

Analysis of Ni²⁺ Metal Adsorption on Chitosan Membrane with Density Functional Theory (DFT) Method

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ABSTRACT

This study aims to modeling the membrane structure of chitosan containing nickel metal and determine the adsorption energy and energy gap of the chitosan molecular structure containing nickel metal. The molecular structure modeling was carried out using a computer using Avogadro software and analyzed with GaussView 6 software. The results of shape optimization using the Density Functional Theory (DFT) method with the basis set B3LYP/LanL2DZ were the total energy of the chitosan-Ni compound. The analysis revealed the interaction between the structure of chitosan and metal Ni. Determination of the structural model of chitosan and Ni metal shows a stable molecular geometry with an electronic energy value of 38826.90 eV in chitosan-Ni with a linear molecular geometry. Modeling the structure of chitosan with nickel metal shows the presence of bonds between nickel metal and chitosan in the inter glycosidic bonding region with a bond length of 1.92 for Ni-N and 1.81 for Ni-O. The adsorption energy of the chitosan structure with nickel is -18.236 eV. The energy gaps in the structure of chitosan-Ni, chitosan, and Ni are 0.10456, 0.23481, and 0.10213 eV.

Keywords: Chitosan, Geometry optimization, Energy adsorption, Bond length, Energy gap

ABSTRAK

Penelitian ini bertujuan untuk memodelkan struktur membran, menentukan energi adsorpsi serta energi gap kitosan yang mengandung logam nikel. Pemodelan struktur molekul dilakukan dengan bantuan komputer menggunakan software Avogadro dan dianalisis dengan software GaussView 6. Hasil optimasi bentuk dengan metode *Density Functional Theory* (DFT) dengan basis set B3LYP/LanL2DZ adalah energi total senyawa kitosan-Ni. Analisis mengungkapkan interaksi antara struktur kitosan dan logam Ni. Penentuan model struktur kitosan dan logam Ni menunjukkan geometri molekul yang stabil dengan nilai energi elektronik sebesar 38826,90 eV pada kitosan-Ni dengan geometri molekul linier. Pemodelan struktur kitosan dengan logam nikel menunjukkan adanya ikatan antara logam nikel dan kitosan pada daerah ikatan interglukosidik dengan panjang ikatan 1,92 Å untuk Ni-N dan 1,81 Å untuk Ni-O. Energi adsorpsi struktur kitosan dengan nikel adalah -18,236 eV. Energi gap struktur kitosan-Ni, kitosan, dan Ni berturut-turut adalah 0,10456, 0,23481, dan 0,10213 eV.

Kata kunci: Kitosan, Optimasi geometri, Energi adsorpsi, Panjang ikatan, Energi gap

INTRODUCTION

Indonesia is an archipelagic country that has abundant natural resources such as gold, nickel, coal and oil. This natural wealth is what drives many companies to open their businesses in Indonesia and encourages the creation of job opportunities for the community. One type of employment is mining. Mining activities are very beneficial for the economy and have an impact on the welfare of the community. But on the other hand it can be a very serious problem. Waste generated from mining that is not processed properly will pollute the environment and can have a negative impact on humans.

Pollution caused by mining waste is very dangerous for the environment, including humans. According to (Sarianto et al., 2016), the impact of nickel mining causes a decrease in water quality and a decrease in fish fit for catching by fishermen caused by a decrease in fish weight. As a result of nickel mining, the fish caught have decreased the weight of the fish. Another impact of heavy metal waste pollution if consumed by humans is disrupting the nervous system, brain damage, paralysis, kidney damage and cancer (Agustina, 2014).

In an effort to reduce the impact of mining waste pollution such as Ni(II) it can be done in several ways including filtration, surface complexation, chemical precipitation, ion exchange, adsorption using activated carbon, electrode positioning, and membrane processing (Jaishankar et al., 2014). Of the several ways to reduce heavy metal pollution, the adsorption technique was chosen to reduce polluted heavy metal levels because it is easier and more effective. Adsorption method is a process of absorption of a substance on the surface of another substance. There are several methods used to adsorb Ni(II) metal, one of which is by using a membrane. The membrane was developed because of its advantages, namely having a large surface area, porosity and number of active groups, so it is good for use in adsorption applications. In addition to these properties, one thing that needs to be developed is a membrane made of environmentally friendly materials (Chairunnisa, 2018).

Chitosan is a natural material that is non-toxic, easily degraded and abundant. Chitosan also has many hydroxyl and amine groups which are effective in binding heavy metals (Chairunnisa, 2018). Chitosan is a natural biopolymer that is polycationic in nature so it can be applied in various fields such as metal adsorbent, textile dye absorbent, cosmetic making material and antibacterial (Iriana et al., 2018).

With the rapid development of technology, many technologies have been developed to achieve maximum results. One of them is in the field of computational chemistry. Computational chemistry studies with quantum chemical calculations are mostly done as a complement to complete experimental evidence. Quantum chemistry studies and molecular simulations involve a large number of molecules characterizing the shape, structure, reactivity, stability, and binding properties of complete molecules as well as molecular fragments and substituents (Sugashini et al., 2015). Computational chemistry studies are carried out in order to minimize the occurrence of trial and error in a study by predicting research results before conducting an experiment.

Density functional theory (DFT) is one of the quantum chemical calculations used to investigate the electronic structure of a system, especially atoms and molecules. DFT can well describe intermolecular interactions, especially van der Waals forces, charge transfer stimuli, transition states, global potential energy surfaces and some other strongly correlated systems, which can be used for a better understanding of system performance (Sugashini et al., 2015).

Research (Braier & Jishi, 2000) on the study of the functional density of Cu²⁺ and Ni²⁺ bonds in chitosan proves that there is a coordination bond between the transition metal and chitosan

biopolymers around the hydroxy and nitrogen groups. This indicates that chitosan can bind to the transition metals Cu²⁺ and Ni²⁺. In his article on the interaction of chitosan and chitin with metal ions Ni, Cu, and Zn using the DFT basis set B3LYP/6-31+G method, it was shown that there was an interaction between metal ions Ni, Cu, and Zn around the hydroxyl and amine groups. Based on the research, it was shown that at the level of stability, the metal ion Ni(I) was more stable than Cu(I) and Zn(I) when bound to chitosan (Gomes et al., 2014).

Based on the results of previous studies, it was shown that there was a bond between Ni metal ions and chitosan which indicated that chitosan was able to adsorb Ni metal. However, in previous studies using different variations of the basis set. In this study, researchers are interested in conducting research on metal adsorption analysis with the basis set B3LYP/LanL2DZ.

METHODOLOGY

Research Tools and Objects

The tool used in this research is a single HP computer hardware with specifications for an Intel Core i5-7200U CPU 2.50 GHz, 500 GB hard disk and 4 GB RAM as well as Gaussian 09W and Gaussian View 6 computational chemistry software. structure of chitosan and Nickel metal.

Work Procedures

This research begins with drawing the structure of chitosan and nickel using Avogadro software. Modeling the molecular structure of chitosan and nickel is modeled in the form of the structure of the chitosan with nickel metal, chitosan structure and nickel metal structure.

Geometry Optimization

The process continued with the optimization of complex molecular geometry using the DFT method with the basis set B3LYP/LanL2DZ. Optimization of complex molecular geometry in the form of calculations to minimize the energy of the molecular structure in order to obtain a stable complex molecular geometry.

RESULTS AND DISCUSSION

Structural Modeling, Optimization of Molecular Geometry and Molecular Interaction

Molecular structure modeling aims to facilitate visualization of the structure of the compound to be studied. Three-dimensional structure modeling of Chitosan molecules, as well as Chitosan and Ni were drawn using the Avogadro application. After the structural modeling is done, the geometry optimization is continued through the GaussView 06 software.

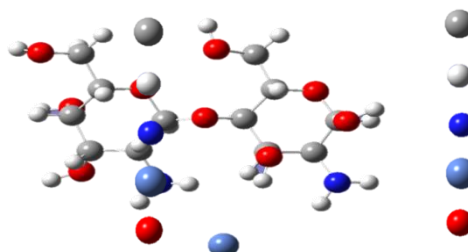


Figure 1. 3D structure of chitosan - Ni²⁺

Modeling the structure shown in figure 1 complex molecules will form different geometries. The molecular geometry formed for the Ni(II)-Chitosan compound can be explained based on the hybridization theory approach.

Based on Figure 2 which explains that the Ni(II)-Chitosan hybridization is sp with linear molecular geometry (Housecroft & Sharpe, 2018). This is because each chitosan ligand binds in coordination with 2 lone pairs of electrons on the Ni^{2+} ion, so the reaction equation and structure of the Ni(II)-chitosan complex ion can be written as follows.

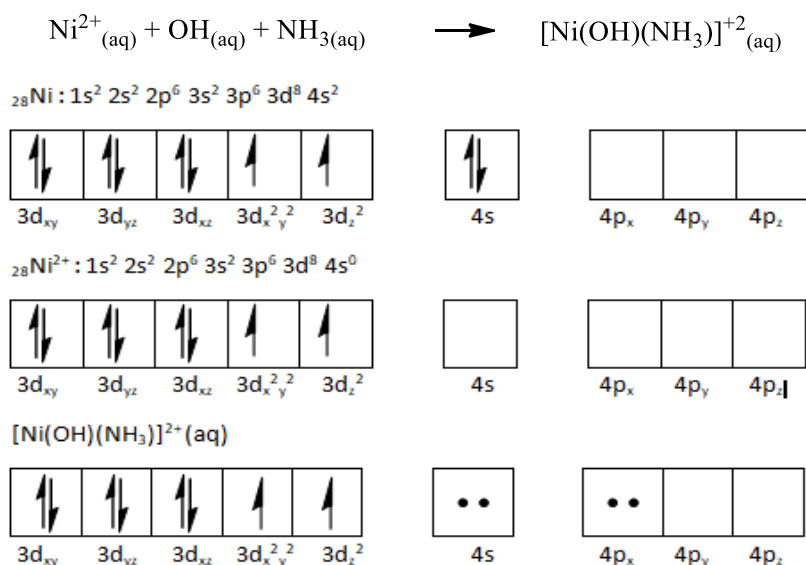


Figure 2. Assumptions for the formation of Ni(II)-chitosan complex based on hybridization approach

The DFT method is a computational method based on the relationship between the total electronic energy and the total electron density. Optimization of complex molecular geometry was carried out using the DFT method with the basis set B3LYP/LANL2DZ, where the formation of the geometry was influenced by the charge value and bond length between the atoms that make up the complex molecule. In addition, there are several optimization parameters of complex molecular geometry which are measured using the DFT method. One of the parameters calculated in molecular optimization using the DFT method is charge and bond length. Following are the results of the charge values and bond lengths in the Ni(II)-Chitosan complex which are shown in table 1.

Table 1. Value of charge and bond length of complex using DFT method B3LYP/ LANL2DZ

No	Charge		Bond length	
	Atom	eV	Atom	Å
1	O ₂₂	-0.568543	O ₂₂ -Ni ₄₈	1.81
2	N ₄₀	0.093650	N ₄₀ -Ni ₄₈	1.92
3	Ni ₄₈	0.698329		

Geometry optimization involved 48 atoms in the Ni(II)-Chitosan complex having different charge values and bond lengths between atoms. The charge values and bond lengths for the Ni(II)-Chitosan complex in Table 1 are specifically for nitrogen atoms, oxygen and the metal ion Ni^{2+} , which are atoms that undergo coordination covalent bonds.

Table 2. Bond angle

Parameter	Structure		
	Ni- N	Ni- O	N - Ni- O
Bond angle	107.8°	110.7°	174.8°

The value of the charge on each atom shows the activity of the atoms involved in bonding to form molecular geometries with stable energy through interactions between electron donors and acceptors. The value of the charge on a complex molecule is the total value of the value of the charge on the atoms bonded together in the complex. Meanwhile, the value of bond length shows the distance between atoms that are bonded to each other, as a result the bond distance will affect the strength of the bonds between atoms in complex molecules. The bond distance between atoms which shows the lowest value causes a stronger bond strength. Based on the optimization results, the O₂₂-Ni₄₈ bond is stronger than the N₄₀-Ni₄₈ bond as shown in Table 2.

According to (Braier & Jishi, 2000) revealed that the coordination of nickel with chitosan is most likely to occur around the inter glycosidic structure of chitosan. This is also supported by an article which reveals that the interaction between nickel metal and chitosan is most likely to occur around the amine and hydroxy groups.

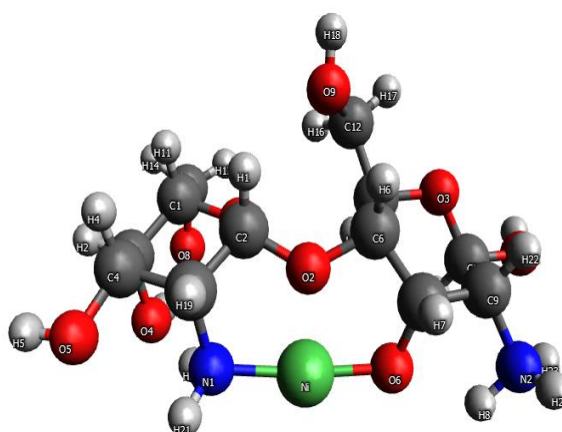


Figure 3. Optimization of chitosan and Ni structure

Based on the optimization results, it was found that there were structural differences between before and after optimizing the Chitosan-Ni²⁺ structure. One metal atom of Ni, which before optimization was far from the chitosan structure, after optimization, approached the chitosan by forming bonds to the nitrogen and oxygen atoms in the chitosan structure around the inter-glycosidic bonding area.

Optimization of molecular geometry is the process of determining the structure/geometry of molecules with low and stable energy values (Pushpavathi et al., 2017). Electronic energy identifies the amount of energy electrons involved in a molecule to be formed. Geometry optimization results data are shown in table 3.

Table 3. Complex property data using the DFT method

No	Parameter	Kitosan - Ni ²⁺
1	Electronic Energy	-38826,90 eV
2	Heat of Forming	267,292 kkal/mol
3	Number of Atoms	48
4	Total Charge	2

Adsorption Energy Value

The adsorption energy is the difference between surface energy + adsorbate, surface energy and adsorbate energy. The surface of this research is chitosan and the adsorbate used is nickel metal. The negative value of the adsorption energy indicates that the corresponding adsorption state is thermodynamically more stable than the unbound state (De Proft et al., 2007). Energy data from the samples used are shown in table 4.

Table 4. Electronic energy data and adsorption energy

Sample	Electronic Energy		E _{ads} (eV)
	(Hartree)	(eV)	
Chitosan-Ni	-1426.862	-38826.900	-18.236
Chitosan	-1258.031	-34232.772	-
Nickel	-168.161	-4575.897	-

Based on table 4, it can be seen that the electronic energy value of each sample is different. The energy value of chitosan that binds nickel metal is lower than the energy value of chitosan before binding nickel metal. The energy value of chitosan-Ni is -1426,862 hartree, which is smaller than the energy value of chitosan before binding nickel metal, which is -1258.031 hartree. This lower energy value indicates that the structure of chitosan that binds to chitosan metal is more stable than the structure of chitosan that has not bonded to nickel metal. From the energy value data obtained, then the adsorption energy value is calculated. The adsorption energy value was obtained from the difference in the energy values of chitosan-Ni, chitosan energy and nickel energy.

From the calculation results, it was found that the adsorption energy value was -18,236 eV. The negative sign obtained indicates that the reaction that occurs between chitosan and metal Ni is a spontaneous reaction. The spontaneous reaction means that the bond between nickel metal and chitosan can occur directly without requiring activation energy. The negative value also indicates that chitosan bonded to nickel is more stable than chitosan which is bonded to nickel metal. The data obtained indicate that chitosan can be used as an adsorbent to be able to adsorb nickel metal.

Energy Gap Value (ΔE)

The energy gap is the difference between the LUMO energy value and the HOMO energy value. HOMO (Highest Occupied Molecular Orbital) is the highest occupied molecular orbital and LUMO (Lowest Unoccupied Molecular Orbital) is the lowest occupied molecular orbital. The value of the energy gap describes the ease with which a molecular system can be excited to a higher electronic state. The small energy gap (Eg 1.1 eV) causes a large absorption power (Oliveira et al., 2019).

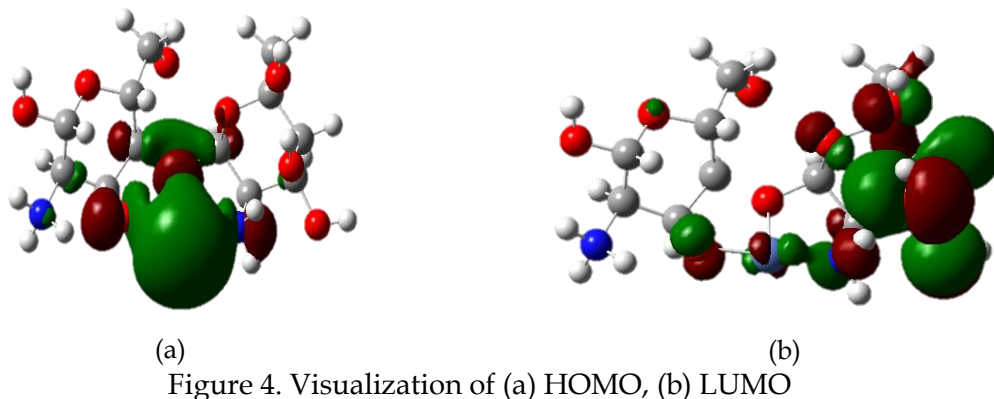
The HOMO value relates to the ability of a molecule to donate electrons and the LUMO value relates to the ability of a molecule to accept electrons (Pamungkas & Sanjaya, 2013). Based on the optimization results, the values of HOMO, LUMO and energy gap are shown in table 5.

Table 5. Data for HOMO, LUMO and energy gap

Sample	E _{HOMO} (eV)	E _{LUMO} (eV)	E _{Gap} (eV)
Chitosan-Ni	-0.4846	-0.38004	0.10456
Chitosan	-0.2087	0.02611	0.23481
Nickel	-1.10279	-1.00066	0.10213

Table 5 illustrates that the value of the energy gap before chitosan binds to Ni metal and after binding to Ni metal. The value of the chitosan energy gap before binding and after binding to

nickel atoms was different. The value of the energy gap of chitosan before bonding is 0.23 eV and the value of the energy gap when binding to Ni metal is 0.10 eV. Based on the results, it was found that the energy gap of chitosan which binds nickel metal is smaller than before binding to nickel metal.



The energy gap of chitosan that binds to nickel is smaller than the energy gap of chitosan that is not bonded to nickel, indicating that electrons are more easily excited in the structure of chitosan and nickel compared to chitosan that is not bonded to nickel. A smaller energy gap value causes a large absorption power. This indicates that the absorption of chitosan on nickel is greater, thus concluding that chitosan can absorb nickel metal well.

CONCLUSION

Structural modeling and molecular optimization using the density functional theory (DFT) method on the basis set B3LYP/LANL2DZ. The molecular geometry for the Chitosan-Ni²⁺ molecule is planar with an angle of 174.8° with an electronic energy of -38826.90 eV. Interactions and bonds between molecules. The interaction between the chitosan molecule and the metal ion Ni²⁺ occurs in the amine group (NH₂) and the hydroxy group (OH) with Ni²⁺ ions. The bond between chitosan and metal occurs in nitrogen and oxygen atoms with a Ni-N bond length of 1.92 and a Ni-O bond length of 1.81 . Energy of adsorption of chitosan membrane structure with metal ion Ni²⁺. The electronic energy of chitosan is -34232.77 eV and the electronic energy of Chitosan-Ni is -38826.90 eV with the adsorption energy of Chitosan-Ni²⁺ formation of -18.236 eV. The value of the gap energy structure of chitosan with nickel metal. The energy gap of chitosan is 0.23481 eV and the energy gap of chitosan-Ni is 0.10456 eV. The energy gap value of chitosan-Ni is smaller than the energy gap value of chitosan

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