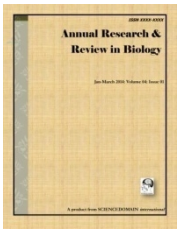

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NMR and Thermodynamic Studies of Pb^{2+} Removal by α-Keratin Nano-Structure in the Environment

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Author's contribution

This whole work was carried out by author LM.

Original Research Article

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ABSTRACT

Aims: In this study is simulated removal of lead ions by human hair. Human hair that has formed of keratin and 14% of keratin is cystine. The approached of Pb^{2+} to cystine is simulated and calculated by Gaussian program package.
Study Design: Density functional methods use for the simulated of keratin and investigation of lead ions removal by keratin. A large number of computational physicists use these methods merely as a recipe, not reflecting too much upon their logical basis.
Methodology: The density functional theory (DFT) method with B3LYP/6-31G is used for calculation energy, chemical shift nucleus magnetic resonance (NMR) and thermodynamics properties for cystine in α-keratin of Human hair in the absence and the presence of heavy metal ions.
Results: Natural hair can be considered as an amphoteric gel containing alkaline and acidic groups with nearly equal and reciprocal strengths. Partial preference of alkaline group accounts for creation of a cation resin quality for hair. When a cation compound gets in touch with a hair having numerous contact sites, an electrochemical bond is formed between the hair and the positive charge.
Conclusion: The results shown, the active site of cystine in this interaction is -S-S- bond and NMR parameters have sharp peak in 2.91nm of ions related to cystine. The thermodynamics properties shown, this interaction is exothermic and spontaneous.

Keywords: Pb^{2+} ions; keratin fibers; human hair; nucleus magnetic resonance (NMR) study; density functional theory (DFT) methods.

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1. INTRODUCTION

Lead is one of the most dangerous four metals for human health [1]. A regular absorption of small amounts of lead may cause serious effects on human health and affecting the body in several ways [2]. There are different methods for elimination of heavy metals and their removal from the environment such as industrial waste waters; these methods include: hydrogen combustion [3], phyto-extraction (removal of environmental pollution by plants) [4], ionic exchange [5], activated charcoal [6], nano-fibers [7], Zeolite [8] and etc [9]. Due to being highly expensive, these procedures are not applied by industry men for preparation and production. Usage of wood ash [10], peanut peel [11], Human hair [12], orange and many other materials has been proved to be effective ways for absorption of metals [13].

In this study simulate lead ions removal by Human hair because structure of Human hair is richer in cystinc and proline that can adsorption heavy metals than other fibers [14].

Recently, the X-ray structures of proteins from α-keratin species crystallize is in PDB web site [15] (Fig. 1). In this study is simulated Pb^{2+} removal by Human hair and is calculated this interaction by DFT-NMR and DFT-IR methods. 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 most important linkages between adjacent keratin chains is the disulfide bond (-S-S-) that makes the keratin extremely resistant to biological and chemical degradation [16,17] and it is active site for lead ions removal. The presence of cystine in the keratin chain leads to characteristic intra- and intermolecular disulphide bonds which determine the properties of keratin (Fig. 2).

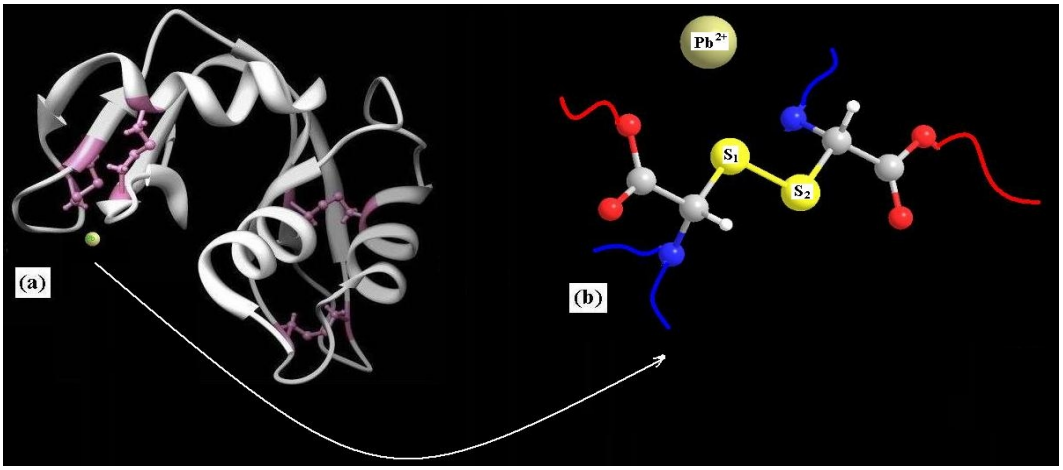

Fig. 1. a) View ribbon crystal structure of α-keratin in human hair, violet color is cystine (bond –S-S-) structure, b) Ball & stick model in interaction with Pb ions in cystine

2. COMPUTATIONAL DETAILS

2.1 Geometry Optimization Quantum Mechanics

The geometry optimizations were performed by means of an all-electron linear combination of atomic orbitals density functional theory (DFT) calculations using the Gaussian program package. The optimizations of solids are carried out including exchange and correlation contributions by means of Beckẻs three parameters hybrid [18-20] and Lee-Yang-Parr (LYP) correlation [B3LYP]; including both local and non-local terms with the program Gaussian program package.

The Gauge Including Atomic Orbital (GIAO) approach was used. The ab initio quantum chemistry methods are computational chemistry methods based on quantum chemistry, that ab initio GIAO calculations of NMR chemical shielding tensors were performed on cystine in α-keratin by means of B3LYP method and 6-31G basis set and the values of symmetric shielding ($\Delta\sigma$), anisotropy (δ), asymmetry shielding (η) and averaging σ over orientations in the magnetic field (σ_{iso}) were calculated by Eqs.(1-4) [21].

$$\Delta\sigma = \sigma_{33} - \frac{1}{2}(\sigma_{11} + \sigma_{22}) \tag{1}$$

$$\delta = \sigma_{33} - \sigma_{iso} \tag{2}$$

$$\eta = \left|\sigma_{22} - \sigma_{11}\right| / \delta \tag{3}$$

$$\sigma_{iso} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) \tag{4}$$

Accurate predictions of molecular response properties to external fields are general significance in various areas of chemical physics. This especially refers to the second-order magnetic response properties (NMR), since the magnetic resonance based techniques have gained substantial importance in chemistry and biochemistry that NMR data is shown with two parameters isotropic (σ_{iso}) and an isotropic (σ_{aniso}) shielding. In the present paper, we report density functional study of isotropic ^{13}C and ^{1}H chemical shifts for neared Pb^{2+} on cystine in α-keratin. All calculations in present work were performed by means of the Gaussian program package.

Compared to Raman spectroscopy, less information about the vibration properties of cystine in α-keratin can be gained from IR spectra. This limitation mainly results from the strong absorption of lead ions on α-keratin in the IR range. The corresponding calculated thermodynamic data, ΔG_{elec}, ΔH and ΔS were determined from the output of the frequency calculation in Gaussian.

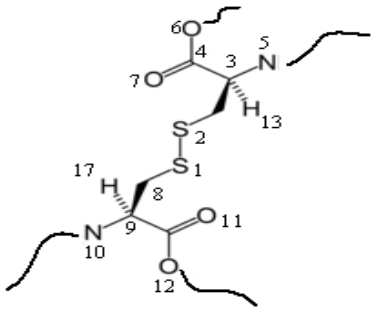

Fig. 2. The structure of two cysteines (shown here in its neutral form) bound together by a disulfide bond in keratin

3. RESULTS

3.1 NMR Parameters

The ab initio GIAO calculations of NMR chemical shielding tensors were performed on the cystine in α-keratin using the B3LYP method with 6-31G basis sets and vibration frequencies of it were calculated in different temperatures and 1atm pressure by using same method and basis set. As it is expected, the results of NMR parameters (σ_{iso}, σ_{aniso}) for atoms of cystine in α-keratin (Fig. 2) are shown in Fig. 3.

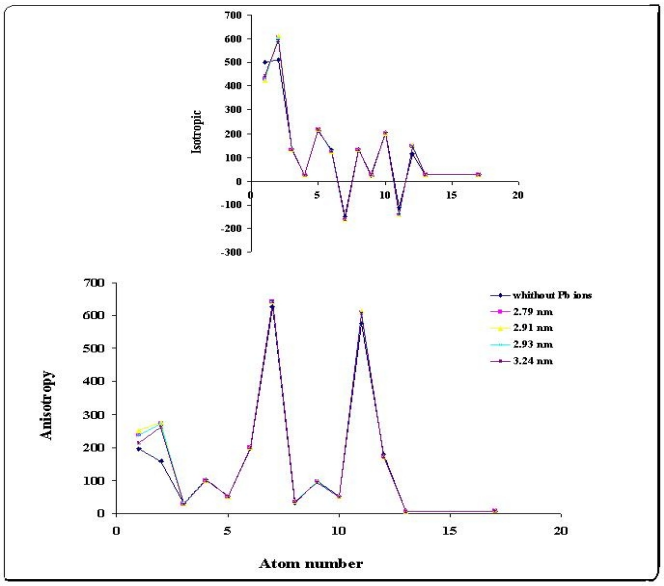

Fig. 3. The isotropy shielding values (σ_{iso}) and anisotropy shielding values (σ_{aniso}) of Pb^{2+} with cystine in α-keratin

The Pb^{2+} ion approached to cystine in different distances, which is the most changing of shielding value for S_1 and S_2 in this diagram, so the -S-S- bond in cystine is active site for Pb^{2+} ion. Other NMR parameters are calculated for S_1 and S_2 atoms. According to Fig. 3, the active site of investigated α-keratin is cystine and the effective atoms on this site can be

contained sulfur atoms and the changing of NMR parameters for other atoms is same in this interaction.

In Table 1, isotropy shielding values (σ_{iso}), anisotropy shielding values (σ_{aniso}), indirect shielding ($\Delta\sigma$), chemical shift tensor (δ), asymmetry parameters (η) and mullikan atomic charge are observed for S_1 and S_2 nuclei in central site of cystine, respect to B3LYP with 6-31G basis set and shown just changing of Pb^{2+} ion approached to -S-S- bond. The σ_{iso}, σ_{aniso}, $\Delta\sigma$, η, δ and mullikan atomic charge (MAC) have similar behavior in different distances and the most changing of NMR parameters is in 2.91 nm of -S-S- bond.

In Table 2, the dipole moment (D) measurement gives an idea about the degree of polarity for approached of Pb^{2+} to human hair. The -S-S- bond is decreasing polar and the electro-negativities of this bond are small, because the dipole moment (D) is decreasing for neared lead ion. The root mean square (RMS) gradient (Kcal/mol·Å) is different for lead ion removal at room temperature. The adsorption energy (E_{ads}) is minimum amount for 2.91 nm.

The kinetic (E_{kin}), potential (E_{pot}) energy and acceptance ratio (ACCR) are calculated for Pb^{2+} in 2.91nm cystine in different temperatures (Table 3) and there was no significant difference between thermo chemical parameters at different temperatures. Thermo chemistry data represented that the highest binding energy (E_{th}), heat capacity at constant volume (C_v), entropy (S_{th}), enthalpy (H_{th}) and Gibbs free (G_{th}) energy provide in B3LYP/6-31G level.

3.2 The other Thermodynamic Properties

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

$$K = \exp\left(-\Delta G_{elec} / RT\right) \tag{5}$$

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

$$\Delta S = \frac{\Delta \mathrm{H}}{T} \tag{6}$$

Where,$\Delta H$is the electronic enthalpy difference. In Tables 4 and 5 are shown the other thermodynamic properties for this interaction such as the heat capacity at constant volume, C_V.

Thermodynamic parameters (ΔG_{ele}, ΔH and ΔS) for the removal of lead ions by Human hair 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 calculation of thermodynamics is evaluated due to the comparison with experimental values. The calculated data are in good agreement with the experimental spectra [12]. The results shown, that the decreasing of ions distance related to keratin fiber is exothermic and hair fiber adsorbed ions to spontaneous and -S-S- bond in keratin is active site for heavy metal removal.

Table 1. The NMR parameters for S1 and S2 in cystine of α-keratin in 298K

steps	atoms	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	σ_{aniso}	$\Delta\sigma$	δ	η	MAC
Cystine without Pb^{2+}	**S_1**	596.495	604.322	302.163	500.993	194.882	-298.246	-198.830	-0.039	0.166
	S_2	612.815	598.162	322.533	511.170	158.272	-282.956	-188.637	0.078	0.152
Distance of Pb^{2+} to cystine (nm)						**S_1**				
2.76		-106.566	-94.239	-8.284	-69.696	43.393	92.119	61.412	-0.107	0.112
2.91		-115.551	-100.454	-12.849	-76.284	56.079	95.153	63.435	-0.130	0.119
2.93		-105.377	-94.325	-7.894	-69.198	42.773	91.957	61.304	-0.098	0.111
3.24		-88.897	-81.900	-0.061	-56.952	19.307	85.338	56.891	-0.065	0.097
Distance of Pb^{2+} to cystine (nm)						**S_2**				
2.76		144.840	60.293	77.037	94.0567	113.287	-25.529	-17.019	0.405	-0.152
2.91		150.554	65.652	85.284	100.497	116.959	-22.819	-15.213	0.411	-0.171
2.93		143.399	59.716	75.448	92.854	113.132	-26.109	-17.406	0.399	-0.150
3.24		130.581	50.235	60.732	80.516	104.492	-29.676	-19.784	0.378	-0.126

Table 2. The RMS, dipole moment and E_{ads} in different distances by NMR parameters

steps	RMS Kcal/molA^o	Dipole moment (D)	E_{ads} Kcal/mol
Cystine without Pb^{2+}	8.58×10^{-9}	2.438	-1363.698
2.76	-4.90×10^{-9}	11.228	-162.130
2.91	-1.57×10^{-9}	10.548	-162.133
2.93	-4.62×10^{-9}	11.356	-162.129
3.24	-3.29×10^{-9}	12.898	-162.122

Table 3. The thermodynamics parameters in different temperatures for distance of Pb^{2+} to cystine 2,91nm

T(K)	ACCR	E_{kin} Kcal/mol	E_{pot} Kcal/mol
298	0.470	20.519	-14971.319
303	0.480	20.863	-14970.163
308	0.440	21.208	-14970.308
313	0.470	21.552	-14971.052

Table 4. 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)
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

4. DISCUSSION

The 17.8% wt of keratin fibers composition are cysteine in human hair that indicate a higher proportion of high-sulphur proteins and has a greater extent of cross-linking than most other fibers [22]. The content of the amino acids with ionic side-chains of human hair is lower than other fibers such as: mohair or wool, thus it has a lower capacity for acids as well as for acid dyes. The metal compounds has been intended to reaction with -SH or -S-S- bonds in alpha keratin, whereas an electron-translucent appearance is considered to be a weak reaction [14].

Lead ions by four distances are neared to -S-S- in cystine of α-keratin and changed all bonds and angles in its structure. The NMR parameters and thermodynamics are calculated by DFT-NMR and DFT-IR methods. All the calculations were carried out using Gaussian program package. The B3LYP with 6-31G basis set is calculated interaction between them. The NMR parameters shown that S_1 and S_2 atoms are active site in cystine and changing of S_1 is more than S_2 in 2.91 nm. The thermodynamics parameters shown, this interaction is exothermic and E_{kin} increase at different temperatures.

In Fig. 1, ball and stick model of interaction and α-keratin with Pb^{2+} is simulated by Chem3D and interaction between them are calculated by Gaussian program package. Energy is calculated for all structures of protein by B3LYP methods with 6-31G basis set. Other basis sets can't calculate them because its structure has lots of atoms. Tables 4 and 5 are thermodynamics parameters for α-keratin and lead ions at room temperature. Configuration interaction (or electron correlation) improves the calculation of energy by means of B3LYP for these electron configurations. The heat of formation (H_{th}) is calculated by subtracting atomic heats of formation from the binding energy for those methods. B3LYP has been used widely to calculate heats of formation, molecular geometries, dipole moments, ionization energies, electron affinities, and other properties. B3LYP are used for calculated of thermodynamics properties of α-keratin.

In Tables 2-5 shown only changes bonds and angles structure of α-keratin in this interaction, for example adsorption energy calculated by:

$$E_{ads} = E_{\alpha-\mathrm{ker}atin+ions} - E_{\alpha-\mathrm{ker}atin} - E_{ions} \quad (7)$$

The cystine adsorbed lead ions in 2.91nm, to reduce distance, disposal of them. RMS gradient (Kcal/mol·Å) is the most amount for this interaction. The dipole moment (D) in neared lead to it in this distance is the least quantity. These places between them are snared Pb^{2+} and can remove it from environment.

Table 5. 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$K$
B3LYP	-0.941	-0.069	0.002	-1.594

The calculations of thermodynamics properties at B3LYP levels are presented in Tables 4 and 5. The enthalpy difference for them is negative, which is interaction exothermic and spontaneous and Pb^{2+} is separated from air- water in environment.

5. CONCLUSION

Lead and lead compounds are generally toxic pollutants. Lead (II) salts and organic lead compounds are most harmful ecotoxicologically. The human body contains approximately 120 mg of lead. About 10-20% of lead is absorbed by the intestines. Organic lead compounds are absorbed quicker, and therefore pose a greater risk. There are a lot of methods for removal of heavy metals. In this study, the lead removal by Human hair is simulated and calculated NMR parameters and Thermodynamics properties by NMR-DFT and IR-DFT. From the NMR and IR results can be concluded:

1 - The active site in cystine- α-keratin is -S-S- bond for Pb^{2+} removal.
2 - The σ_{iso}, σ_{aniso}, Δσ, η, δ and mullikan atomic charge have the most changing in 2.91 nm to -S-S- bond.
3 - The thermodynamics properties are shown changing in same distance. The dipole moment (D) is decreasing for neared lead ion.
4 - The increasing temperature has no significant difference for this interaction.
5 - The entropy, enthalpy and Gibbs free energy (the most negative) is exothermic and hair fiber adsorbed ions to spontaneous.

The human hair can adsorb a significant amount of metal ions; thus keratin fibers are being used to remove metal ions. In future study, human hair can be a cheaper alternative method to purify water supplies and can investigate the best condition for heavy metals in environment by experiment.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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