

## Research Article

# Use of Ethylenediaminetetraacetic Acid as a Scavenger for Chromium from “Wet Blue” Leather Waste: Thermodynamic and Kinetics Parameters

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One serious consequence of the current consumer society is the transformation of the environment into a waste receptacle arising from human activities. Because of the potential toxic effects of chromium solid waste containing this metal there are grounds for serious concern for the tanning and leather processing industry. The application of tannery waste as organic fertilizer has led to extensive contamination by chromium in agricultural areas and may cause the accumulation of this metal in soils and plants. This work evaluated the extraction of  $\text{Cr}^{+3}$  and  $\text{Cr}^{+6}$  contained in solid waste from the leather industry through density functional theory (DFT) calculations. The Gibbs free energy calculations reveal that the chelator ethylenediaminetetraacetic acid (EDTA) forms more stable complexes with metal ions of chromium compared with the structures of the complexes  $[\text{Cr}(\text{NTA})(\text{H}_2\text{O})_2]$  and  $[\text{Cr-collagen}]$ , the latter used to simulate the protein bound chrome leather.

## 1. Introduction

Chromium compounds are used in various industrial processes such as the manufacture of dyes, paints, leather tanning, and plating [1]. Although most of the waste from these processes contains  $\text{Cr}^{+3}$ , which is much less toxic than  $\text{Cr}^{+6}$ , there is the concern expressed about the possible mutagenic and carcinogenic risks of  $\text{Cr}^{+6}$  formed as a result of  $\text{Cr}^{+3}$  chemical oxidation [2]. Presence of light, heat, pH above 5, and reaction with the oxidized fat are some of the situations that cause the oxidation of  $\text{Cr}^{+3}$  to  $\text{Cr}^{+6}$  [3], since, in basic solutions, the oxidation by oxidants such as peroxide occurs more easily [4]. However, the use of chromium in some industry sectors, including mainly the leather industry, due to lack of new processes that can compete with those based on Cr chemistry, is unlikely to be abandoned, in terms of both costs and the quality of the final product [1].

In tanneries, the animal skin goes through processing steps preparing it for the tanning process. The “wet blue”

leather, as the chrome tanned leather is called, has a chromium content of  $20 \text{ g}\cdot\text{L}^{-1}$  and its function is to act as a bridge, linking the protein groups of leather, providing greater end product mechanical and chemical stability [5]. Surveys conducted have shown that approximately 600,000 tons of solid waste is produced each year worldwide by the leather industry and about 40–50% of all leather obtained is lost in shavings [6]. These shavings are small pieces of leather in a variety of forms, mainly composed of collagen complexed with chromium [7]. However, all the methods available for reuse of the tanned leather residue require drastic treatments, chemical or thermochemical processes, causing the complete hydrolysis of leather and adding little value to the final material [8].

In recent years, a viable alternative to recycle these wastes is gaining prominence as an excellent solution to the problem [8]. It is the transformation of the waste (splinters, flaps, and sanding dust) into nitrogen-rich fertilizer. The method consists of the complete dissolution of the solid, removing

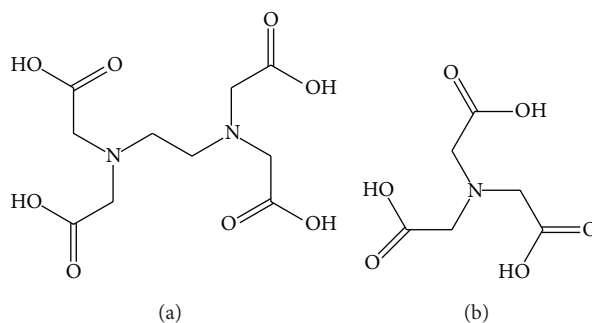


FIGURE 1: Structure of the EDTA (a) and NTA (b).

the precipitate as Cr hydroxide, and use of the protein remaining in the organic liquid as fertilizer [8]. A crucial step in the realization of the method is the use of sequestering agents which may complex the chromium from the organic matter of the leather, consisting mainly of collagen.

Among the most important classic reagents containing many industrial applications which can be used to remove toxic metal ions from contaminated water and soil stand out ethylenediaminetetraacetic acid (EDTA) [9–12] and nitrilotriacetic acid (NTA) [13–15] (Figure 1). These ligands, in the form of alkali metal salt, contain the respective polyacetate anion forming very stable complexes with most metallic ions. The evidenced importance of these ligands as chelating agents supports the need for an exploration of their properties. Given these concepts, theoretical studies concomitant with the experimental, addressing the understanding of the phenomenon involving a metal complexation by organic ligands, are always needed. However, due to the variety of possible geometries and different oxidation states of the metal, theoretical calculations for metal complexes are generally complicated [16]. The *ab initio* calculations (Hartree-Fock) [17] used to describe the complexes formed between metals and organic ligands are limited by the complexity of the system being studied. On the other hand, the method of the density functional theory (DFT) has been increasingly used to study interactions between biomolecules and metals [18, 19]. This approach is interesting because it includes the effect of electron correlation and enables the calculation for larger systems [20, 21]. Thus, the objective of this work is to use molecular modeling methods and DFT calculations to evaluate the thermodynamics of formation of  $\text{Cr}^{+3}$  and  $\text{Cr}^{+6}$  complexes formed by EDTA and NTA ligands, relating them to the respective structures of Cr-collagen complex used to simulate the interaction between the protein leather and chrome. In addition, experimental kinetics studies were carried out in order to obtain the kinetics parameters for the studied complexes.

## 2. Computational Methods

Initially, the structures of ligands and complexes were modeled using the PC Spartan Pro program [22]. The models were submitted to optimization by the semiempirical and DFT methods, PM3 [23], and BP86/6-31G for the atoms C,

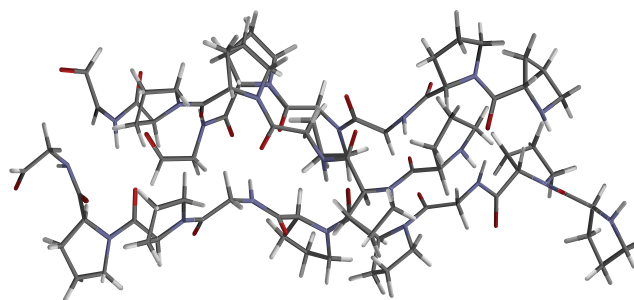


FIGURE 2: Structure of collagen. The red color represents the oxygen atom; blue: nitrogen, gray: carbon, and white: hydrogen.

H, O, and N and LANL2DZ for the metal. To simulate the interaction between the target protein and chromium ions, the three-dimensional structure of collagen was obtained from Protein Data Bank (PDB) (<http://www.rcsb.org/pdb>) (code: 1A3I), Figure 2.

This protein has been used as a model structure for studies of collagen [24], the most abundant protein in mammals and responsible for the complexation of chromium in the leather [25]. Because of the size of this protein, there was a possibility of complexation with two or even three chromium atoms. However, this work focuses on the complexation reaction for a Cr-ligand ratio of 1:1. Thus, the protein structure was adjusted by cutting the edges, altering the size of the structure to an approximate radius of 17 Å. To investigate the thermodynamic properties of the complexation between chromium ( $\text{Cr}^{+3}$  and  $\text{Cr}^{+6}$ ) and the ligands EDTA, NTA, and collagen, electronic structure calculations were performed on another level. For this, all structures were exported to the GAUSSIAN 09 [26] program, where the vibrational frequency calculations were performed using the method of Density Functional Theory (DFT) [12, 27] combined with functional exchange-correlation (XC) BP86 [28]—expression Becke for exchange and Perdew for correlation—and the basis set 6-31G [29] for the atoms C, H, O, and N and LANL2DZ [30, 31] for the chromium atom. The latter, by including pseudopotential, is indicated for atoms that are from the fourth period of the periodic table.

The complexation of a metal ion with a chelating agent usually occurs in aqueous medium. In order to simulate

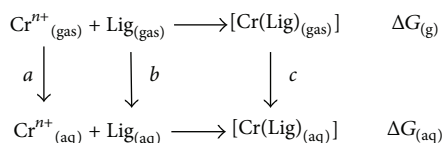


FIGURE 3: Thermodynamic cycle.

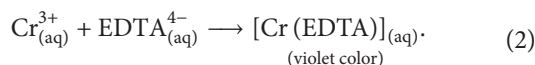
this situation, we have employed a thermodynamics cycle (Figure 3). Since the theoretical calculations were performed for the gaseous state and the interest is in obtaining the free energy of reaction in solution, a new series of calculations were performed in GAUSSIAN 09 to evaluate the solvation energy of the species involved. The solvent effects have been taken into account with the Polarizable continuum model (PCM) developed by Shimizu et al. [32]. To get the Gibbs free energy of complexation reaction solution ( $\Delta G_{(\text{aq})}$ ) shown in Table 1, calculations were made using the thermodynamic cycle below [12, 18] and the following:

$$\Delta G_{(\text{aq})} = \Delta G_{(\text{g})} + [c - (a + b)], \quad (1)$$

where  $a = \Delta G_{\text{solv}}(\text{Cr}^{n+})$ ,  $b = \Delta G_{\text{solv}}(\text{Lig})$ , and  $c = \Delta G_{\text{solv}}([\text{Cr}(\text{Lig})])$ .

To justify the difference in stability between the complexes, analysis of natural bond orbitals (NBO) [33] was performed with the BP86 functional and the basis functions 6-31G (C, H, O, N) and SDD [34] (Cr). Furthermore QTAIM calculations were carried out by using the program AIM11 [35].

**2.1. Experimental.** To evaluate the kinetics of complexation of trivalent chromium with EDTA [36] the following reagents were used: Merck PA: chromium salt ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and EDTA (disodium). Furthermore, we used thermostatic bath (Tecnal TE-210) and an UV-Vis spectrophotometer (Shimadzu UV-160 IPC). For the Cr-EDTA complex formation (2),  $\text{Cr}^{3+}$  and EDTA solutions were prepared at concentrations of 1000 and 7158 ppm, respectively, so that the stoichiometry of the reaction 1 : 1 was obeyed:



5 mL of each solution was placed in contact in several containers with in order to measure the absorbance of the solution at different reaction times. The temperature was controlled by a thermostatic bath using temperatures of 25, 40, 50, 60, and 70°C. After removing the sample from thermostatic bath it was placed in an ice bath to stop the reaction and the solution was read in a UV-Vis spectrophotometer.

### 3. Results and Discussion

**3.1. EDTA and NTA Complex with the Cr Ion.** The EDTA ligand is hexadentate and the atoms responsible for coordinating with the chrome are four oxygen atoms of the carboxylic groups and two nitrogen atoms of the amine groups. In order to develop different isomers of Cr-EDTA complex, relative

TABLE 1: Variation of the Gibbs free energy for complexation reaction in kcal·mol<sup>-1</sup>.

Complex	Charge on the Cr atom	$\Delta G_{(\text{aq})}$	$\Delta \Delta G_{(\text{aq})}$
[Cr(EDTA)]	+6	-322.75	0.00
[Cr(EDTA)]	+3	-316.99	5.76
[Cr(NTA)(H <sub>2</sub> O) <sub>2</sub> ]	+6	-311.02	11.73
[Cr(NTA)(H <sub>2</sub> O) <sub>2</sub> ]	+3	-305.93	16.82
[Cr(collagen)]	+6	-289.70	33.05
[Cr(collagen)]	+3	-286.66	36.09

positions between the two nitrogen atoms in the structures were considered. However, for structures that are initially different in the disposition of the atoms in the coordination sphere, after optimization and minimization of energy, it was found that all converged into a common structure with a more stable rearrangement (Figure 4(a)). Regarding the NTA, coordination occurs between three carboxyl groups and the nitrogen and thus a tetradentate ligand. In this case, as the objective was to investigate complexes with octahedral geometry, since they tend to be more stable, for development of the structures two water molecules were used as ligand, thus completing the valence six of the chromium. As with EDTA, after optimization of the structure, all converged into a single (Figure 4(b)).

**3.2. Free Energy Calculations.** After optimization, all calculations of frequency (in the gaseous state and implicit solvent) were performed in GAUSSIAN 09 program, as mentioned in the methodology section. Thus, it was possible to obtain the Gibbs free energy total for each species as per

$$G_{\text{tot}} = \sum_{E,T,G} + E_{\text{corr}(G)} + E_{\text{ZPE}}, \quad (3)$$

where  $G_{\text{tot}}$  = Gibbs free energy of the total,  $\sum_{E,T,G}$  = sum of electronic, thermal, and free Gibbs energy,  $E_{\text{corr}(G)}$  = Gibbs free energy correction, and  $E_{\text{ZPE}}$  = zero-point energy correction.

From the total free energy values ( $E_{\text{tot}}$ ) of the species (reactants and products), it was possible to perform the calculation of the thermodynamic cycle and find the change in free energy for each complexation reaction in solution ( $\Delta G_{(\text{aq})}$ ) and the corresponding relative free energy change ( $\Delta \Delta G_{(\text{aq})}$ ), as shown in Table 2.

According to the results shown in Table 3, the stability order for the complexes is as follows:  $[\text{Cr}^{+6}(\text{EDTA})] > [\text{Cr}^{+3}(\text{EDTA})] > [\text{Cr}^{+6}(\text{NTA})(\text{H}_2\text{O})_2] > [\text{Cr}^{+3}(\text{NTA})(\text{H}_2\text{O})_2] > [\text{Cr}^{+6}(\text{collagen})] > [\text{Cr}^{+3}(\text{collagen})]$ . This means that the complexation reaction between chromium and EDTA is more favorable to occur in relation to the complexes  $[\text{Cr}(\text{NTA})(\text{H}_2\text{O})_2]$  and Cr-collagen, for both oxidation states of the chromium. It may also be noticed that, for the same ligand, the complex formed with  $\text{Cr}^{+6}$  is more stable when compared to the corresponding complex with  $\text{Cr}^{+3}$ . This is due to the fact that there is a correlation between the complexation capacity and size of the metal ion, because the metal-ligand affinity proves to be the inverse of the ionic radius [37]. Thus,

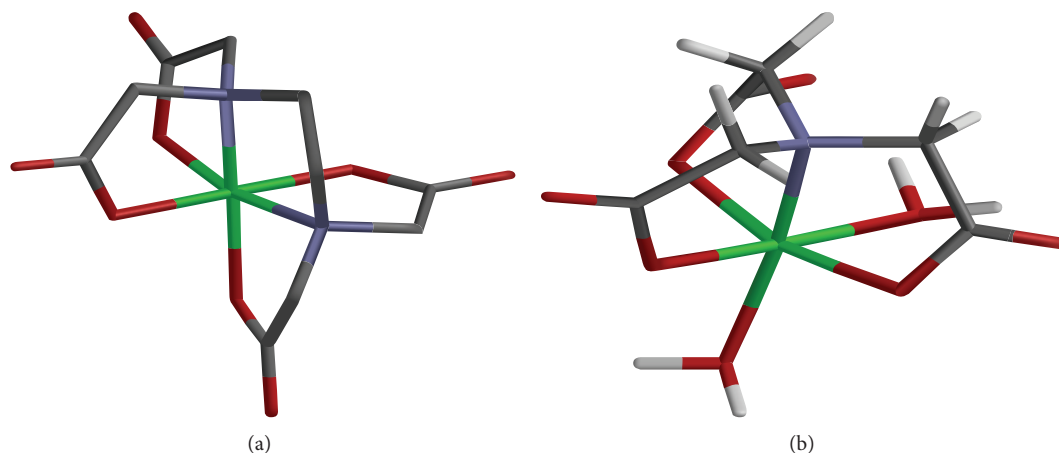


FIGURE 4: Optimized structures of the complexes [Cr(EDTA)] (a) and [Cr(NTA)(H<sub>2</sub>O)<sub>2</sub>] (b). The green color represents the chrome atom; red: oxygen, blue: nitrogen, and gray: carbon.

TABLE 2: Relative Gibbs free energy values for the complexation reaction in solution ( $\Delta\Delta G_{(aq)}$ ).

Complex	Chromium load	$\Delta\Delta G_{(aq)}$ kcal·mol <sup>-1</sup>
[Cr(EDTA)]	+6	0.00
[Cr(NTA)(H <sub>2</sub> O) <sub>2</sub> ]	+6	11.73
[Cr(collagen)]	+6	33.50
[Cr(EDTA)]	+3	5.76
[Cr(NTA)(H <sub>2</sub> O) <sub>2</sub> ]	+3	16.82
[Cr(collagen)]	+3	36.09

TABLE 3: QTAIM parameters obtained by the main interatomic interactions in the isomer (B) of the Cr-EDTA complex, the Cr-NTA(H<sub>2</sub>O)<sub>2</sub>, and Cr-collagen complex in a.u.

	BCP	$\rho$	$\nabla^2\rho$	Hc
Cr-EDTA	Cr-O1	0.175	+0.649	-0.064
	Cr-O2	0.122	+0.533	-0.018
	Cr-O3	0.135	+0.777	-0.025
	Cr-O4	0.170	+0.488	-0.062
	O1-C5	0.273	-0.449	-0.270
Cr-(NTA)(H <sub>2</sub> O) <sub>2</sub>	Cr-O2	0.035	+0.100	-0.007
	Cr-O5	0.052	+0.135	-0.017
	Cr-O8	0.081	+0.198	-0.033
	Cr-O9	0.086	+0.241	-0.034
Cr-collagen	Cr-N11	0.099	+0.236	-0.039
	Cr-O1	0.055	+0.087	-0.008
	Cr-O2	0.055	+0.068	0.009
	Cr-O3	0.058	+0.067	-0.012
	Cr-O4	0.086	+0.046	-0.031

the results are consistent with the difference in size between the ions, 0.76 [38] and 0.44 Å [39] for Cr<sup>+3</sup> and Cr<sup>+6</sup>, respectively. In addition, molecular orbital and electronic structure

TABLE 4: Higher energies of nonbonding interactions between NBOs in the coordination sphere for complexes of Cr<sup>+6</sup> kcal·mol<sup>-1</sup>.

Cr <sup>+6</sup> (EDTA)	Cr <sup>+6</sup> (NTA)(H <sub>2</sub> O) <sub>2</sub>	Cr <sup>+6</sup> (collagen)
$n_{O4} \rightarrow d^*_{Cr}$ 9.11	$n_{O8} \rightarrow d^*_{Cr}$ 4.45	$n_{O3} \rightarrow d^*_{Cr}$ 2.81
$n_{O1} \rightarrow d^*_{Cr}$ 7.15	$n_{O5} \rightarrow d^*_{Cr}$ 3.90	$n_{O1} \rightarrow d^*_{Cr}$ 2.63
$n_{O2} \rightarrow d^*_{Cr}$ 6.44	$n_{O2} \rightarrow d^*_{Cr}$ 3.74	$n_{O2} \rightarrow d^*_{Cr}$ 2.52
$n_{O3} \rightarrow d^*_{Cr}$ 2.37	$n_{O9} \rightarrow d^*_{Cr}$ 2.63	$n_{O4} \rightarrow d^*_{Cr}$ 1.21

calculations can be used to more deeply investigate the molecular basis for rationalizing the complexation reaction.

**3.3. Natural Bond Orbitals Analysis (NBO).** The NBO analysis provides information about the electronic structure of a complex. For example, the interaction between the occupied and vacant orbitals represents the deviation of the molecules from the Lewis structure, and the respective energies can be used as a measure of structure stability [18, 40]. Table 4 shows the most energetic interactions involving the transfer of electrons between orbitals (donor  $\rightarrow$  acceptor) and energies in the coordination sphere of the structures formed with Cr<sup>+6</sup>, through which it is possible to justify the difference in stability between the respective complexes. As can be seen, the interactions mentioned in relation to [Cr<sup>+6</sup>(EDTA)] complex are relatively much higher than the correspondents in the structures of the [Cr(NTA)(H<sub>2</sub>O)<sub>2</sub>] and [Cr(collagen)] complexes. These results indicate a greater stability for the Cr-EDTA complex, being in accordance with the Gibbs free energy variation obtained from the thermodynamic cycle. In order to investigate the electronic and steric effects that modulate the complexation reaction with chromium ions, we have performed NBO and AIM calculations.

**3.4. Quantum Theory of Atoms in Molecules (QTAIM).** The topological analysis of the electron density can provide valuable information about the properties of the system under consideration. The properties of electron density measurements in the so-called Bond Critical Point (BCP), such as the

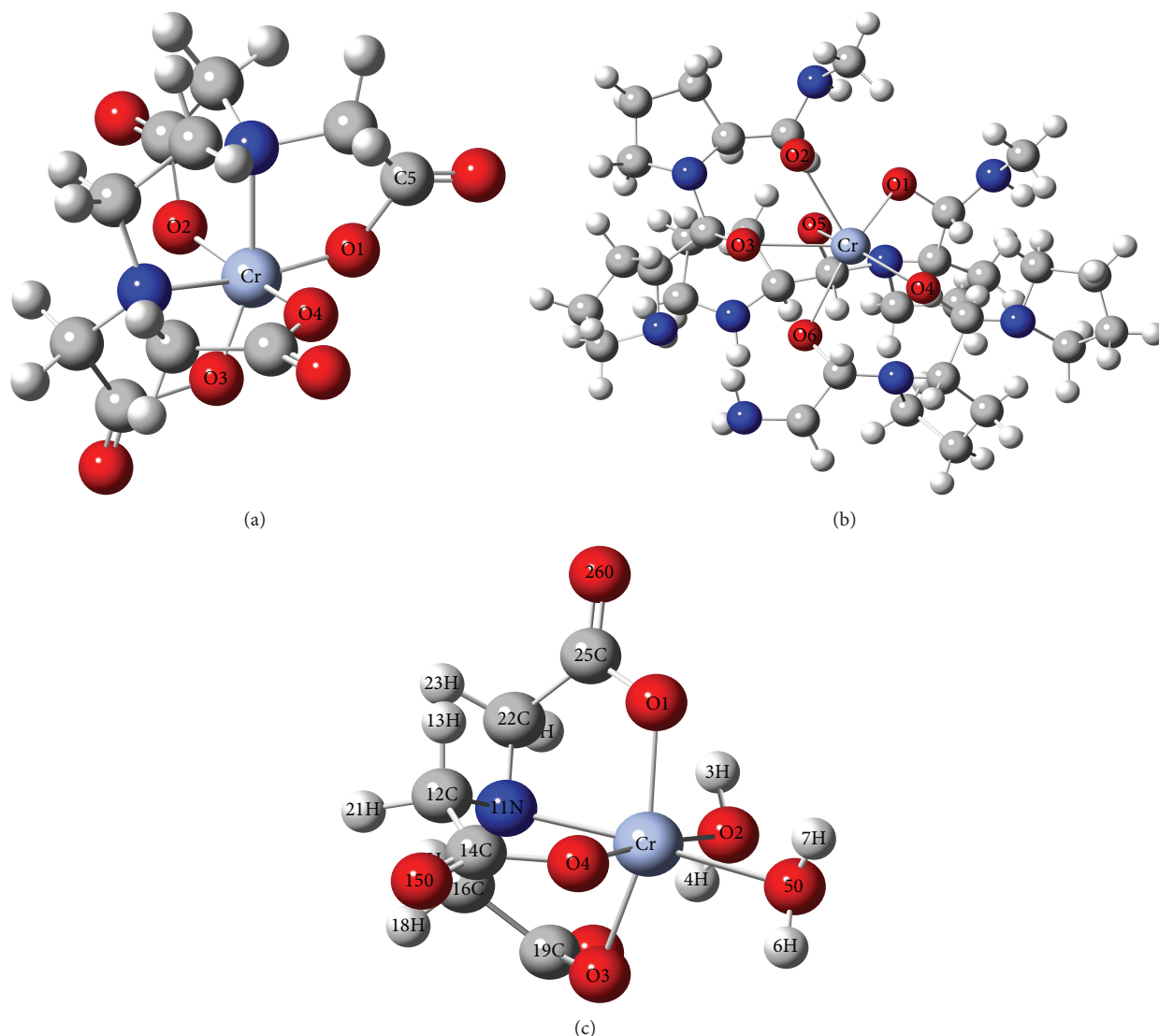


FIGURE 5: Structures of the isomer “B” of the Cr-EDTA complex (a), Cr-collagen complex (b), and Cr-NTA complex (c).

electronic density at BCP ( $\rho$ ), the Laplacian of the electron density ( $\nabla^2\rho$ ), the potential energy ( $V_c$ ), kinetic energy ( $G_c$ ), and the total electron energy ( $H_c$ ), are useful for detecting and characterizing the chemical bonds such as covalent bonds, metal-ligand interactions, hydrogen bonds, and other weak noncovalent intramolecular interactions [41]. For example, for bonds predominantly covalent,  $\rho$  is generally  $>0.20$ ,  $\nabla^2\rho < 0$ , and  $H_c < 0$ , while for the bond of an electrostatic nature (ionic)  $\rho$  is generally lower ( $\sim 10^{-2}$  for hydrogen bonding and  $\sim 10^{-3}$  for Van der Waals interaction) with  $\nabla^2\rho > 0$  and  $H_c$  relatively higher [13, 42]. Table 3 shows the properties of BCPs for the most relevant interactions that occur among the atoms in the  $\text{Cr}^{+6}$  complexes shown in Figure 5. As with the data in Table 4, it can be seen that the interactions established between chromium and the oxygen atom are electrostatic in nature, with ionic bonding characteristics, wherein the core supports the entire load concentration ( $\nabla^2\rho > 0$  and relatively high  $H_c$ ), in contrast,

for example, with the values of the covalent bond O1–C5. The QTAIM analysis did not reveal relevant intramolecular interaction, such as hydrogen bonding, for example. However, the topological analysis revealed a greater electron density in the coordination sphere region for Cr-EDTA complex than with the complexes collagen-Cr and Cr-(NTA)( $\text{H}_2\text{O}$ )<sub>2</sub>. Moreover, the electron density ( $\rho$ ) values in the coordination sphere of BCPs for these two complexes were much lower, indicating that electrostatic interactions are less.

### 3.5. Formation Kinetics of Cr-EDTA Complex

**3.5.1. Experimental.** Since our theoretical findings point out EDTA as the best ligand used for the complexation reaction with chromium at both oxidation states,  $\text{Cr}^{+3}$  and  $\text{Cr}^{+6}$ , we have performed the experimental part focused on EDTA complex. The formation of the Cr-EDTA complex in relation to time can be evidenced by the gradual formation of its

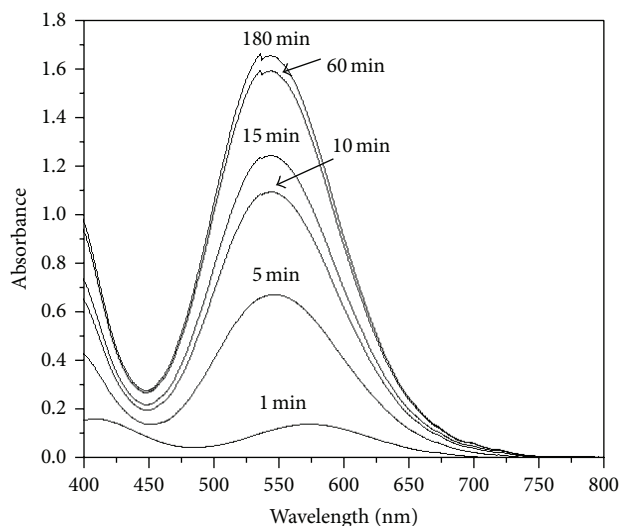


FIGURE 6: UV-Vis spectra of the Cr-EDTA complex at 70°C.

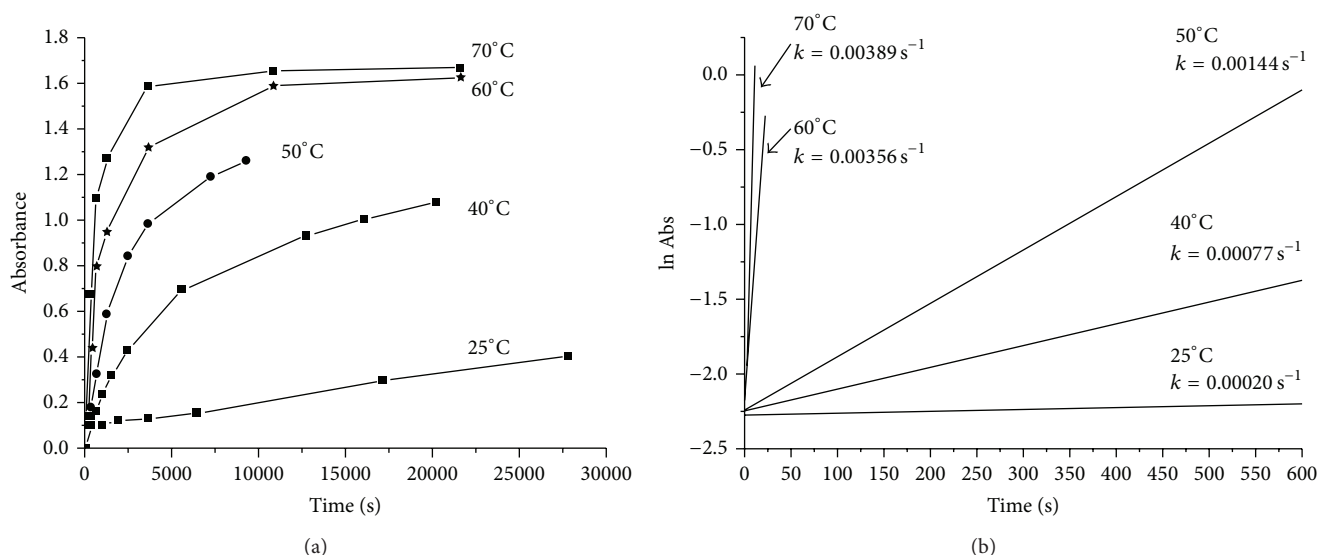


FIGURE 7: The formation kinetics of the Cr-EDTA complex at different temperatures (a) and the linearization of the equation speed ( $\ln [\text{Abs}] = kt$ ) with the respective constants (b).

absorption band in the visible region at 546 nm (Figure 6). The spectra show that at 70°C the formation of the complex can be studied with extreme speed; only 5 min of reaction is necessary. The formation kinetics of Cr-EDTA complex was studied at 546 nm at various temperatures, as shown in Figure 7(a). It can be observed that increasing the temperature increases the rate of complex formation, observing the increase in absorbance for the same time. In addition, considering an approximately linear curve in short times, one can determine the rate constants for complex formation, by linearizing the velocity equation  $\ln [\text{Abs}] = kt$ , shown in Figure 7(b). Using the Arrhenius equation [43] (4) and with the data obtained in this experiment it was possible to

determine the activation energy required for the formation of the complex ( $E_a = 59 \text{ kJ}\cdot\text{mol}^{-1}$ ):

$$\ln K = \ln A - \frac{E_{\text{at}}R}{T^{-1}}. \quad (4)$$

**3.6. Effect of pH.** Complexation reactions involving metals by ligands of aminopolycarboxylic acids are very dependent on pH, such that, according to the acidity of the reaction medium, there will be a greater or lesser prevalence of a species of ligand at equilibrium. At very low pH the nonionized species of the ligand predominates, so that, for the reaction to occur, the metal ions must be able to remove the ionizable hydrogens

of the molecule. On the other hand, in strongly basic solutions, such hydrogens are removed by reaction with hydroxide ions. However, the ligand in its anionic form will “compete” with the hydroxyl in the complexation with the metal, and many metal ions tend to hydrolyze and precipitate as hydroxides [2]. The formation of  $[\text{Cr}^{+3}(\text{EDTA})]$  complex shows to be favored between pH 4.5 and 7, and according to the basicity increase, the species is gradually replaced by  $[\text{Cr}^{+3}(\text{EDTA})(\text{OH})]$ , tending to form the hydroxide  $\text{Cr}^{+3}$  [44].

#### 4. Conclusion

In this work the stability of complexation of chromium (trivalent and hexavalent) with the structures of the polydentate ligands EDTA and NTA and collagen was studied. According to our results we observe that the formation of the Cr-EDTA complex from the  $\text{Cr}^{+6}$  is energetically more favorable; that is, the complex is more stable. The fact that the  $\text{Cr}^{+6}$  has a similar electronic configuration to a representative element and a smaller ionic radius compared to  $\text{Cr}^{+3}$  can justify this greater stability. The kinetics of formation of complex with  $\text{Cr}^{+3}$  was also investigated. The results showed that increasing the temperature increases the rate of formation of the complex and at 70°C only 5 min of reaction is required with a rate constant equal to  $k = 0.00389 \text{ s}^{-1}$ .

By comparing the Gibbs free energy of Cr-EDTA,  $[\text{Cr}(\text{NTA})(\text{H}_2\text{O})_2]$  and Cr-collagen structures complexation, the following order of stability was found:  $[\text{Cr}^{+6}(\text{EDTA})] > [\text{Cr}^{+3}(\text{EDTA})] > [\text{Cr}^{+6}(\text{NTA})(\text{H}_2\text{O})_2] > [\text{Cr}^{+3}(\text{NTA})(\text{H}_2\text{O})_2] > [\text{Cr}^{+6}(\text{collagen})] > [\text{Cr}^{+3}(\text{collagen})]$ . Thus, in this work it was noticed that although the EDTA and NTA ligands can be used in the process, the formation of the Cr-EDTA complex is energetically more favorable; therefore, EDTA has greater ability to “sequester”  $\text{Cr}^{3+}$  as well as  $\text{Cr}^{6+}$ , which are connected to the waste from the leather industry (chips, shavings, and dust from sanding) before they are discarded or reused for other purposes. Thus, from a thermodynamics, as well as kinetics point of view, our theoretical and experimental findings point out EDTA as a promising scavenger for chromium, forming a more stable metallic complex with chromium with a lower activation energy, from “wet blue” leather waste.

#### Conflict of Interests

The authors declare that there is no conflict of interest regarding the publication of this paper.

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