Electronic Properties of Cellulose Through Molecular Modeling Technique for Wastewater Treatment

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ABSTRACT

Improvement of cellulose electronic properties is one of the promising strategies used in wastewater treatment. The aim of this work is to study the properties of cellulose (Ce) enhanced by combining with chitosan (Cs) and TiO_2 nano-particles, as molecular modeling using certain naturally revised blends can help in eliminating heavy elements from the waste-water environment. TiO_2, as water management mediators, was admitted in the chitosan/cellulose blend. The nano-component cellulose/ TiO_2 and cellulose/chitosan/TiO_2 (Ce/TiO_2 and Ce/Cs/TiO_2) was utilized to detect the optimized geometrical structures and some electronic properties of the samples.

The consequences of polymer nano-composites (PNCs) showed an expansion of the contact between the contiguous atoms when adjusting the optimized geometry, higher dipole moment, and lower ionization potential and slight HOMO-LUMO energy gaps compared to their original constituents of pure Ce. Thus, the ability of the nano-composites mix improved its ability to remove heavy-metal pollutants from wastewater.

Key Words: Cellulose/chitosan blend, Electronic Properties, Gaussian09, Nano-metal Oxide TiO_2.

INTRODUCTION

Water purification is the technique of eliminating undesirable biological contaminants, chemicals, suspended solids and some gases from water. The purification of wastewater is an ecological challenge. Using efficient of anti-bacterial systems can improve the standard of living, reduce environmental degradations, and encourage a healthier hygienic lifestyle. cellulose/ chitosan and polymeric materials are the major contenders of these anti-bacterial systems. Bio-degradable and alternative properties of both cellulose and chitosan encourage their use compared to polymeric materials (Blantocas *et al*., 2017). This kind of material is considered a potential source of low price, eco-friendly, cellulose-based adsorbents. Polymers such as cellulose (Ce) can easily be incorporated with nano-metal oxides. The chitosan/ TiO_2 compound nano-fibrous adsorbents is fabricated by two methods, namely TiO_2 coated chitosan nanofibers and entrapped method (Razzaz *et al*., 2016; Li *et al*., 2017) through site-directed surface oxidation chemistry, the hydroxyl groups of BC were successfully oxidized into aldehyde groups that served as anchors for covalent immobilization of laccase (Lac. Electrospun cellulose acetate/ TiO_2 adsorbents were set by the electrospinning method. The adsorbents were examined with the Brunauer-Emmett-Teller area examines, FTIR spectroscopy, field release FESEM, and X-ray spectroscopy characterization techniques. The influences of several adsorption factors like, pH, the quantity of TiO_2, interaction time, the kinetics of metallic element uptake, and temperature were determined through a set of adsorbent experimentations (Gebru and Das, 2017) Fourier transform infrared (FTIR. chitosan, due to the occurrence of hydroxyl and amine clusters, can be traditionally used for the excretion of heavy components from water (Aliabadi *et al*., 2014) cobalt and nickel ions from aqueous solution was investigated. The prepared nanofiber membranes were characterized by FTIR, SEM and BET analysis. A response surface methodology based on Box-Behnken Design (BBD). This was based on the results of interaction energies that energetic substances form steady complexes of cellulose and chitosan. These complexes became stable by making hydrogen bonding with adsorbates and adsorbents. Cellulose exhibit poor ability to eliminate the FOX-7, TNT, DNAN, and NQ munition composites from normal water solution (Gurtowski *et al*., 2017). Blantocas *et al*. (2017) proposed a molecular program package for this task with the objective to perpare theoretical modeling on the basis of the interaction of chitosan/TiO_2. A competent element adsorbent from quaternary ammonium cellulose was effectively established by the quick elimination of Cr from aquatic solution (Neagu, 2009; Taha *et al*., 2012; Zhou *et al*., 2011; Hajeeth *et al*., 2014). The effect of HOMO-LUMO energy gaps and some electronic properties on the immobilization and heavy metal absorption process was examined (Chaban, 2016; Shtepliuk and Yakimova, 2018).

The purpose of this study is to create organic materials using quantum mechanical estimations and to investigate their essential structures. Some polymer resources, as chitosan and cellulose are extremely significant in biological, chemical substances and environmental purposes. This specific class of composites, particularly when blended with nano-particles could assist as a significant and clean tool in the removing of pollutants from the environment. Various aspects of these compounds were studied earlier, however, the present work, molecular modeling is employed in order to use some naturally revised blends to eliminate heavy elements from the environment. TiO_2 will be used as water management mediators to be admitted in the chitosan/cellulose blend.

MATERIALS AND METHODS

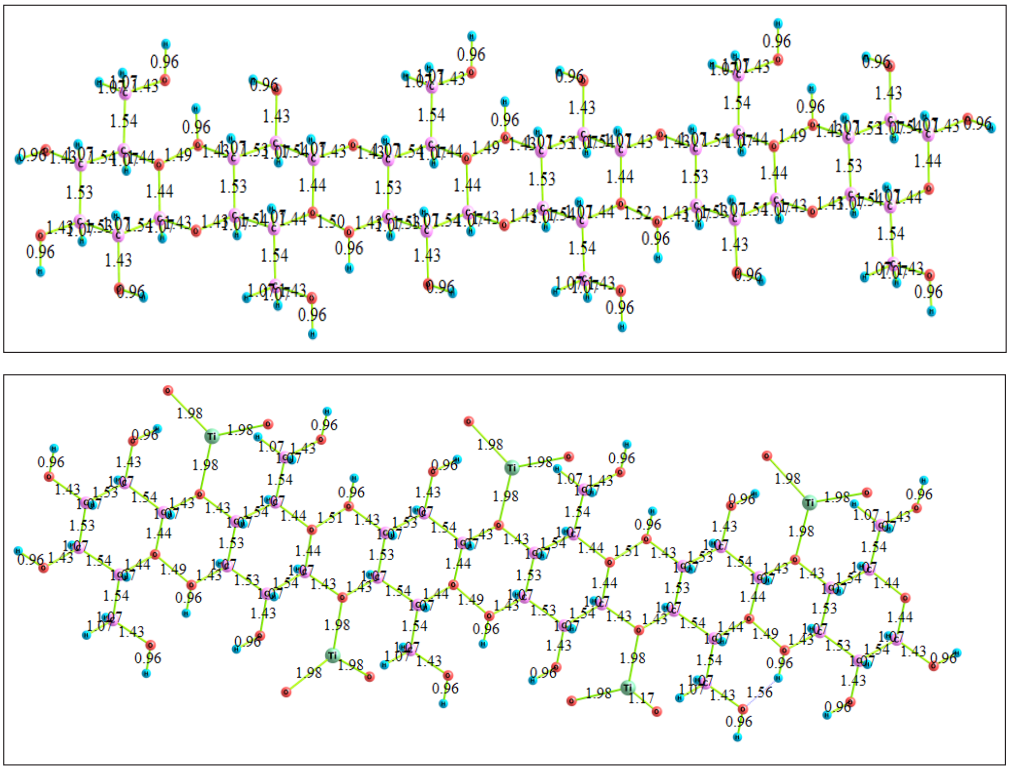
Semi-empirical method PM6 has been used by applying Gaussian09W and GaussView 5.0 as the central tool for simulation, modeling, and execution (Frisch *et al*., 1990). The model of cellulose compound has been made from six units of "*b*-D Glucose1-4 linkage", whereas a possible model of the nanocomposite blends (Cs/Ce, Ce/ TiO_2 and Cs/Ce/ TiO_2) has been applied. The characterization of molecular modeling, the geometrical structure of the blend, band gap energy, and ionization potential of the samples were assessed since these factors have important roles in wastewater treatment.

RESULT AND DISCUSSION

Optimized Geometry

The structural factors of cellulose and cellulose/chitosan substances have been computed. It was found that there are no enhancements made on the construction of the polymers after the blending process as shown in Figures 1 and 2.

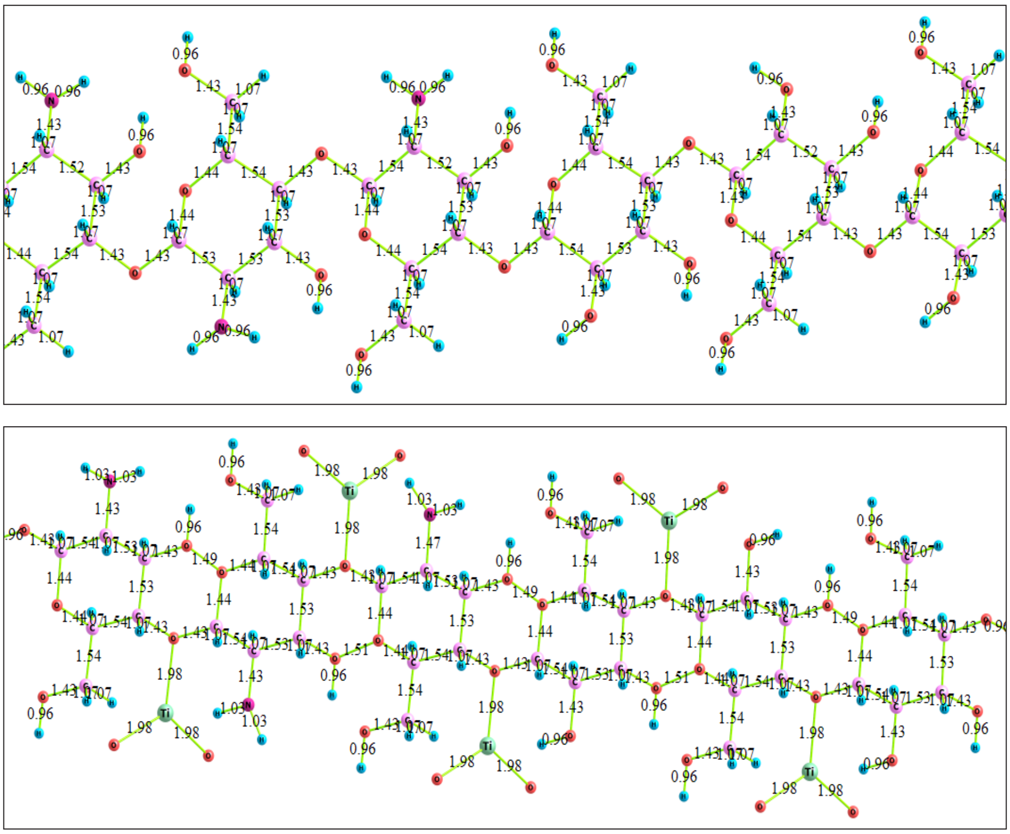
The blending of chitosan and cellulose improves the capability of heavy metal adsorbent. This is probably due to the reorientation of its crystal structures and eventually intensifications the composite's reactivity. Simulation indicates that the reorientation has no influence on the blends' molecular construction and increasing the appreciation of the chains of polymer to draw metal oxides such as TiO_2 via the (C-O-C) glycosidic bond. There were no changes in the molecular fabric of both parent matters chitosan and cellulose despite the fact that they are combining with TiO_2.



(a)

(b)

Figure 1. Optimized structure (bond lengths) of ball and stick model of (a) cellulose, (b) Physical interaction of TiO_2 with cellulose.



(a)

(b)

Figure 2. Optimized structure (bond lengths) of ball and stick model of (a) cellulose/chitosan, (b) Physical interaction of TiO_2 with cellulose/chitosan.

Ionization Potential

Ionization potential is a measure of the total energy required to take away an electron from a natural compound in its ground state to create ions in exciting conditions. If a compound has low ionization potential, then it requires low energy to form excited states and consequently, it is mostly considered by means of particular reactive. The ionization potential of the bio-polymers decreases as it turns to multi-faceted, especially when TiO_2 is added. Low ionization energy, particularly for the chitosan/cellulose/ TiO_2 nanocomposite displays that these blends are possibly very effective pollutant adsorbents as illustrated in Table 1.

Table 1. Calculated total ionization potential for the studied cellulose, cellulose/chitosan molecules and their blend with TiO_2

Molecule	Ionization Potential (eV)
Cellulose	10.1279
Cellulose-chitosan	9.75617
Cellulose/TiO_2	9.70352
Cellulose/chitosan/TiO_2	8.804

Band Gap Energy

The narrow HOMO/LUMO energy gap implies slight kinetic balance, because it is energetically favorable to include electrons to LUMO and take electrons from HOMO (Diener and Alford, 1998; Moran *et al*., 2003; Yang *et al*., 2013). Along with the frontier orbital theory, very stable and slow reactive compounds have a big HOMO/ LUMO gap, while unstable and active mixture has an insignificant HOMO/LUMO gap. Likely the most exciting feature is that the blending of both cellulose/chitosan alone and/or with nano-metal oxides (TiO_2) increases its reactivity. For illustration, from Figure 3 and Table 2, it can be determined that the cellulose/chitosan/ TiO_2 blend gets a narrower energy band gap that offers improved responsiveness for the blend. Therefore, the capability of the cellulose/ chitosan/ TiO_2 blend should have been improved in order to absorb heavy-metal pollutants in wastewater.

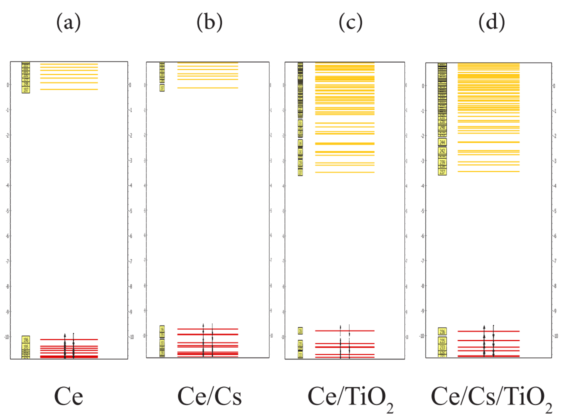


Figure 3. Energy levels for (a) cellulose (b) cellulose/chitosan (c) cellulose/TiO_2 (d) cellulose/chitosan/TiO_2.

Table 2. Calculated frontier orbits and energy gaps for cellulose, cellulose/chitosan, cellulose/TiO_2, and cellulose/chitosan/TiO_2 blend.

Molecule	HOMO (ev)	LUMO (ev)	EG (ev)
Cellulose	-10.127885404	-0.200821608	9.927063796
Cellulose/chitosan	-9.756174948	-0.126261824	9.629913124
Cellulose/TiO_2	-9.76352208	-3.468662652	6.294859428
Cellulose/chitosan/TiO_2	-9.834000124	-3.444172212	6.389827912

Total Dipole Moment

The total dipole moment of cellulose and the individual TiO_2 blended compound were estimated and illustrated in Table 3. The total dipole moment of cellulose/chitosan blend is greater than that of the dipole moment of cellulose alone which is 13.4946 Debye. By doping TiO_2 into the composite, the total dipole moment increased substantially to 53.6619 Debye. Doping TiO_2 into the different blends increase the dipole moment. The increasing of the total dipole moment enhances the construction and reactivity of a compound with the surrounding elements. This moment rise may improve the ability of blend's adsorption for hard metals and natural pollutants originate in wastewater. So, an immediate relationship between the total dipole moment and adsorption rates can be observed. It was found that the higher adsorbing could be due to the increase of the total dipole moment of the composite.

Table 3. Calculated total dipole moment for the studied cellulose, cellulose/chitosan and their blend with TiO_2.

Molecule	X	Y	Z	Total dipole moment (Debye)
Cellulose	9.3119	-3.6283	0.1257	9.6502
Cellulose/chitosan	13.2353	-1.4789	-2.1782	13.4946
Cellulose/TiO_2	-58.6148	-10.7593	-1.6054	59.6157
Cellulose-chitosan/TiO_2	53.1679	7.0784	1.6340	53.6619

Electrostatic Potential (ESP) Maps

Electrostatic Potential (ESP) maps is also known as "Electrostatic Potential Energy Maps", or "Molecular Electrical Potential Surfaces". The electrostatic potential maps support the visualize charge distribution, and other charge associated properties of molecules. Knowledge of the charge distributions can be used to determine how molecules interact with one another. To make the electrostatic potential energy data easy to interpret, a color spectrum, with red as the lowest electrostatic potential energy value and blue as the highest, is employed to convey the varying intensities of the electrostatic potential energy values. The molecular electrostatic potential (map) ESP for cellulose and cellulose/chitosan molecules are shown in Figures 4a and 5a respectively, whereas, Figures 4b and 5b show the ESP of each molecule with TiO_2 additive. The figures show that negative ESP increases when every one of the molecules is blended with TiO_2, especially with the polarity of the fragments. The TiO_2-blended mixtures is an extra reactive, easily built with enhanced stability as compared to pure cellulose.

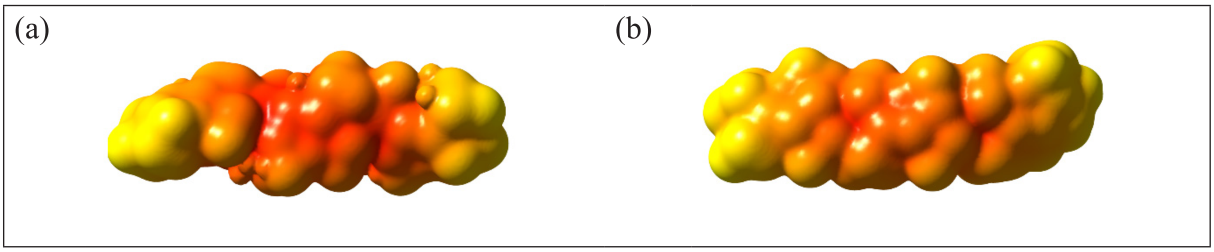


Figure 4. ESP of cellulose and Physical interaction of TiO_2 with cellulose, respectively.

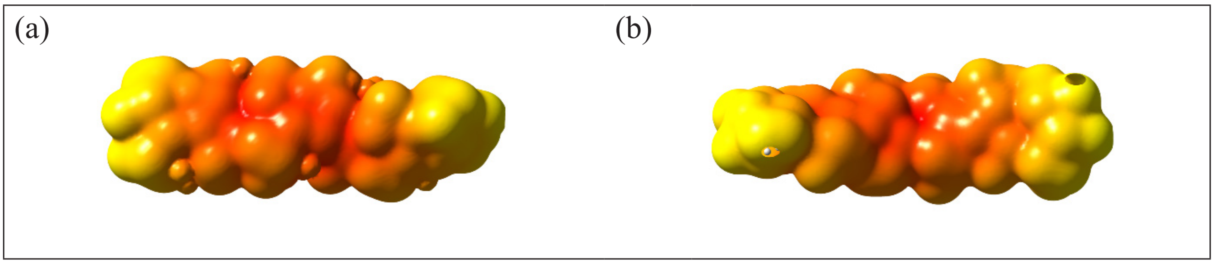


Figure 5. ESP of cellulose/chitosan blend and Physical interaction of TiO2 with cellulose/chitosan blend, respectively.

CONCLUSION

The results of the simulation process demonstrate that blending process of Ce, Cs/Ce, and TiO_2 changed them into one structural unit via glycosidic bond, (C-O-C), of the glucose engagement ring. However, the blended process did not change the molecular construction of the polymers and the nano-metal oxide. This blending process produced optimized geometries that contain higher dipole moment, lower ionization potential, and low HOMO-LUMO energy gaps compared to their original constituents of pure Ce. In particular, the electrostatic potential map of the patterned blends showed increasing in negative energies that indicate enhancement instability. Consequently, the capability of the nano-blend improved the order to absorption of heavy-metal pollutants in wastewater.

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الخواص الإلكترونية للسليولوز من خلال تقنيات النمذجة الجزيئية لمعالجة المياه غير الصالحة للشرب

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الملخص
محاولة تحسين الخصائص الإلكترونية للسليلوز هي واحدة من التقنيات المهمة التي استخدمت في تطوير وسائل معالجة المياه غير الصالحة للشرب. الهدف من هذا العمل هو دراسة خصائص السليولوز Ce من خلال تحسين تركيبه بخلطه مع الشيتوزان Cs وأيضا مع ثاني أكسيد التيتانيوم النانومتري TiO_2، وقد تم تطعيم أو تشويب مزيج Cs/Ce بإدخال TiO_2. استخدم توظيف النمذجة الجزيئية لمزيج أو خليط معدل طبيعيًّا في امتصاص العناصر الثقيلة من البيئة المائية غير الصالحة للشرب. واستخدمت المركبات النانوية الناتجة (Ce/TiO_2)، ($Ce/Cs/TiO_2$) لإظهار التركيب الهندسي الأمثل وبعض الخصائص الإلكترونية للعينات. ونتيجة لذلك، ولتطعيم البوليمرات تحت الدراسة، تم الحصول على "nano-composites (PNCs) polymer" مركبات البوليمرات النانومترية (PNCs) وبها زيادة في طول روابط الاتصال بين الذرات المتجاورة لتتكيف مع التركيبات الهندسية المحسنة optimized geometry كما وجدت زيادة في عزم ثنائي القطب، وانخفاض في جهد التأين وقيمة طاقة الفجوة HOMO-LUMO مقارنة مع مكوناتها الأصلية من Ce النقي. وبالتالي فإن قدرة المزيج النانوي قد تحسنت من أجل امتصاص ملوثات المعادن الثقيلة في المياه غير الصالحة للشرب.

الكلمات المفتاحية: ثاني أكسيد التيتانيوم النانومتري TiO_2، الخصائص الإلكترونية، مزيج (السليلوز/ الشيتوزان)، نموذج جاوسيان.