the same used for geometry optimization, as well as in dynamic interaction study. The bases function double numerical zeta with polarization (DZVP) are useful in this type of interaction calculations between molecules. The Density Functional Theory (DFT) is appropriate for determining structural and the electronic property changes with excellent accuracy. In the case of the RUC interacting with ADM, they were used to study dynamic interaction, the initial point is considered when there is a separation between the two representative molecules. They were chosen in the interval of a Cartesian step maximum 0.0015 Bohr and a convergence 0.0015 Hartree/Bohr for the energy gradients. In the interaction, it is chosen that the dynamics allow knowing the nature of the particles associated with the nuclei; it is at this point when a deeper understanding of dissociation mechanism and the bonds at atomic systems is obtained²¹. These bond changes can be associated as reaction mechanisms, under the Born-Oppenheimer approach^{22,23}. Another selection is that the whole system is not charging with a neutral charge, and with a multiplicity of 1. The electronic wave function is obtained under an assumption where electrons are immersed in a field of instantaneously fixed nuclei, indicating that the nuclei are immersed in an average

electronic field. For the nuclei their masses and the spatial part are relatively short in comparison with the electrons, this simplifies the methodology when considering the nuclei as a classical particle. In the analysis of the dynamics, the temperature ensemble is constant using Berendsen's thermostat, where is the external temperature with a default of 298.15 K, each nucleus follows a Newtonian trajectory due to the quantum forces derived from the potential of the electron plus the electrostatic force exerted by the other nuclear particles. The step time in dynamics is 1 fs. The self-consistent approach is considered to be converged or terminated when the tolerance is of the order of 10^{-5} for both energy and density ²⁴.

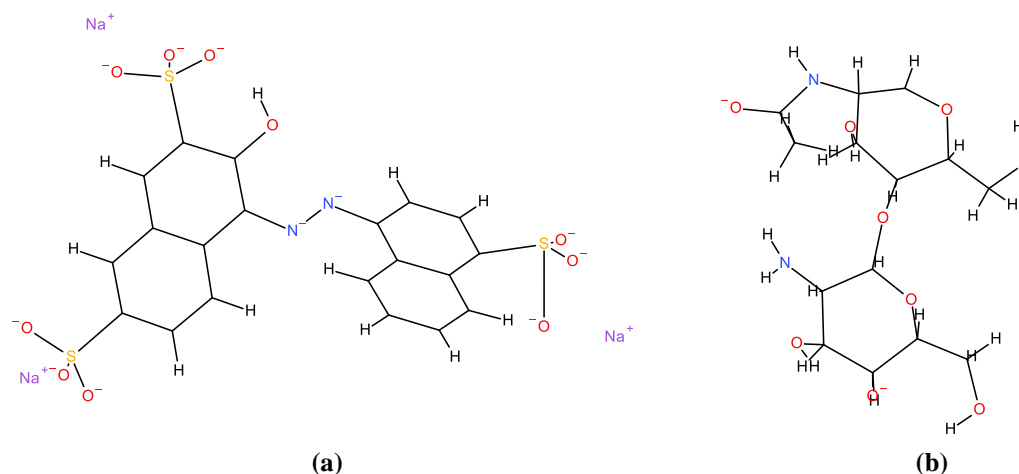


Figure 1. Charge distribution in the optimization result applying DFT to: (a) ADM and (b) RUC

On the one hand, in a dynamics study, it was considered to place an orientation by selecting functional groups SO_3 at the front of the dye, in a collision direction against NH_2 of chitosan for model i. In the case of model ii, the orientation at the starting point was considered as SO_3 against OH on the RUC, with a considerable separation between both, simulating a gaseous state of the system. During the dynamics, the energy values calculated are reported in the graph of Figure 3. The variables are total energy and time. The graphs of the total energy as a function of time were made for both models i and ii; the molecules have different changes in the molecular structure of the dye and the RUC. Considering the quantity and size of atoms involved in the interaction, it is important to take criteria in the preferential direction for the molecular interaction.

Interaction between the ADM and the NH_2 of the RUC for model i

The molecules with a RUC and ADM have been considered as model i; the possible collision was selected in the direction of the functional groups SO_3 of the dye against the NH_2 of the chitosan. Figure 2 reports the different structural changes occurring when these molecules interact. Along dynamics simulation, changes involved in the length of atomic bonds are observed, and at the end, the possible

Results and Discussion

The stable structures obtained by the optimization calculations of the ADM geometry and the RUC using DFT are shown in Figure 1.

It is observed that in Figure 1(a) the sodium atom in dye molecule is released by the stability of the molecule after optimization, but it is kept close to the oxygen by van der Waals forces. Figure 1(b) shows the result of the optimization of RUC by DFT. Both molecules are those that were initially split by dynamics study.

reaction products. This analysis considers intervals of 50 fs as is to be described.

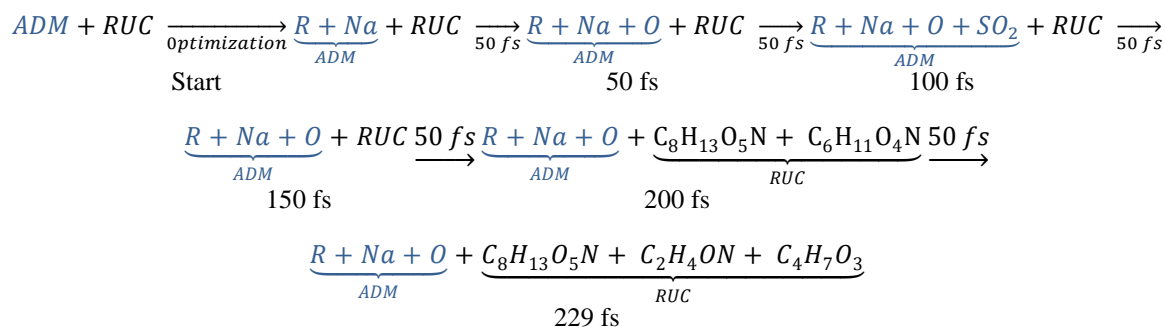
As a starting point we have the molecules separated at certain distance (Figure 2a), between SO_3 and NH_2 is around 6.5 Å, and we observe instants later in the calculation of the dynamics, the distance of $\text{S1-O3} = 9.7$ Å, $\text{S1-H10} = 9.6$ Å, $\text{O1-O3} = 10$ Å, $\text{O1-H10} = 9.8$ Å, $\text{O2-O3} = 9.8$ Å, $\text{O2-H10} = 9.7$ Å and $\text{O3-H10} = 8.4$ Å, an interaction where bonds oxygen-sulfur and oxygen-sodium reach a distance that implies a breaking.

In the interval 1-50 fs, oxygen-sulfur bond (labelled 1) grows up to break. Then oxygen-1 remains oriented to RUC (Figure 2b). From 50 to 100 fs (Figure 2c) the carbon-sulfur bond (C3-S1) is broken, allowing as products of the initial dye molecule: SO_2 , O-1, Na-1, Na-2 and Na-3. In the range 100-150 fs (Figure 2d) the SO_2 released from the dye molecule re-joins carbon 3 due to the proximity of the functional group NH_2 of RUC. It is also observed that oxygen (O-5) detached from S-1 approaches the O-5 of RUC. Also at chitosan, the H-6 attached to C-4 is detached from it to join the O-2 of C-3, and there is a rearrangement of C-8, C-9 and C-10 as well as their respective hydrogens. In the range 150-200 fs, the SO_2 bound to the dye molecule is arranged to bind to the NH_2 of the RUC. To the latter the C-6—O-5 bond nearby to O-1 previously

detached from SO₃ of the ADM is broken. This provides two products of the RUC: C₈H₁₃O₅N and C₆H₁₁O₄N, as seen in Figure 2e. From 200 to 229 the orientation and closeness of the dye molecule with RUC produce another break carbon-carbon bond (C-4—C-5) fractionating RUC into three products: C₈H₁₃NO₅, C₂H₄NO and C₄H₇O₃, seen in Figure 2f. The bond distance when they present an increase from 3 angstroms is considered bond broken that has already been widely reported, in comparison of energy calculation results obtained for this collision

between the molecules are observed equivalent results showing that SO₃ and NH₃ are important of reaction to obtained products SO₂ and H₂NOH as results reported, confirming the importance of having a preferential orientation selected when the interaction between the functional groups SO₃ and NH₃ is carried out²⁵.

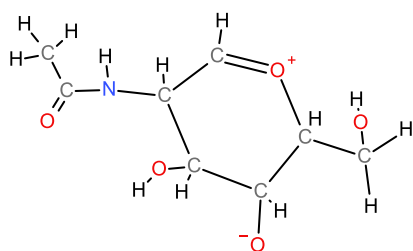
The changes occurred in the ADM and RUC molecules described above are summarized in the following reaction:



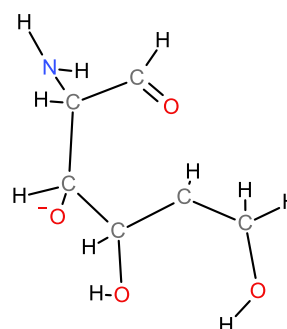
Where RUC refers to the repetitive unit of chitosan, ADM represents Amaranth dye molecule, R represents one part of the ADM. The latter remains when the sodium and oxygen atoms are released to

ADM, or when in addition to these two atoms the sulfur dioxide is also released at 100 fs.

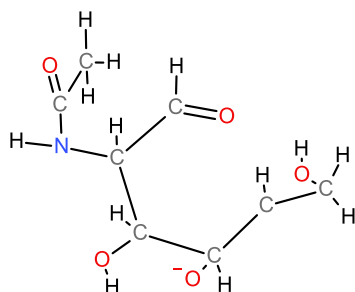
Where the products structure are:



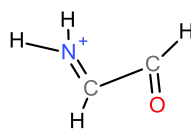
C₈H₁₃O₅N
(2S,3R,4R,5R)-5-acetamido-4-hydroxy-2-(hydroxymethyl)-2,3,4,5-tetrahydropyran-1-ium-3-olate



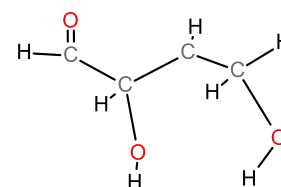
C₆H₁₁O₄N
(2R,3S,4R)-2-amino-4,6-dihydroxy-1-oxo-hexan-3-olate



C₈H₁₃O₅N
(3S,4R,5R)-5-acetamido-1,4-dihydroxy-6-oxo-hexan-3-olate



C₂H₄ON
2-oxoethylideneammonium



C₄H₇O₃
(2R)-2,4-dihydroxybutanal

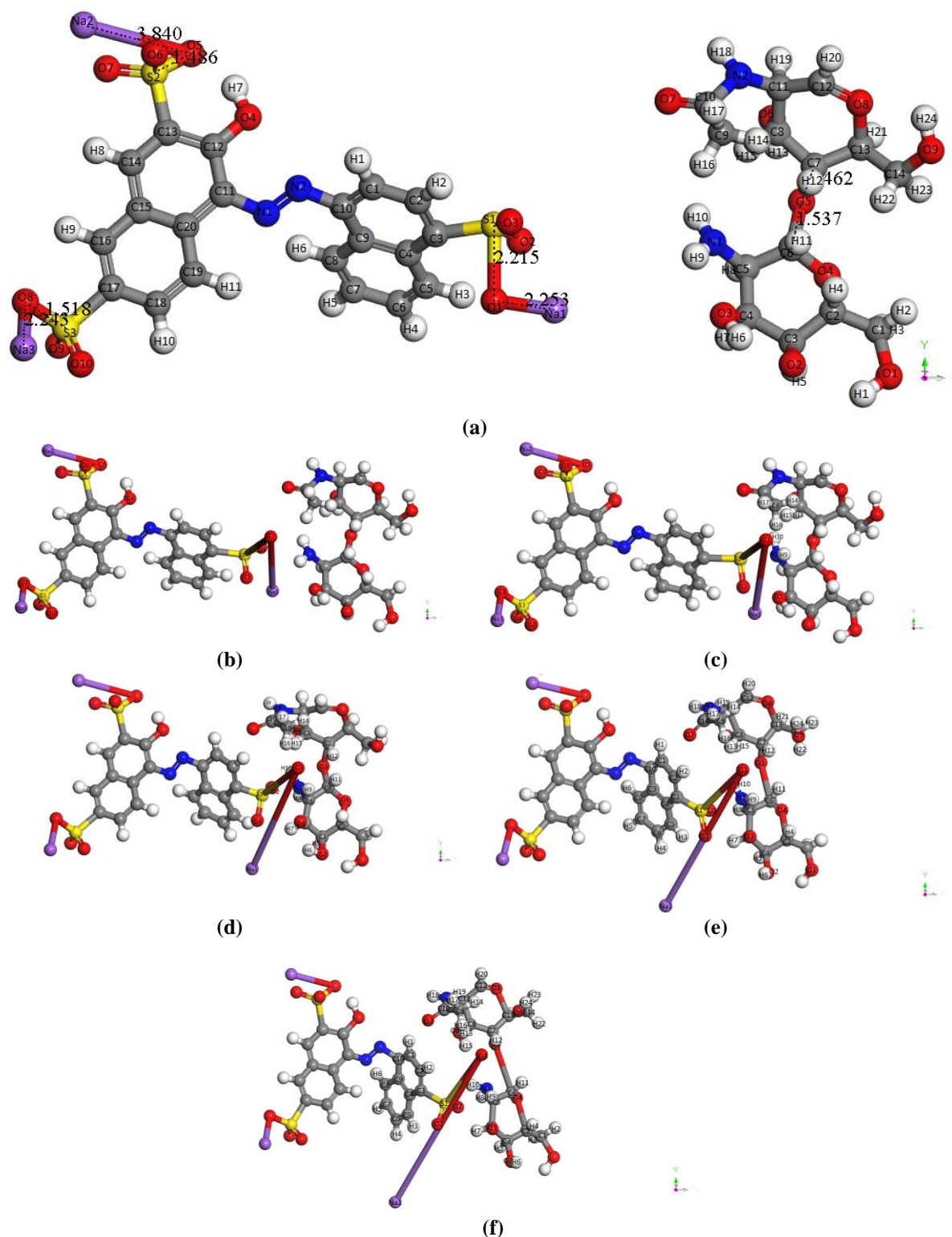


Figure 2. Case i. Dye molecule against the RUC (a) at the start of its study, (b) at 50 fs, (c) at 100 fs, (d) at 150 fs, (e) at 200 fs (f) at 230fs for the attractive position.

The interaction that simulates possible adsorption, it is represented graphically by the changes in energy due to changes in electronic structure and bond lengths (Figure 3). The energy changes are associated with the relaxation of the molecules, in particular angles variation are due to the interaction of the functional groups of RUC with

ADM for the first model. The NH_2 of chitosan is one of the adsorption sites of anionic contaminants.

In the initial stage of the dynamics, the NH_2 bonds maintain a stable length, while the lengths of the SO_3Na bonds increase as decreases the distance between the two molecules. A minimum energy value in the range 0-15 fs is observed when the interaction starts. This is associated with the movement of the

oxygen, carbon and hydrogen atoms of the ADM with a value of -87 kcal/mol. In the range of 20 to 50 fs a maximum value is obtained associated with the approach of RUC to the dye, so the hydrogen, oxygen and carbons of the dye start to vibrate with greater intensity. The representative values shown are mainly due to the variation of the bonds of the SO_3Na of the dye that is in front of the RUC, where there is an elongation of the oxygen bond and reduction of the bond of another oxygen that is bound to the sodium of the dye. The maximum energy of 25 kcal/mol indicates a change in bond lengths, lengthening an oxygen bond with the sulfur of the dye when approaching the RUC.

The energy of the system increases between 75 to 175 fs gradually as the dye approaches the RUC, until generating an energy barrier whose maximum value is 225 kcal/mol at 175 fs, this takes place when the SO_3Na that is in front of the adsorbent molecule presents changes in its bonds, mainly the elongation of the sulfur-oxygen bond, until considering the rupture of the sulfur-oxygen bond and another of sodium-oxygen. In the RUC, the reorganization of hydrogen, oxygen and carbons that make up the dye molecule takes place. Taking the molecules with a neutral pH, it is shown that there are changes just in the place where the adsorption of the dye is carried out on the chitosan. This agrees with experimental adsorption measurements carried out only at acid pH⁹.

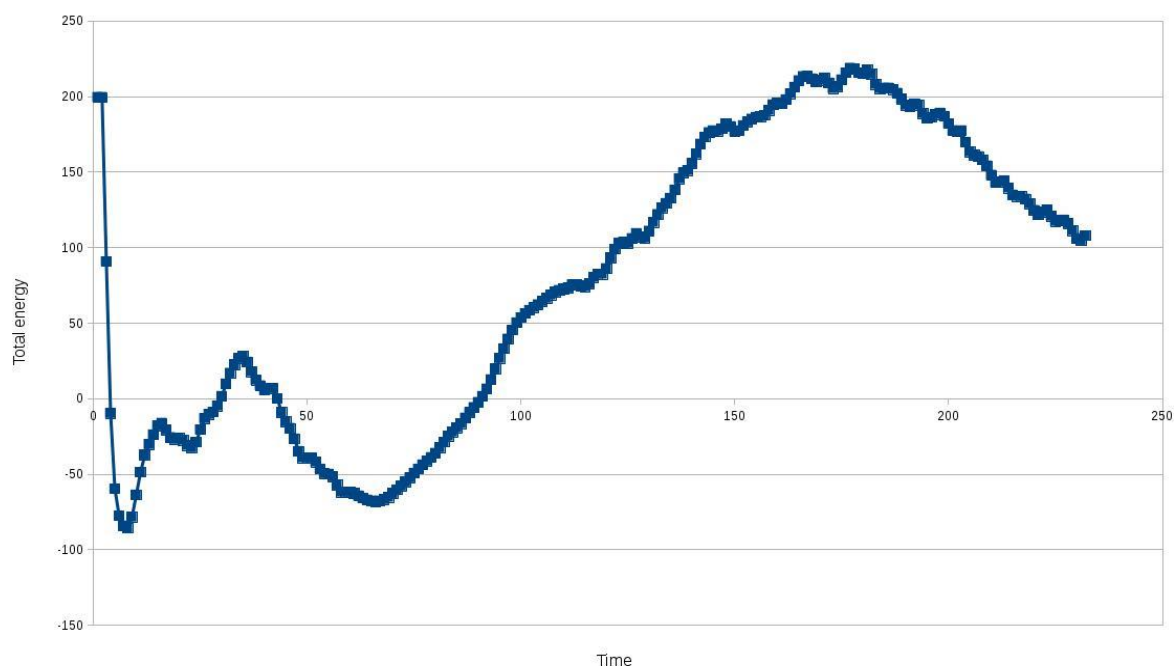


Figure 3. Generated graphic of attractive interaction

Impact of ADM on the OH of the RUC for model ii

In an equivalent manner to model i, dye molecule and RUC were placed with a considerable separation by situating SO_3 of dye against OH of RUC as shown in Figure 4a. As the dynamics run dye molecule approaches to RUC, causing different changes in its structure and bond lengths, but without reaching a representative breaking during the dynamics. The effect described above during dynamics provides criteria to mention that these two structures have a repulsive effect, that is, the dye molecule avoids collision with RUC, thereby indicating that ADM is not related to OH, nevertheless NH_2 does it is, as shown in the case of the previous model. Furthermore, the address taken by the dye seeking to the NH_2 , which has some affinity for the functional group SO_3 as shown in Figure 4b-i, where amaranth dye and chitosan molecules suffer several changes.

These different structural changes observed in the calculation of dynamics are outlined in Figure 4 as follows: Figure 4a shows how amaranth dye and chitosan molecules are found at the beginning. Figure 4b represents the change from the start to 50 fs where it is already observed that for the dye molecule there is a detachment of SO_3 when the C-3—S-1 bond breaks. Figure 4c does not show much change concerning 4b, which indicates that for the range 50-100 fs the variations are similar. From 100 to 150 fs (Figure 4d) the SO_3 functional groups of ADM come off, which indicates breakage of carbon-sulfur bonds, meaning the C-3—S-1, C-13 —S-2 and C-17—S-3 bonds were broken. Figure 4e shows the molecules at 150-200 fs, where two of the functional groups SO_3 of the dye rejoin the carbon from which they had separated, this happens because C-13—S-2 and C-17—S-3 bonds turn back to be together. In the range 200-250 fs (Figure 4f) ADM is again complete with the three functional groups attached to it as it was in the beginning, by also joining C-3—S-1 bond.

Although at this range, we must notice that as the dye molecule avoids OH functional group of RUC, the dye is addressed to seek NH_2 . From 250 to 300 fs (Figure 4g) dye molecule continued to progress without having an affinity for RUC. For the range, 300-350 (Figure 4h) the SO_3 functional groups of dye close to RUC are released from the dye molecule

indicating a breakdown of two of the carbon-sulfur bonds (C-3—S-1 and C-13—S-2). Finally, Figure 4i shows the molecules in the range 350-382 fs where the dye molecule at this range causes the RUC to split into two products when the carbon-oxygen bond breaks (O-5—C-9), leaving $\text{C}_6\text{H}_{11}\text{O}_4\text{N}$ and $\text{C}_8\text{H}_{13}\text{O}_5\text{N}$ (Figure 5).

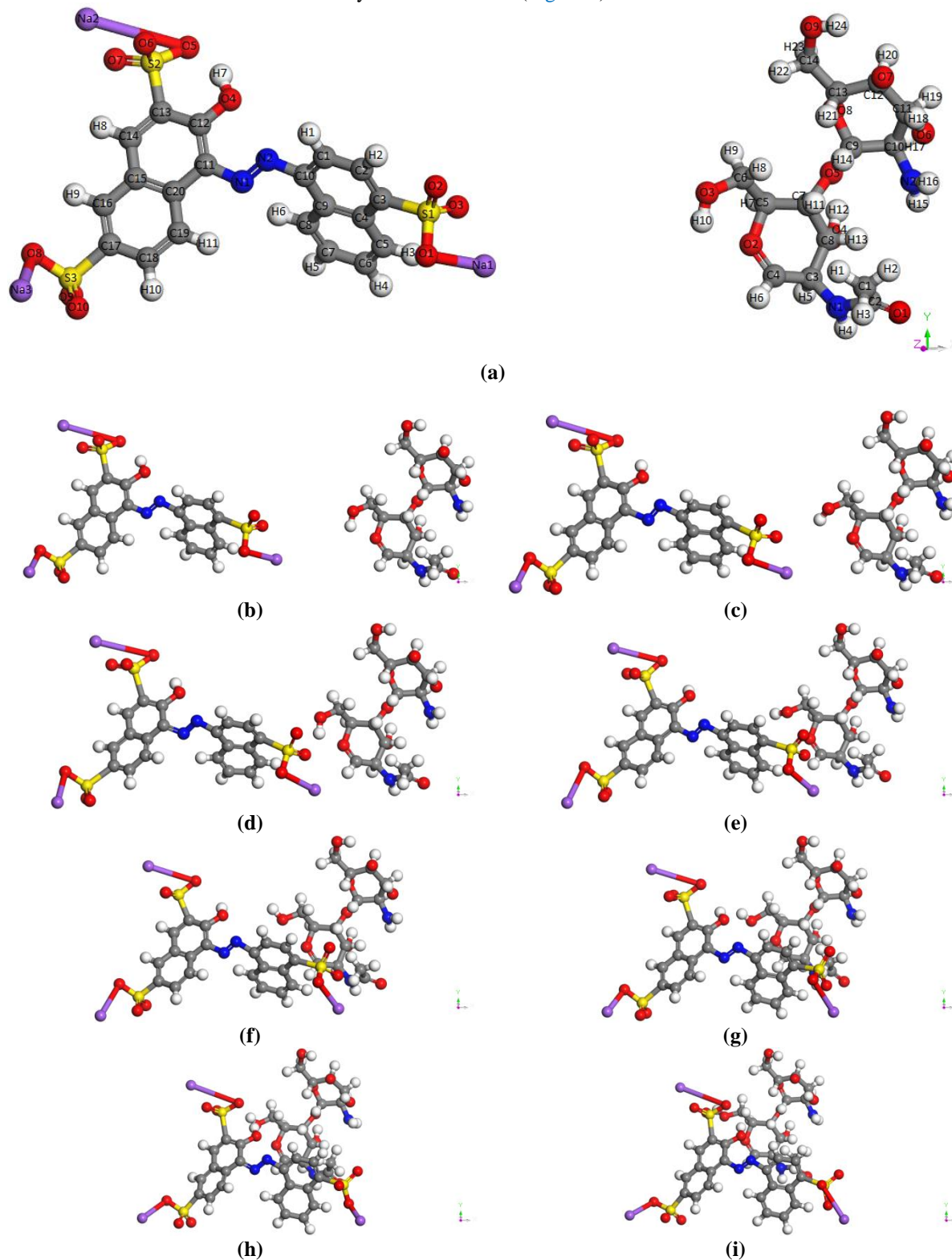


Figure 4. Case ii. Unattractive position of dye molecule against RUC (a) at the start of its study, (b) 50 fs, (c) 100 fs, (d) 150 fs, (e) 200 fs (f) 250 (g) 300 fs, (h) 350 fs and (i) 382 fs.

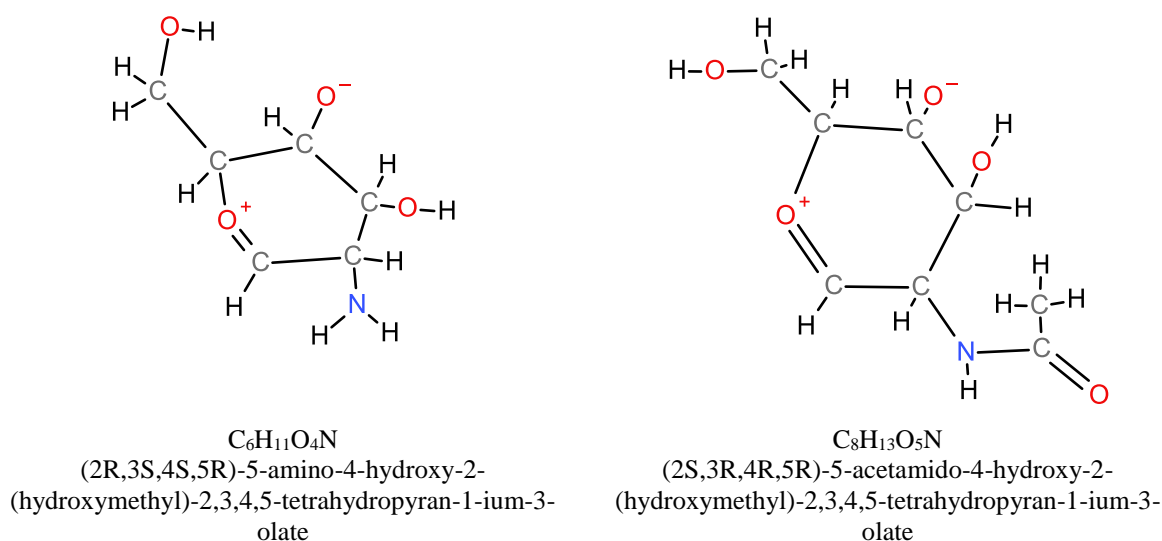


Figure 5. Products of RUC generated at 382 fs.

In the second model, energy values are plotted in [Figure 6](#) where changes in energies from the interaction between the two molecules are observed, all with respect to step time. This interaction presents important changes in comparison to the other model, reflected when the interaction of RUC with ADM is carried out. The OH of chitosan is one of the adsorption sites of anionic contaminants. For this case, it is observed that the collision of dye molecule is repelled from RUC forming an angle of deviation less than 90° .

In comparison to the previous model, several oscillations are observed throughout the simulation, indicating that in the simulation both molecules present a great variety of energy maximum and minimum values that are associated to the vibrations and modifications of atomic bonds between the two molecules during all exposure, what we see is that hydrogen, carbons, oxygen, sulfur and nitrogen are involved in energy changes.

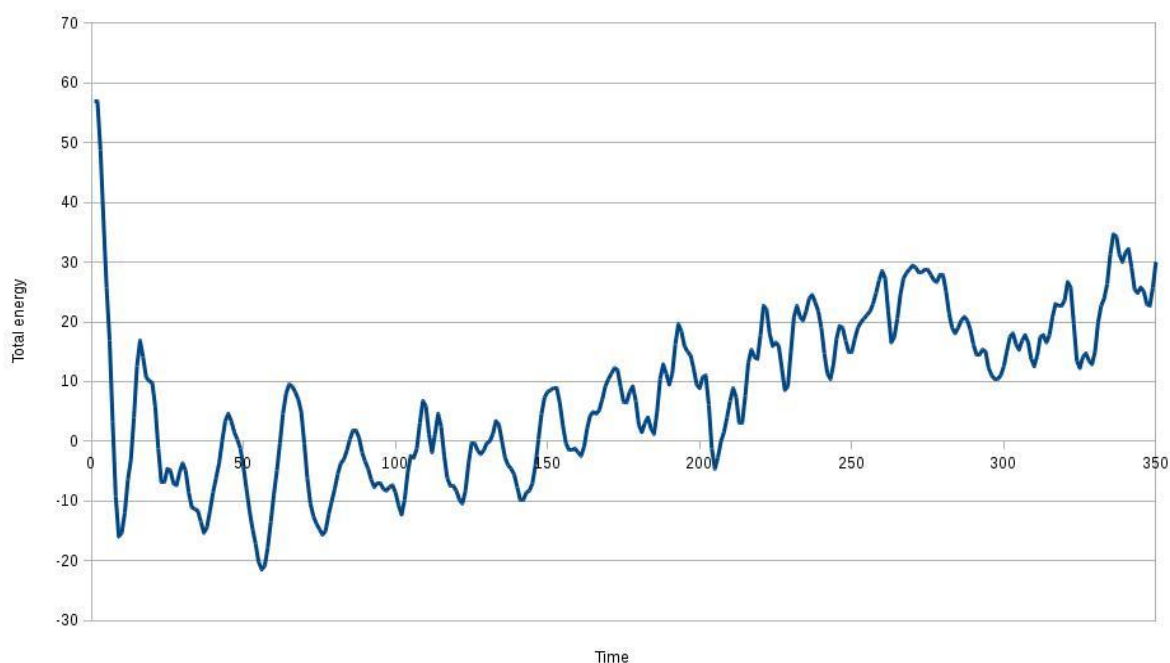


Figure 6. Generated graph of the repulsive interaction.

Conclusions

There is different freedom grade for atoms collision on molecules, considering the magnitude of molecules we only select two possibilities taking the

experimental results of other authors, where initial conformation are molecules obtained by geometry optimization calculation to get stable molecules. In the interaction between chitosan and colorant molecules, the results show structural changes in the

molecules. Thus determining the existence of a preferential direction in the interaction, that indicates the possibility of adsorption between the molecules for the different models that represent different parts of the interaction, showing that one of them has an attraction effect between the functional groups SO₃ and NH₂, and the other, one of repulsion between SO₃ and OH, of the dye and RUC respectively as initial stage.

The dynamics calculations provide the energy values obtained from the interaction between the ADM and the RUC, producing reaction mechanisms between each other, characterizing them by the atomic bonds growing to be considered as a bond break. In particular, the carbon-sulfur, sulfur-oxygen and oxygen-sodium bonds of the ADM were identified at a certain particular time. Bond breaks are also observed in the RUC, splitting the molecule into two products when carbon-oxygen bonds are broken, and up to three products when in addition to carbon-oxygen, a carbon-carbon bond also breaks. The results of the increase in the bond distance sometimes depend on the temperature but in this case, it corresponded to preferential interaction for an orientation found by elements that are the main promoters of the reactions indicating a temperature of 298.15 K can be found a reaction that allows modifying the dye without changing the ambient temperature.

The structural changes and the modification of the molecules to obtain fragments considered as products of the reaction, allow us to conclude that based on the results, the relative direction of interaction between the molecules occurs only for model i. For model ii, the ADM and RUC do not present reaction mechanisms that allow them to be considered as adsorption from their direct interaction.

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