Electronic Properties of Cellulose Through Molecular Modeling Technique for Wastewater Treatment

Abdel-baset H. Mekky\textsuperscript{(1)(2)}, Abdulaziz. S. Alaboodi\textsuperscript{(3)}

(1) Physics Department, College of Science and Arts El-Mozneb, Qassim University, El-Mozneb, Kingdom of Saudi Arabia
(2) High Institute of Engineering and Technology, Buhaira, Egypt
(3) Mechanical Engineering department, College of Engineering, Qassim University

Received 14 January 2019 - Accepted 30 January 2020

https://doi.org/10.37575/b/sci/2046

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\textsubscript{2} nano-particles, as molecular modeling using certain naturally revised blends can help in eliminating heavy elements from the waste-water environment. TiO\textsubscript{2}, as water management mediators, was admitted in the chitosan/cellulose blend. The nano-component cellulose/ TiO\textsubscript{2} and cellulose/chitosan/TiO\textsubscript{2} (Ce/TiO\textsubscript{2} and Ce/Cs/TiO\textsubscript{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\textsubscript{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\textsubscript{2} compound nano-fibrous adsorbents is fabricated by two methods, namely TiO\textsubscript{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\textsubscript{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\textsubscript{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 prepare theoretical modeling on the basis of the interaction of chitosan/TiO₂. 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. TiO₂ 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 “β-D Glucose1-4 linkage”, whereas a possible model of the nanocomposite blends (Cs/Ce, Ce/TiO₂ and Cs/Ce/TiO₂) 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 TiO₂ 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 TiO₂.
Figure 1. Optimized structure (bond lengths) of ball and stick model of (a) cellulose, (b) Physical interaction of TiO$_2$ with cellulose.

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.

![Image](image.png)

**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.

![Image](image.png)

**Table 1.** Calculated total ionization potential for the studied cellulose, cellulose/chitosan molecules and their blend with TiO$_2$

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ionization Potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>10.1279</td>
</tr>
<tr>
<td>Cellulose-chitosan</td>
<td>9.75617</td>
</tr>
<tr>
<td>Cellulose/TiO$_2$</td>
<td>9.70352</td>
</tr>
<tr>
<td>Cellulose/chitosan/TiO$_2$</td>
<td>8.804</td>
</tr>
</tbody>
</table>

**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

![Image](image.png)

**Table 2.** Calculated frontier orbits and energy gaps for cellulose, cellulose/chitosan, cellulose/TiO$_2$, and cellulose/chitosan/TiO$_2$ blend.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>EG (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>-10.127885404</td>
<td>-0.200821608</td>
<td>9.927063796</td>
</tr>
<tr>
<td>Cellulose/chitosan</td>
<td>-9.756174948</td>
<td>-0.126261824</td>
<td>9.629913124</td>
</tr>
<tr>
<td>Cellulose/TiO$_2$</td>
<td>-9.76352208</td>
<td>-3.468662652</td>
<td>6.294859428</td>
</tr>
</tbody>
</table>
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$_2$.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>Total dipole moment (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>9.3119</td>
<td>-3.6283</td>
<td>0.1257</td>
<td>9.6502</td>
</tr>
<tr>
<td>Cellulose/chitosan</td>
<td>13.2353</td>
<td>-1.4789</td>
<td>-2.1782</td>
<td>13.4946</td>
</tr>
<tr>
<td>Cellulose/TiO$_2$</td>
<td>-58.6148</td>
<td>-10.7593</td>
<td>-1.6054</td>
<td>59.6157</td>
</tr>
<tr>
<td>Cellulose-chitosan/TiO$_2$</td>
<td>53.1679</td>
<td>7.0784</td>
<td>1.6340</td>
<td>53.6619</td>
</tr>
</tbody>
</table>

**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.

ACKNOWLEDGMENT(S)
The authors express their gratitude and respect to “King Abdulaziz City for Science and Technology - KACST” for the significant financial funding to conduct this project No., (35 – 156).

REFERENCES


الخواص الإلكترونية للسليلوز من خلال تقنيات التخليص الجزيئي لمعالجة المياه غير الصالحة للشرب

عبد العزيز مكي، عبد العزيز سليمان العبودي

(1) كلية العلوم والآداب بالدرب، جامعة القصيم، المملكة العربية السعودية
(2) المعهد العالي للهندسة والتكنولوجيا، البحيرة، مصر
(3) قسم الهندسة الميكانيكية، كلية الهندسة، جامعة القصيم، المملكة العربية السعودية

استلام 14 يناير 2019م - قبول 30 يناير 2019م

https://doi.org/10.37575/b/sci/2046

الملخص

محاولة تحسين الخصائص الإلكترونية للسليلوز هي واحدة من التقنيات المهمة التي استخدمت في تطوير وسائل معالجة المياه غير الصالحة للشرب. اهدف من هذا العمل هو دراسة خصائص السليلوز من خلال تحسين تركيبه بخلطه مع الشيتوزان Ce غير الصالحة للشرب. استخدمت تقنية TiO2 وCs/Ce أيضاً مع ثاني أكسيد التيتانيوم النانومتري. وقد تم تعزيز أو تنشيط مزيج Ce/CS TiO2. استخدم توظيف النمذجة الجزيئية لزيادة أو خليط معالج تحت تأثير تخليص العناصر الثقيلة من البيئة المائية غير الصالحة للشرب. واستخدمت المركبات النانوية كاملاً وخصوص الخصائص الإلكترونية لتأكيد التركيب النانو-الوني(Ce/Cs/TiO2) للعينات. ونتيجة لذلك، وتطبيقات البوليميرات تحت الدراسة، تم الحصول على مركبات البوليميرات النانومتري (PNCs) وزيادة في طول روابط الاتصال بين الذرات المجردة لتلكيف مع تركيبات اندسية المحسنة. كما وجدت زيادة في عمل ثاني القطب وانخفاض في جهد الطيف وقيمة طاقة الفجوة HOMO-LUMO مقارنة مع مكوناتها الأصلية من Ce النقي. وبالتالي فإن قدرة المزيج النانوي قد تحسن من امتصاص ملوثات المعادن الثقيلة في المياه غير الصالحة للشرب.

الكلمات المفتاحية: مركب نانوي TiO2، الخصائص الإلكترونية، مزيج (السليلوز/الشيتوزان)، نموذج جاوسين.