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Simulation of Heavy Metal Removal by α-Keratin Nano-Structure of Human Hair from Environment

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Abstract

Including heavy metals are environmental pollutants that human exposure through some of their water and food poisoning can be acute and chronic and sometimes dangerous to establish. Lead can enter the human body and animals by entering the food chain through the feeding and breathing polluted air and they will cause poisoning. In this study, keratin fibers nano-structure is used for Pb^{2+} removal from environment. The keratin fibers using are low cost related to other methods. The interaction of them is simulated and the ab intio calculations at the density function level of theory (DFT) showed energy and thermodynamic properties changing for this interaction. The cystine in α-keratin is simulated and calculated approached to Pb ions in different distances. There is disulfide bond (-SS-) in cystine, for cation ions adsorbed in hair human fibers. The results shown this method is exothermic, spontaneous and favourable for heavy metals in environment.

Keywords: Heavy Metal, α-Keratin, Cystine, Simulation, DFT Method, Environmental.

1 Introduction

Lead, the most abundant heavy metal in Earth's crust, is a highly toxic metal which adversely affects the red blood cells of the human's nervous system and kidneys [1]. Lead, though affects every system in the body, and is detrimental to developing brain and numerous systems of children and fetus [2, 3].

There are different methods for removal of heavy metals from the environment such as industrial waste waters; these methods include: hydrogen combustion [4], phytoremediation of metals, cation and anion exchange, activated carbon, nano-fibers, zeolite and etc. Most of these methods are not applicable because of the high costs to industry and the environment [5-9]. The researchers are trying to obtain methods, are been low cost, safe, high adsorption capability, selective operation, easy and etc. such as: wood ash [10], peanut peel [11], orange, hair and many other materials has been proved to be effective ways for adsorption of metals [12, 13].

In this study, Pb^{2+} removal by hair human is simulated by computational chemistry calculation, is shown Figure 1.

Hair is composed of a group of proteins (α-keratins) that interconnect to form stable fibrils. The α-keratin protein chains are very complex both histological and chemically due to the multiplicity of the cross-linked protein molecules. One of the more important linkages between adjacent keratin chains is the disulfide bond (-SS-) that makes the keratin extremely resistant to biological and chemical degradation. As a waste material keratin should be very cheap source for many applications.

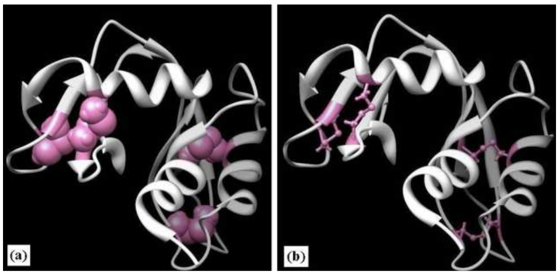

Fig.1: View Ribbon Crystal structure of α-keratin in human hair, red color is cystine (bond –SS-) structure: a) Space filling, b) Ball & stick model in interaction with Pb ions.

From the view point of polymer science, keratin is a biopolymer that is insoluble in water and common solvent [14, 15]. The presence of cystine in the keratin chain leads to characteristic inter and intermolecular disulphide bonds which determine the properties of keratin (Fig.2).

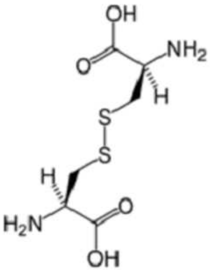

Fig.2: The structure of two cysteines (shown here in its neutral form) bound together by a disulfide bond in keratin.

Lead ions near to cystine of α-keratin and changed all bonds and angles in its structure. The thermodynamics and electronic properties are calculated by MNDO and DFT-IR methods. All the calculations were carried out using Gaussian program package. The BLYP and B3LYP with 6-31G basis set calculate them interaction. The

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results show a sensitivity enhancement in resistance and electric properties when Pb^{2+} is neared to the cystine of α-keratin.

2 The Computational Methods

The geometry optimizations were performed using an all-electron linear combination of atomic orbital density functional theory (DFT) calculations using the Gaussian program package. Unlike of Hartree-Fock (HF) method which only is calculated exchange energy of electrons, in DFT method is both exchange energy and the electron:

$$E_{KS} = \nu + \langle hp \rangle + 1/2 \langle P_j(\rho) \rangle + E_{\chi(\rho)} + E_{C(\rho)} \qquad (1)$$

Where, $E_{\chi(\rho)}$ is the exchange function and $E_{C(\rho)}$ is the correlation functional. The correlation unction of Lee, Yang and Parr includes both local and nonlocal term. For the Minimum energy structures and cluster size, we employ commercial soft ware from MSI [16] and carry out both linear combinations of atomic orbital (LCAO) and plane wave pseudo potential (PWPP) calculations at the DFT± GGA level. The LCAO basis functions are one-electron orbital of free atoms and free ions [17]. Another advantage is that for specific and well-parameterized molecular systems, these methods can calculate values that are closer to experiment than lower level *ab initio* techniques.

Semi-empirical quantum mechanics method used for calculation all thermodynamic parameters of this interaction. Because, we can use the information obtained from semi-empirical calculations to investigate many thermodynamic and kinetic aspects of chemical processes. Energies and geometries of molecules have clear relationships to chemical phenomena. The accuracy of semi-empirical quantum mechanics method depends on the database used to parameterize the method [18, 19]. MNDO gives better results for some classes of molecule.

- Closed-shell singlet ground states
- Half-electron, excited singlet states
- Half-electron, doublet, triplet, and quartet open-shell ground states.

MNDO is a Modified Neglect of Diatomic Overlap method based on the neglect of diatomic differential overlap (NDDO) approximation.

To be able to compute the typical qualities from the microscopic description of a real system, one shall examine integrals around stage space. It may be calculated for an *N*-particle process within an collection with distribution function $\boldsymbol{P}(r^N)$, the experimental price of a property $A(r^N)$ from:

$$\langle A(r^N) \rangle = \int A(r^N) P(r^N) dr^N \qquad (2)$$

The problem with direct evaluation of this multi-dimensional integral (apart of the huge number of phase space points as a sample) is that most of the configurations sampled contribute nothing to the integral. Having energy is so high that the probability of their occurrence is vanishing small [20, 21].

The root-mean square average (RMS) is the gradient vector Cartesian components. For multi-dimensional potential energy materials an easy way of measuring the gradient vector could be the root-mean-square (RMS) gradient explained by RMS Gradient:

$$(3N)^{-1} \left[\sum_A \left(\frac{\partial E}{\partial X_A}\right)^2 + \left(\frac{\partial E}{\partial Y_A}\right)^2 + \left(\frac{\partial E}{\partial Z_A}\right)^2 \right]^{1/2} \qquad (3)$$

For a molecular mechanics calculation the energy and the gradient are essentially the only quantities available from a single point calculation. Ball-and-stick models of the α-keratin are showed in Fig.1 that Lead ions are near to α-keratin simulated by program package and the adsorption, electric, binding nuclear energy, RMS gradient, heat of formation and Gibbs free energy are calculated by MNDO methods in semi empirical quantum by Gaussian program package.

3 Results & Discussion

There are lot methods for removal of heavy metals but most of them are highly expensive so researchers have been highly considered methods that their low cost, high adsorption efficiency, selective operation, easy and hazard less application such as hair human (Fig.3) [13], ionic exchange, activated charcoal, nano-fibers and etc. In this study is simulated interaction between lead ions and α-keratin of hair human. Recently, the X-ray structures of proteins from α-keratin species crystallize is in PDB web site [22].

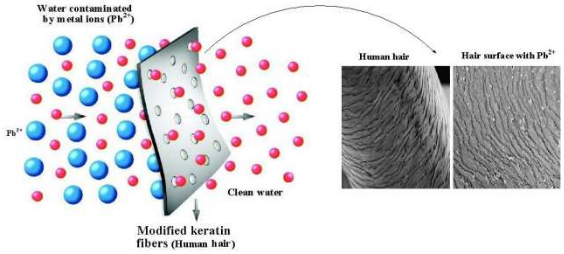

Fig.3: The removal of lead ions by modified keratin fibers.

In figure 1, ball and stick model of interaction and α-keratin with Pb^{2+} is simulated by Chem3D and interaction between them is calculated by Gaussian program package. Energy is calculated for all structures of protein by MNDO, BLYP and B3LYP methods with 6-31G basis set. Other basis sets cannot calculate for it because its structure has lots atoms. Table 1 is thermodynamics parameters for α-keratin without lead ions at room temperature.

Configuration interaction (or electron correlation) improves energy calculations using MNDO for these electron configurations. The heat of formation is calculated for these methods by subtracting atomic heats of formation from the binding energy. MNDO has been used widely to calculate heats of formation, molecular geometries, dipole moments, ionization energies, electron affinities, and other properties. BLYP and B3LYP are used for calculated of thermodynamics properties of α-keratin.

The structure and thermodynamics properties of lead neared to cystine in α-keratin are calculated by MNDO and DFT-IR. In tables 2-4 shown only changes bonds and angles structure of α-keratin in this interaction, for example adsorption energy calculated by:

$$E_{ad} = E_{\alpha-\text{keratin}+ions} - E_{\alpha-\text{keratin}} - E_{ions} \qquad (4)$$

The cystine adsorbed lead ions in 2.91nm, to reduce distance, disposal of them.

Table.1: The structure properties of α-keratin at 298K with 6-31G basis set.

MNDO method							
E_{ads} (Kcal/mol)	RMS Kcal/mol•Å	E_{elec} (V)	E_{bin} (Kcal/mol)	H (Kcal /mol)	G_{elce} (Kcal /mol)	Dipole Moment (D)	E_{nuc} (Kcal /mol)
-64248.72	16.86	-686.42	-1848.33	-150.92	12780283.64	2.22	-1848.33
BLYP method							
G_{th} (Kcal/mol)	H_{th} (Kcal/mol)	E_{th} (Kcal/mol)	S_{th} (Kcal/mol)			C_V (Kcal/mol)	
63.58	90.92	90.41	91.77			31.51	
B3LYP method							
G_{th} (Kcal/mol)	H_{th} (Kcal/mol)	E_{th} (Kcal/mol)	S_{th} (Kcal/mol)			C_V (Kcal/mol)	
65.42	94.677	94.05	98.36			35.39	

RMS gradient (Kcal/mol·Å) is different for this interaction. Exposure to lead ions decreased the conductance of α-keratin, such as that in 2.76 nm distance, the E_{ele} for them is -56.26V, so it is decreased to reduce distance.

The G_{ele} (Kcal/mol) for these interactions have a minimum amounts in 2.91nm to cystine. Theirs dipole moment (D) of lead interaction with cystine in this distance is the least quantity. These places between them are snared for Pb^{2+} and can eliminate it in environment. The nuclear energy for lead removal is observed in table 2. It has most among in 2.76nm, because the field of α-keratin on Pb^{2+} is the most amounts.

The total energy (E_{total}) shown in figure 4. In the table 2, the heat of formation (enthalpy H) and the binding energy (E_{bin}) calculated by MNDO increase for this interaction, their changing is been fitting together. The electric resistance for them is following as:

$$E_{elec} = RI \tag{5}$$

Where, E_{elec} is electric energy (V), R (Ω) is electric resistance and I (A) is electric intensity that is $I = \frac{q}{t}$ and q(C) is electric charge and t is time interaction, in experimental data, it is so:

$$R = \frac{E_{elec} t}{nF} \tag{6}$$

Where, n, F and t are electron number of conversion, faraday constant and time (h) respectively.

The calculations of thermodynamics properties at BLYP and B3LYP levels are presented in Table 3. They indicate the consistency between the two calculation methods (DFT-IR). The enthalpy difference for them is negative, which is interaction exothermic, spontaneous and favourable and Pb^{2+} is separated from air- water in environment.

4 The Other Thermodynamic Properties

Thermodynamic equilibrium constants, K, for these interactions were calculated by the related standard Gibbs free energy difference (ΔG_{elec}):

$$K = \exp\ (-\Delta G_{elec}/RT) \tag{7}$$

where, T is the transition temperature and R is gas constant. The entropy difference (ΔS) at the phase transitions are given by:

$$\Delta S = \frac{\Delta \mathrm{H}}{T} \tag{8}$$

where, $\Delta \mathrm{H}$ is the electronic enthalpy difference. In table 4 is shown the other thermodynamic properties for this interaction.

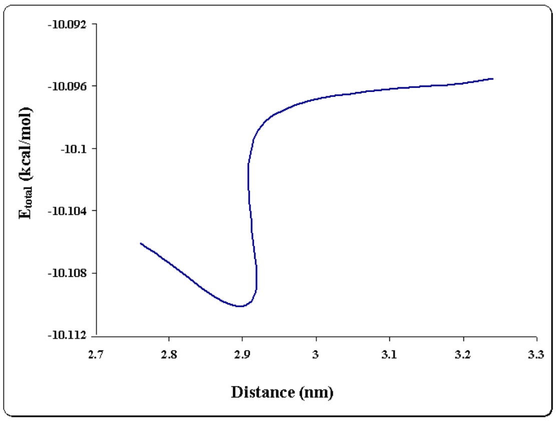

Fig.4: The total energy of interaction Pb^{2+} with α-keratin by MNDO method.

In this interaction, calculation data are converted to (in table 2) the electrical resistance (Ω) that showed in figure 5.

Table.2: The structure properties of interaction Pb^{2+} with α-keratin at 298K by MNDO method.

Distance (nm)	E_{ads} (Kcal/mol)	RMS Kcal/mol·Å	E_{elec} (V)	E_{bin} (Kcal/mol)	H (Kcal /mol)	G_{elec} (Kcal /mol)	Dipole Moment (D)	E_{nuc} (Kcal /mol)
MNDO method								
2.76	-10.106	15.41	-56.26	0.149	0.340	4399.677	1.573	85.653
2.91	-10.110	14.23	-54.49	0.147	0.327	4161.202	1.519	83.609
2.93	-10.098	15.68	-54.86	0.153	0.348	4290.167	1.732	83.277
3.24	-10.095	16.89	-52.44	0.155	0.350	4200.439	1.734	79.151

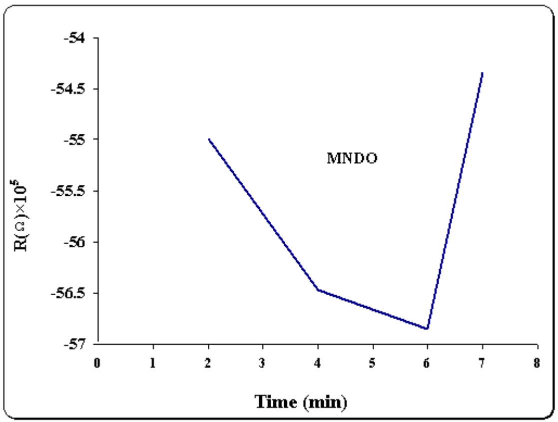

Fig.5: The electric resistance of interaction Pb^{2+} with α-keratin by MNDO method.

Thermodynamic parameters (ΔG_{ele}, ΔH and ΔS) for the removal of lead ions by hair human were calculated and the results suggest that the nature of adsorption is exothermic, spontaneous and favorable. This method is best for removal for Pb^{2+} ions in environment. The calculated of thermodynamics are evaluated via comparison with experimental values. The calculated data are in good agreement with the experimental spectra[13].

Table.3: The properties thermodynamic of interaction Pb^{2+} with α-keratin at 298K by DFT-IR method.

Distance (nm)	G_{th} (Kcal/mol)	H_{th} (Kcal/mol)	E_{th} (Kcal/mol)	S_{th} (Kcal/mol)	C_V (Kcal/mol)
BLYP/6-31G					
2.76	1.525	-0.941	1.505	8.155	3.605
2.91	2.089	-2.822	2.069	16.486	5.651
2.93	2.084	-3.072	2.069	17.168	5.661
3.24	1.448	-2.006	1.442	11.681	3.748
B3LYP/6-31G					
2.76	1.512	-0.627	1.505	6.933	3.603
2.91	1.485	-0.815	1.254	7.596	3.663
2.93	1.478	-0.878	1.505	7.810	3.674
3.24	1.442	-1.568	1.436	9.918	3.747

The thermodynamic properties of hair are based on the properties of the keratin strands and amino acids that combine into a 'coiled' structure. This structure lends too many of the hair properties, such as its ability to stretch and return to its original length. In keratin fibers, long stretches of alpha helix are interspersed with globular (more compactly folded) regions in figure 1.

Table.4: The properties thermodynamic of interaction Pb^{2+} with α-keratin at 298K by DFT-IR method.

methods	ΔG_{elec} (Kcal/mol)	ΔH (Kcal/mol)	ΔS (Kcal/mol)	$\ln K$
BLYP	-1.066	-0.063	0.003	-1.806
B3LYP	-0.941	-0.069	0.002	-1.594

Cysteine amino acids terminate in an -SH group that can form a disulfide bond (-SS-) with a similar group on a cystine in the same protein or in an adjacent protein (Fig.2). Ten to fourteen percent of α-keratin is composed of cystine which these disulfide bonds lend strength and a certain amount of rigidity to keratin proteins and to hair. The disulfide bonds adsorbed lead ions in environment. The results shown, decreased distance of ions related to keratin fibers is exothermic and ions adsorbed by hair fiber are spontaneous.

5 Conclusions

Hair, wool and etc., inside their natural state, fit in with several proteins named α-keratins. The keratin is utilized in study is polypeptide consists of some 18 several types of α-L-amino acid remains of the typical formula $NH_2CHRCOOH$. The side groups R differ markedly in proportions and chemical nature; they could be hydrophobic, acidic or basic.

The human hair is containing alkaline and acidic groups with equal and reciprocal strengths, so is an amphoteric gel. Human hair has the highest percentage of Cys amino acid than wool or other animal hair; the values of Cys in α-keratin are 17.08 gr per 100 gr^{-1} of human hair [23]. These differences probably indicate a higher proportion of high- sulphur proteins, as it is known that human hair has a greater extent of cross-linking than most wool fibers. However, the alkaline groups on human hair are suitable for metal cations adsorption in water environment, an electrochemical bond is formed between the hair and the positive charge.

Cation compounds are remarkably significant in keratin bundles. Due to being non-polar, these compounds are capable of neutralization and removal of imbalance of electrical charges between varieties of hairs. In this study is simulated α-keratin for Pb^{2+} ions removal in environment. The structure and thermodynamics properties shown this method is favorable and is in good agreement with the experimental data.

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