DFT: B3LYP/ LANL2DZ Study for the Removal of Fe, Ni, Cu, As, Cd and Pb with Chitosan

Hend Ezzat [1], A. A. Menazea [2,3], Wessam Omara [4,5], Osama H. Basyouni [5,6], Samah A. Helmy [7], Aya A. Mohamed [8], Walid Tawfik [9], Medhat Ibrahim [3,*]

[1]   Nano Technology Unit, Solar and Space Research Department, National Research Institute of Astronomy and Geophysics (Nano NRIAG), 11731 Helwan, Cairo, Egypt
[2]   Laser Technology Unit, National Research Centre, 12622 Dokki, Giza, Egypt
[3]   Spectroscopy Department, National Research Centre, 12622 Dokki, Giza, Egypt
[4]   Materials Science Department- Institute of Graduate Studies and Research, Alexandria University, Alexandria, Egypt
[5]   Egypt Nanotechnology Center, Cairo University, El-Sheikh Zayed, 6th October, Giza 12588, Egypt
[6]   Department of Physics, Faculty of Science, Kafrelsheikh University, Kafrelsheikh 33516, Egypt
[7]   Physics Department, Special Physics Branch, Faculty of Science, Ain Shams University, 11566 Cairo, Egypt
[8]   Physics Department, Faculty of Science, Cairo University, Cairo, Egypt
[9]   National Institute of Laser NILES, Cairo University, Cairo, Egypt
*   Correspondence: medahmed6@yahoo.com;

Abstract: Human activities are responsible for the existence of heavy metals in the environment. The accumulation of these metals in the environment causes several risks, such as toxicological, mutagenic, and carcinogenic effects. Chitosan (Cs) based materials have been explored its competitive efficacy in heavy metals removal from contaminated water. In this study, an attempt is presented to develop a natural, reliable, and cost-effective biopolymer structure of Cs with a high ability to entrap some heavy metals, which can be found in polluted water. The correlation between Cs-heavy metals and its stability was studied by density functional theory (DFT) using B3LYP together with the basis set LANL2DZ. The observed results revealed that the bandgap energy values for Cs, Cs- Fe, Cs-Ni, Cs-Cu, Cs-As, Cs-Cd and Cs-Pb were 2.571, 0.6147, 0.7176, 0.3396, 0.6648, 1.5007 and 0.4128 eV, respectively. The later showed that Cs structure has high selectivity and binding affinity to Cu and Pb hydrated metals, respectively rather than Fe, Ni, As and Cd. The examined correlation between Cu and Pb with Cs revealed that Cs could be applied for sensing and removing of Cu and Pb from wastewater.

Keywords: Chitosan; DFT; LANL2DZ; heavy metals; wastewater.

1. Introduction

Heavy metal pollution has occurred worldwide due to industrialization, mining, and manufacturing. Heavy metals removal from wastewater attracted high interest for all environmental agencies and communities all over the world [1]. The removal of these heavy metals from drinkable water takes a high priority because of its toxicity due to the formation of complexes inside the body cells; these complexes are not biodegradable [2,3]. In industrial wastewater, many toxic metals are often detected from the metal coating, battery industries, printing, painting and pigment industries, etc. [4, 5].

Cadmium Cd, Lead Pb, and Nickel Ni are among the most dangerous heavy metal pollutants generated from the electroplating industry, batteries, phosphate fertilizers, pigments, stabilizers, and alloys into the aquatic environment. They have possessed several risks to

human health, causing hypertension, insomnia, pain, dizziness, anemia, irritability, muscle weakness, hallucinations, and renal damage hepatic damage, dysfunction of central nervous systems, cancer, and mutation [6-8].

Several techniques have been commonly used to remove toxic metals from wastewater, such as exchange of ions, chemical precipitation, complexation, extraction of liquid-liquid, reverse osmosis, the process of oxidation-reduction, evaporation, separation, adsorption, and Pulsed Laser Deposition [9-14]. However, these approaches are costly and ineffective, particularly when heavy metal ions are involved in wastewater at low concentrations. Adsorption is one of the most economical, practical, and widely used methods for the removal of toxic metals from the aqueous environment [15, 16].

Cs is an amino polysaccharide produced from chitin that is found naturally in some fungi. It is regarded as one of the most important and easiest bio-polymers used in different applications, such as protein and metal adsorption, medication guidance and gene delivery, magnetic resonance imaging, tissue design, and enzyme immobilization, food preservation, medical uses, particularly in medicinal products for obesity and high cholesterol disease, expanding their uses as a chelating agent and substantial metal trapper and in water treatment [17].

Cs is the most versatile biopolymer for a broad range of applications due to its biocompatibility, biodegradability, and antibacterial property. It demonstrates a successful biological action against pathogenic grams that is unusual in a linear biocompatible and biodegradable polysaccharide natural polymer extracted through the chitin deacetylating process, normally found in the hard external skeleton of shellfish, mollusks, and insects. Cs with low molecular weight usually demonstrate higher water dissolvability and better antibacterial properties compared to high molecular weight; Cs 's chemical modifications are the right choices for advancing its properties to be implemented in a wide field [18].

In recent days, researchers are interested in using Cs because this material is regarded as an ideal adsorbent where a polymer film is capable of heavy metal adsorption from wastewater. The removal of heavy metals such as; Cd, Pb, and Ni by Cs is considered a clever, low-cost idea in our life without any complicated experiments and could be very easy in use [19]. Cs include reactive hydroxyl–OH (non-specific binding site) and amino –NH_2 groups (specific binding site), which can attach heavy metals and serve as chelating and reaction sites. Pure Cs has the property of agglomerating and forming a gel in aqueous media so that most hydroxyl and amino groups are inaccessible for binding metals [20,21]. Researches have been found that NH_2 groups are the main reactive groups for adsorption of metal ions. Based on this, OH groups may also involve in adsorption mechanism. A different mechanism, such as electrostatic attraction and chelation, may involve adsorption of metal ions onto these different fictional groups in which the pH is an important factor. The free lone pair electrons on nitrogen may bind metal cations at pH close to neutrality (or weak acidity). At the same time, the protonation of amine groups in acidic solutions makes polymer behave in a cationic manner and, consequently, the potential for attracting metal anions. The chelation of metal cations by ligands in solution may result in the formation of metal anions, which therefore convert the chelation mechanism on Cs to an electrostatic attraction mechanism on protonated amine groups of the polymer [21,22].

The mechanism of selective adsorption was well explained by incorporating ionic scale effect and DFT analysis. Limited information is available on the microscopic complexation process between heavy metals and polar adsorbents, but theoretical calculations using quantum

mechanical approaches have been used with great success. The DFT is a robust and efficient electronic structure method for describing metal systems. Recent studies have combined DFT techniques with experimental methodologies to describe the adsorption process and the interaction between heavy metals, including [Cd (II), Ni (II), Pb (II)], and Cs [23-25]. It is worth mentioning that DFT, as well as other molecular modeling tools, show potential applications for Cs as well as other members of biopolymers. Applications include understanding the electronic properties of biopolymers as well as their derivatives [26-32]. It is stated that understanding the electronic properties is an important step toward the functionalities of such emerging materials. They are investigating electronic properties of Cs as well as other biopolymers not only important for environmental applications but also in many other applications, whereas such classes of materials show the potential applications according to their unique properties [33- 39].

In this work, the possible interaction between Cs and some heavy metals such as Fe, Ni, Cu, As, Cd, and Pb is tried. This study is performed using molecular modeling DFT:B3LYP/LANL2DZ level of theory. The study including the geometrical stability and electronic properties of Cs with hydrated heavy metals.

2. Materials and Methods

Model molecules of Cs and Cs with hydrated metals as Fe, Ni, Cu, As, Cd, and Pb were built. All the studied models were computed by the GAUSSIAN09 program [40] at Spectroscopy Department, National Research Centre, Egypt. Studied models were optimized with DFT theory at the B3LYP [41-43] level, together with the LANL2DZ basis set. Total dipole moment (TDM) and HOMO-LUMO bandgap energy, the contour of molecular electrostatic potential (MESP), were also calculated at the same level of theory.

3. Results and Discussion

3.1. Model Structure.

Model structures were built for simulating the possibility of using Cs as heavy metals removal. Models presented as three units of Cs representing the main model molecule. For simulating heavy metals in the aquatic environment, each of the studied heavy metals was correlated weakly with 6 water molecules (H_2O) as M- $6H_2O$ where M is Fe, Ni, Cu, As, Cd and Pb respectively. The correlation between Cs and each hydrated metal was represented as an adsorbed state. Figure 1 shows models for Cs and Cs with hydrated metals Fe, Ni, Cu, As, Cd, and Pb, respectively. If the metal is going to interact with Cs through one bond, this could be instead of one water molecule if the metal is going to interact through two bonds then it will be through two water molecules. All model structures were computed using DFT theory at the B3LYP level and LANL2DZ basis set. HOMO-LUMO band gab energy and MESP were calculated at the same level of theory for all structures. It is stated earlier that physical parameters such as TDM, HOMO-LUMO band gap energy, and MESP are good descriptors for the reactivity of a given compound [44-46].
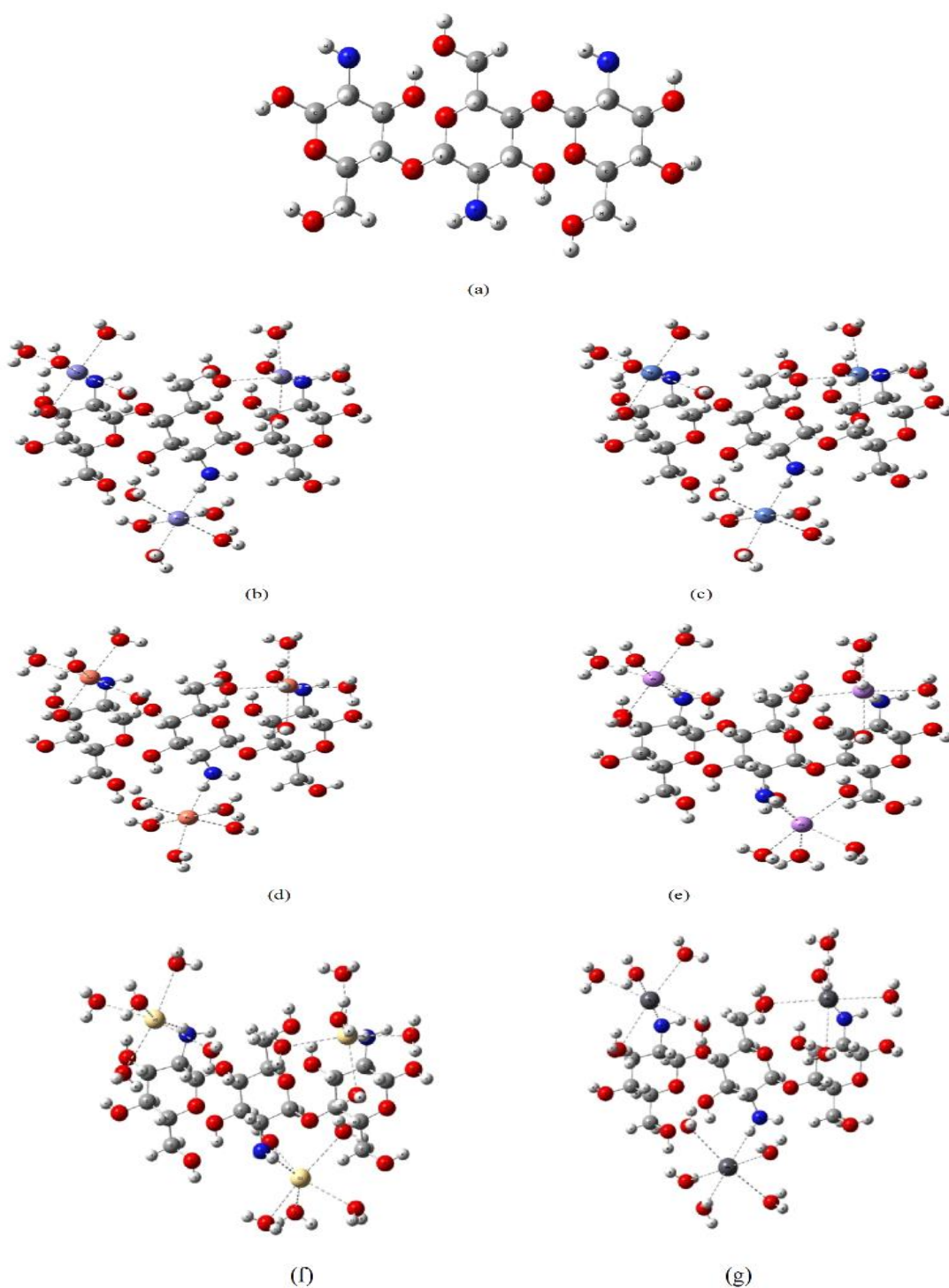
Figure 1. B3LYP/LANL2DZ calculaed optimized structure for (a) Chitosan; (b) Chitosan + Fe; (c) Chitosan + Ni; (d) Chitosan + Cu; (e) Chitosan + As; (f) Chitosan + Cd; (g) Chitosan + Pb.

3.2. HOMO-LUMO calculations.

HOMO-LUMO bandgap energy and TDM for proposed structures Cs and Cs with M-6H$_2$O where M=Fe, Ni, Cu, As, Cd, and Pb were computed at the same level of theory. Figure 2 represents the calculated HOMO-LUMO band gap, which represents the distribution of orbitals around the molecule. For Cs, the orbitals distributed uniformly around the three units. When Cs interacted with metals, orbital distribution was localized around metals. Conversions appeared in HOMO-LUMO bandgap energy and TDM listed in table 1. For Cs, three units

model bandgap energy were 2.5712 eV and TDM were 4.0939 Debye. However, Cs with M-6H$_2$O where M=Fe, Ni, Cu, As, Cd, and Pb recorded changes in the two parameters. Accordingly, Cs + Fe HOMO-LUMO bandgap decreased to 0.6147 eV, and TDM increased to 13.2259 Debye, which means that Cs affected by Fe. Also, Cs + Ni bandgap and TDM changed as 0.7176 eV and 15.6366 Debye, respectively, which also means that Ni effect on Cs.

Furthermore, Cs + Cu recorded a change in bandgap and TDM as 0.3396 eV and 27.8830 Debye, respectively. Cs + As also bandgap and TDM changed to 0.6648 eV and 19.0923 Debye. Similarly, Cs + Cd changed to 1.5007 eV and 17.3977 Debye. Equally, for Cs + Pb bandgap and TDM were 0.4128 eV and 17.6536 Debye. When the TDM increased while the bandgap energy decreased, this means that the interaction occurrence ability is high. From all data, Cs could interact with all studied metals but have more ability to interact with Cu and Pb that they have the highest TDM value and the lowest band gap value.
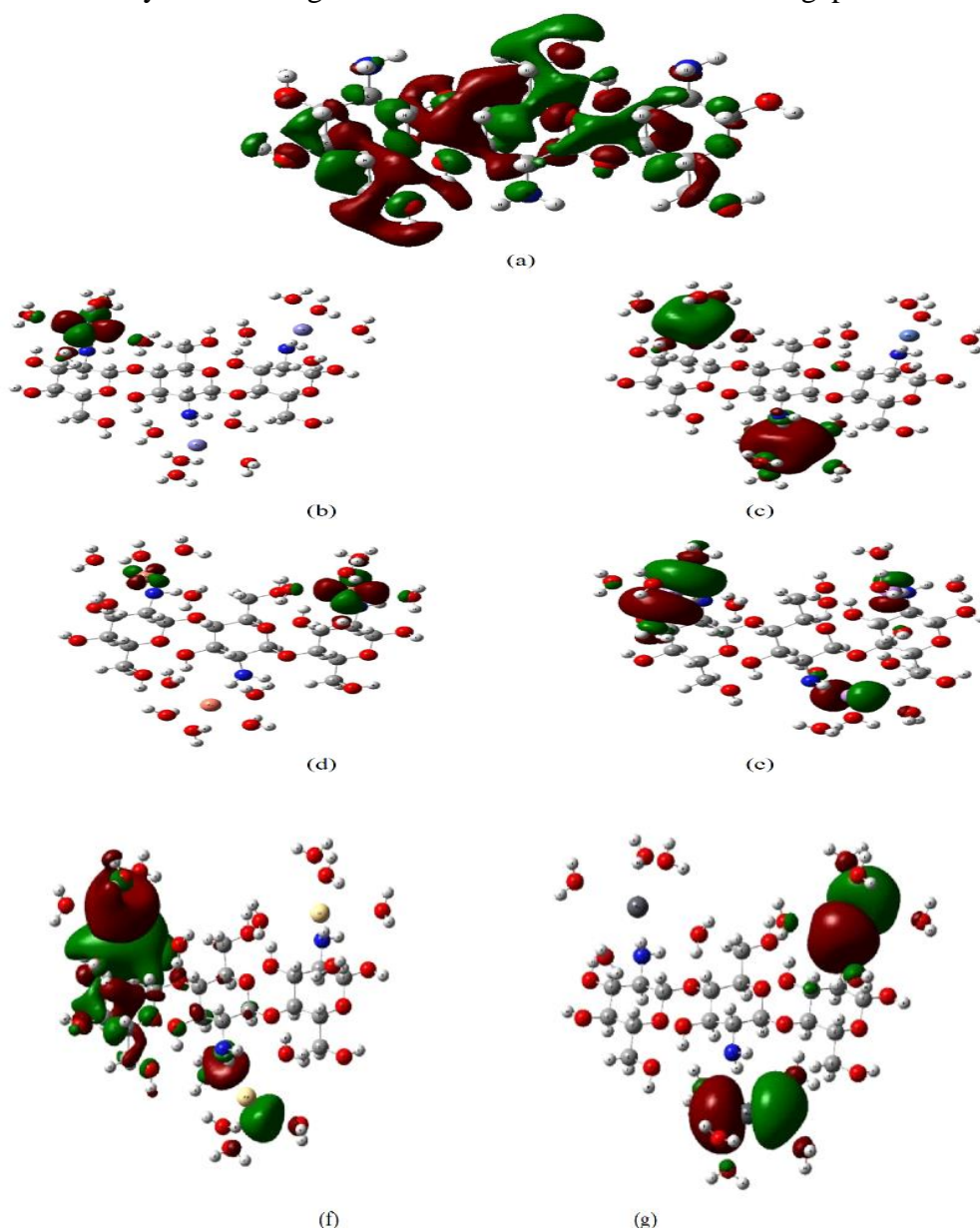

Figure 2. Calculated B3LYP/LANL2DZ HOMO-LUMO band gap energy for (a) Chitosan; (b) Chitosan + Fe; (c) Chitosan + Ni; (d) Chitosan + Cu; (e) Chitosan + As; (f) Chitosan + Cd; (g) Chitosan + Pb.

Table 1. Calculated TDM (Debye) and HOMO-LUMO bandgap energy ΔE (eV) using B3LYP/LANL2DZ for Chitosan, Chitosan + Fe, Chitosan + Ni, Chitosan + Cu, Chitosan + As, Chitosan + Cd and , Chitosan + Pb

Structure	TDM	ΔE
Chitosan	4.0939	2.5712
Chitosan + Fe	13.2259	0.6147
Chitosan + Ni	15.6366	0.7176
Chitosan + Cu	27.8830	0.3396
Chitosan + As	19.0923	0.6648
Chitosan + Cd	17.3977	1.5007
Chitosan + Pb	17.6536	0.4128

3.3. Molecular electrostatic potential.

MESP characterizes the number of neighboring charges, nuclei, and electrons' strength at a certain location. The interpretation of MESP clarified according to the color extended gradually as red, orange, yellow, green, and blue, respectively. Ranged color represents the MESP intensities variation, where red color signified the lowest MESP value, and the blue color signified the highest MESP value. The importance of MESP calculation is knowing the molecule active site and its interaction ability with neighboring.

Figure 3a represents MESP for Cs, a low potential red region signifies electrons abundance. Accordingly, the active sites of Cs are the NH_2 active groups. Figures 3b, c, d, e, f, and g illustrate the contour MESP for the adsorption of hydrated metals Fe, Ni, Cu, As, Cd, and Pb. MESP contour specified that the structures be more reactive according to the interaction where the red region localized. The present computational work proves that molecular modeling at DFT level is providing valuable data for the removal of heavy metals from the environment using biopolymers, which is in good agreement with previous findings [47-50].
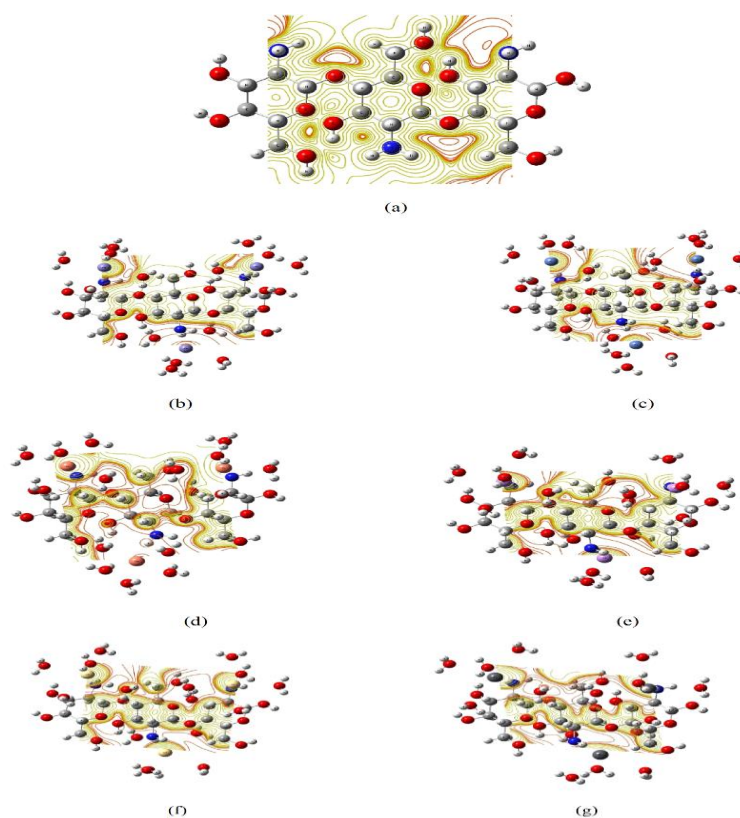

Figure 3. Calculated B3LYP/LANL2DZ MESP for (a) Chitosan; (b) Chitosan + Fe; (c) Chitosan + Ni; (d) Chitosan + Cu; (e) Chitosan + As; (f) Chitosan + Cd; (g) Chitosan + Pb.

4. Conclusions

DFT: B3LYP/LANL2DZ model was used to study the ability of Cs to interact with heavy metals in hydrated form. This interaction is an important step for applying a green method for the remediation of heavy metals from the aquatic environment. Results showed that Cs can interact with all studied hydrated metals but has more ability to interact with Cu and Pb that they have the highest TDM and the lowest bandgap energy. Cs structure has high selectivity and binding affinity to Cu and Pb hydrated metals, respectively, rather than Fe, Ni, As, and Cd. The examined correlation between Cu and Pb with Cs revealed that Cs could be applied for sensing and removal of Cu and Pb from wastewater. This computational study dedicated Cs in nanoscale as a green selective tool for the remediation of heavy metal from the aquatic environment.

Funding

Acknowledgments

Conflicts of Interest

The authors declare no conflict of interest.

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