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Spectrophotometric studies for the interaction of Pb^{+2} ion with some chelators

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ABSTRACT

Lead is one of the toxic heavy metal when presented in a high level over it allowable limit. To detoxify this heavy metal a chelators were used as in a chelation therapy. This work studies the complexation of some chelators (penicillamine and quercetin) with Pb II ion. A spectrophotometric techniques were applied in water and water-ethanol mixture as a solvent, at four different temperature. A shift in it λ_{max} and decrease in absorbance indicating the complex formation. The stoichiometry of these complexes were determined by a method of the continuous variation (Job's) method, it was found that Pb-quercetin (1:1), and Pb-penicillamine (2:1). These chelator's have a high tendency to complex with Pb II ion which were reflected by its high values of their equilibrium constants. Thermodynamic parameters indicate a spontaneous interaction (negative free energy change ΔG^o), and the enthalpy changer have negative ΔH^o which depends on type of the interaction and the structures of the complexes. The kinetic calculations shows a second order interaction.

KEYWORDS

Chelating agents;
Penicillamine;
Quercetin;
Kinetic parameters;
Thermodynamic parameters and complexation.

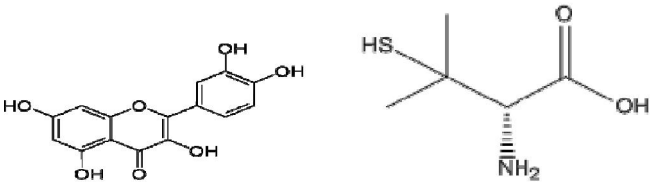
INTRODUCTION

Chelation describes a particular way that ions and molecules bind metal ions, chelation involves the formation or presence of two or more separate coordinate bonds between a polydentate ligand and a single central atom. Usually these ligands are organic compounds[1]. Called chelators. A medical procedure that involves the administration of chelators to remove heavy metals from the body called chelation therapy. Detoxification of heavy metal by the administration of chelators, forms a stable complex and prevents the toxic heavy metal species from attacking the biological targets[2].

Penicillamine is a well-known heavy metal chelator, classically used in the treatment of Wilson disease, rheumatoid arthritis, and cystinuria. From a dermatologic standpoint, penicillamine was found to be useful in the treatment of systemic sclerosis. The pharmaceutical form is D-penicillamine, it is an α-amino acid metabolite of penicillamine[3].

Quercetin is a flavonoids found in many fruits, vegetables, leaves and grains. It can be used as an ingredient in supplements, beverages, or foods.

Quercetin widely distributed in nature. The name has been used since 1857, and is derived from



Quercetin Penicillamine

Figure 1 : Chemical structures of the studied compounds

quercetum (oak forest), after Quercetin[4]. It is a naturally occurring polar auxin transport inhibitor[5]. Quercetin has anti-oxidant and anti-inflammatory effects, it scavenge damaging particales in the body known as free radicals, which damage cell membranes, tamper with DNA and even causes cell death. Flavonoids were significantly more effectine inhibitors of iron ion-dependent lipid peroxidation systems due to chelating iron ions with the formation of inert iron complexes unable to inhibit lipid peroxidation. At the same time these complexes retained their free radical scavenging activities[6].

Lead is a chemical element in the carbon group with symbol Pb and atomic number 82. Lead is a soft, malleable and heavy post-transition metal. Metallic lead has a bluish-white color after being freshly cut, but it soon tarnishes to a dull grayish color when exposed to air. Lead has a shiny chrome-silver luster when it is melted into a liquid. It is also the heaviest non-radioactive element. Lead is a bright and silvery metal with a very slight shade of blue in a dry atmosphere[17]. Upon contact with air, it begins to tarnish by forming a complex mixture of compounds depending on the conditions. The color of the compounds can vary. The tarnish layer can contain significant amounts of carbonates and hydroxyl carbonates[7][8].

EXPERIMENTAL

Chemicals and solutions

Penicillamine Fluka AG. Chem. Fabrik CH-9470 Buchs and quercetin from Aldrich chemical company, Methanol from scharlau, Lead nitrate from Hopkin & Williams LTD (CHADWELL HEAT ESSEX ENGLAND).

Way to prepare (penicillamine and quercetin)

The stock solution of. The stock solutions of Penicillamine (10^{-2}M) was prepared by dissolving (0.2982 g) in 100mL volumetric flask using 50% ethanol/distilled water mixture as a solvent. The stock solution of Qurecetine (10^{-2}M) was prepared by dissolving (0.3382 g) in 100mL volumetric flask using 80% ethanol/distilled water mixture as a solvent.

Pb (II) solution

The stock solution of lead (II) (10^{-2}M) was prepared by dissolving (0.3312 g) of lead nitrate ($Pb(NO_3)_2$) in (100 ml) volumetric flask using water as a solvent.

Absorption spectroscopy

All spectral measurements were recorded on a double beam UV-Visible spectrophotometric, shimadzue – model - 160A, using a 1cm path length quartz cell. Absorbance value of EDTA, penicillamine, genistein and qurecetine in the presence and absence of Pb (II) solution were made in the range of (200-600nm).

Stoichiometry analysis

The stoichiometry of the complexes ligands (penicillamine and quercetin) with lead (II) ion were determined by continuous variation method (Jobs method)[9][10] equimolar concentrations (10^{-4}M) of a ligand and Pb (II) ion were prepared, and Job's method was applied by placing 1 to 9 mL of (10^{-4}M) ligands solution into a series of 10 mL volumetric flask, this was followed by placing 9 to 1 mL of (10^{-4}M) Pb (II) ion solution, and the absorbance were measured at the maximum wave length.

RESULTS AND DISCUSSION

Absorption spectroscopy

The optimized solvent mixture (ethanol/water) was obtained by measuring the Uv-Vis absorption spectra of penicillamine and qurecetine in various mixture compositions as shown in TABLE (1). This Table shows penicillamine and qurecetine absorption band. The band do not exhibit any significant changes in λ_{max} with the variation of solvent composition, whereas the absorbance does. Figures (2 and

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TABLE 1 : Optimized condition for the absorbance of the ligands

No.	ligands	Ethanol%	Wave length (nm)		Absorbance	
			λ_{II}	λ_{I}	II	I
1	(10^{-4}M) Quercetin at λ_{max} = 372nm in ethanol/water mixture	40	254	372	2.128	2.327
		50	254	372	2.127	2.232
		60	254	372	2.129	2.296
		70	254	372	2.13	2.266
		80	254	372	2.136	2.353
2	(10^{-4}M) Penicillamine at λ_{max} = 194nm in ethanol/water mixture	0	194	-	0.522	-
		40	194	-	0.504	-
		50	194	-	0.594	-
		60	194	-	0.592	-
		70	194	-	0.265	-
		80	194	-	0.436	-

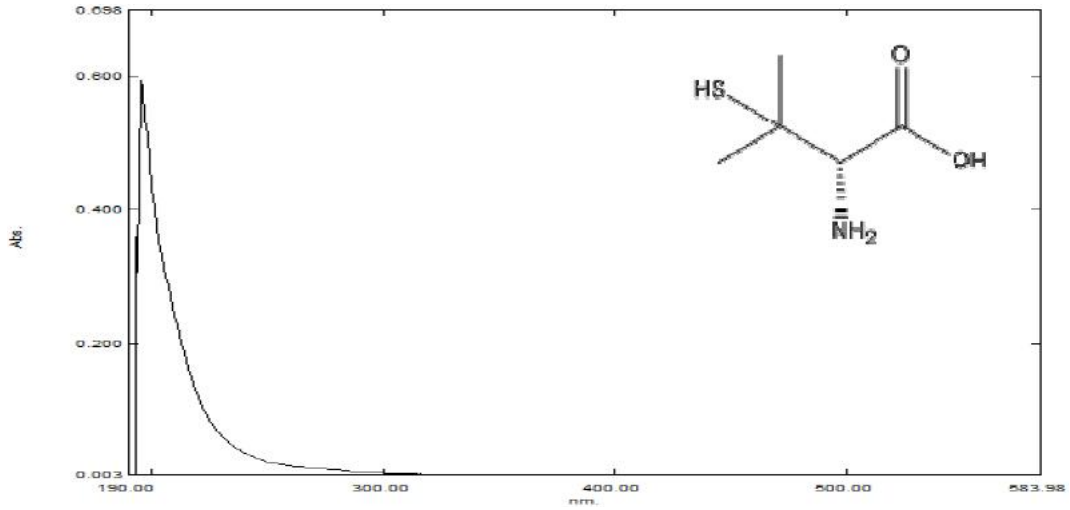

Figure 2 : UV-Visible absorption spectra of (10^{-4}M) penicillamine in 50% ethanol/water mixture

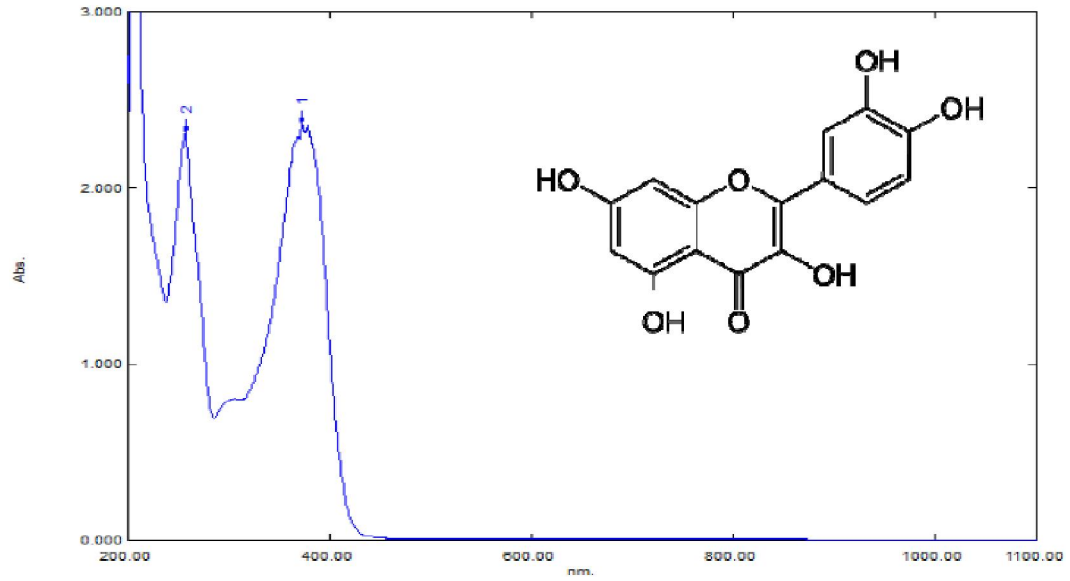

Figure 3 : UV-Visible absorption spectra of (10^{-4}M) quercetin in 80% ethanol/water mixture

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TABLE 2 : Electronic spectral data of (10^{-4}M) Pb (II) with the chelators

Compound	λ_{max} nm	Absorbance	Assignment
Penicillamine	194	0.593	n→ π*
Pb(II) –Penicillamine	268	0.07	
Quercetin	372	2.353	
	256	2.306	n→ π*
Pb(II) – Quercetin	425	0.213	π→ π*
	260	0.328	

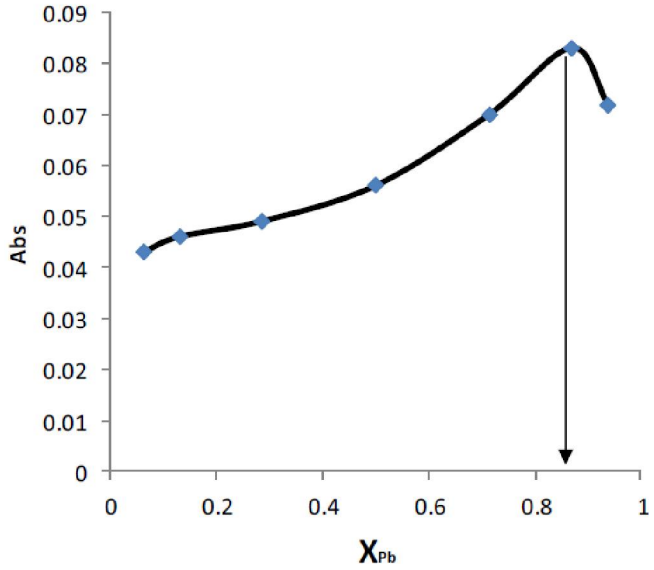

Figure 4 : Job's plot for the composition of Pb (II) - penicillamine complex at λ = 268nm

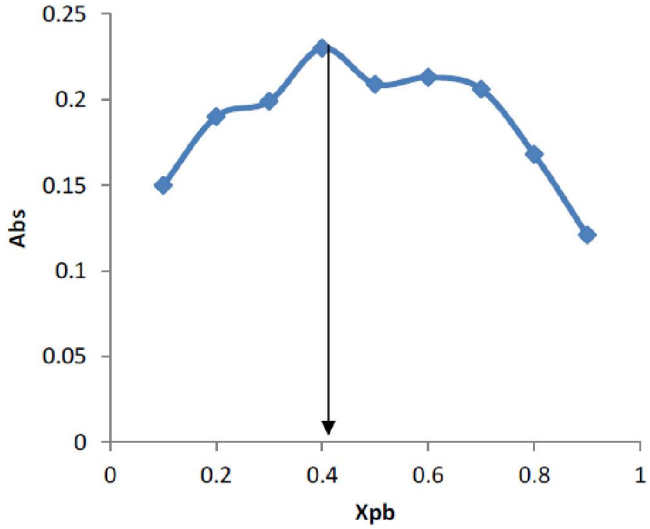

Figure 5 : Job's plot for the composition of Pb (II) - quercetine complex at λ = 425nm

3) and TABLE (1)

Upon addition of lead (II) solution to (10^{-4}M) chelating agents solutions, significant changes were observed in the electronic spectra, as shown in TABLE (2). This Table shows that the electronic spectra shifts λ_{max} to a longer wave length (bathochromic shift) upon addition of Pb (II) ion and a decrease in absorbance, these two evidence indicate a complex formation between the studied chelators and Pb (II) ion.

Stoichiometry of the formed complexes

The stoichiometric ratio of Pb (II) to chelating agents (penicillamine and quercetin) in the complexes were determined by Jobs method of equimolar solutions. The curve displayed maxima absorbance at mole fraction X_{max}, which indicates the formation of complexes with metal ion to ligands ratio, Figures (4 and 5).

$n = X_{max} / 1 - X_{max}$, n represent coordination number of the complexes, X_{max} represent mole fraction corresponding to the maxima absorbance.

Stability constant (K_{eq}): The equilibrium constant can be calculated using the continuous variation method[11].

Metal ion + chelators ⇋ [metal ion – chelators] $_{complex}$

$$K_{eq} = \frac{[(metal\ ion - chelators)_{complex}]_{eq}}{[metal\ ion]_{eq}\,[chelators]_{eq}} \quad (1)$$

$$K_{eq} = \frac{[\frac{Amax}{\varepsilon l}]}{\left[C_{Pb} - [\frac{Amax}{\varepsilon l}]\right]\left[C_{chel.} - [\frac{Amax}{\varepsilon l}]\right]} \quad (2)$$

A_{max} = the maximum absorbance of the complex

ε = molar absorptivity of the complex (L. mole^{-1}. cm^{-1})

l = path length. cm.

C_{Pb} = Initial concentration of the Lead

$C_{chel.}$ = Initial concentration of chelating agents.

$$[Pb\ II - chelators]_{eq} = Absorbance_{(max)} / \varepsilon l \quad (3)$$

$$[Pb]_{eq} = [Pb] - [Pb - chelators]_{eq} \quad (4)$$

$$[Chelators]_{eq} = [chelators]' - [Pb - chelators]_{eq} \quad (5)$$

The molar absorptivities of the complexes were calculated by recording the absorbance of a various concentration of the complexes at its stoichiometric

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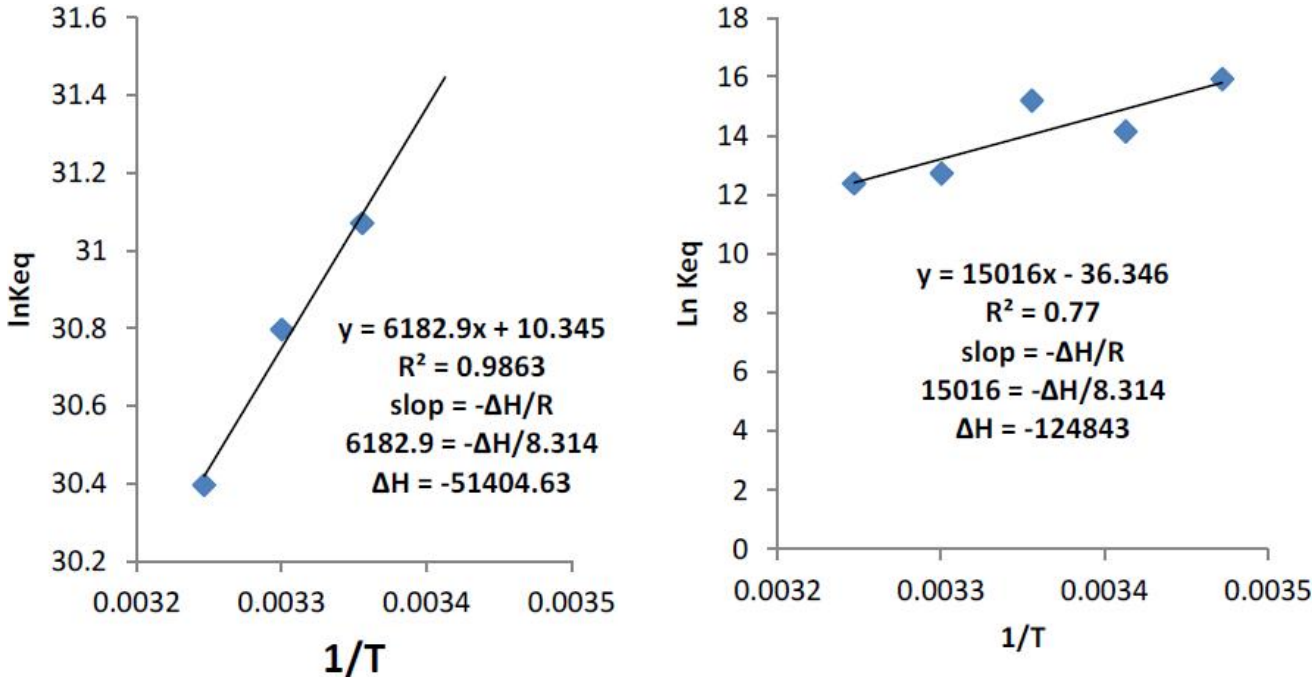

A B

Figure 6 : Vant hoff plot for interaction of: A/ penicillamine – 2Pb (II). B/ quercetine – Pb (II)

TABLE 3 : Thermodynamic parameters for 2Pb (II) - penicillamine complex

T(K)	K_{eq}	ΔG^0 (J/mole)	ΔH^0 (J/mole)	ΔS^0 (J/mole)	ε
293	103×10^{13}	-84208.5	-51404.6	111.95	6126.8
298	3.117×10^{13}	-76979.3		85.82	6240
303	2.37×10^{13}	-77580.7		86.38	6312.2
308	1.588×10^{13}	-77835.6		85.81	6362.3

TABLE 4 : Thermodynamic parameters for Pb (II) - quercetine complex

T(K)	K_{eq}	ΔG^0 (J/mole)	ΔH^0 (J/mole)	ΔS^0 (J/mole)	ε
293	1.397×10^{6}	-34456.8	-124843	-308.48	10187
298	3.94×10^{6}	-37626.1		-292.67	10787
303	0.334×10^{6}	-32040.7		-306.27	11497
308	0.24×10^{6}	-31723.1		-302.33	11807

values of each complexes and plotting of the absorbance of the complexes against concentration given a straight line with the slope equal to (□) L. $Mole^{-1}$. Cm^{-1} as shown in TABLES (3 and 4).

The values of K_{eq} obtained by the continuous variation method were determined in five temperatures (293 - 308K) as shown in TABLES (3 and 4), then allows us to calculate ΔG^o at different temperatures[12] [13].

$$\Delta G^o = \% RT \ln K_{eq} \quad (6)$$

Thermodynamic parameters: TABLE (3 and 4) reported the thermodynamic parameters of the complexation of Pb (II) with studied chelators.

The enthalpy change were calculated by substituting the values of the slope of vant Hoff plot (log K_{eq} vs 1/T) as in equation (7) and figure (6)

$$\ln Keq = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (7)$$

Slope = -ΔH/R, R = gas constant

Entropy change for the system can then be calculated from:

$$\Delta G^o = \Delta H^o - T\,\Delta S^o \quad (8)$$

These tables' shows that the equilibrium constant values decrease with increase in temperature

TABLE 5 : Data for application the second order equation for (2:1) Pb (II)-penicillamine complex, at 293K, λ_{max} = 268 nm

Time (min)	Abs	1/Abs
0	0.3	3.33333333
5	0.297	3.36700337
10	0.295	3.38983051
15	0.293	3.41296928
20	0.29	3.44827586
25	0.287	3.48432056
30	0.285	3.50877193

TABLE 6 : Data for application the second order equation for (1:1) Pb (II)-quercetine complex, at 293K, λ_{max} = 425 nm

Time (min)	Abs	1/Abs
0	0.097	10.30928
5	0.096	10.41667
10	0.089	11.23596
15	0.084	11.90476
20	0.083	12.04819
25	0.081	12.34568
30	0.076	13.15789

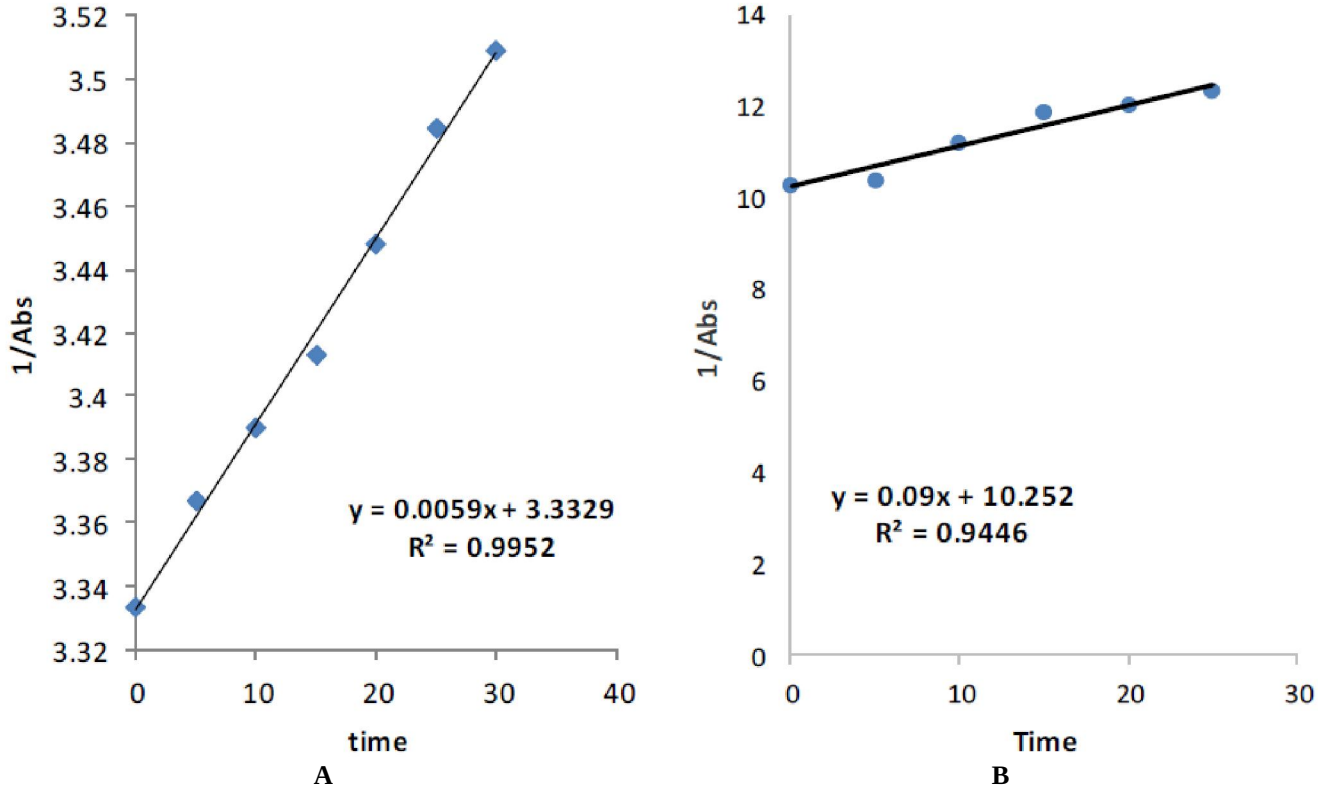

Figure 7 : The application of the second order reaction equation for complex of Pb (II) with: A/ Penicillamine. B/ Quercetin

of Pb (II) with (penicillamine, and quercetin). The negative value of Gibbs free energy for these interaction indicate the spontaneous process in the direction of equilibrium. The positive value or negative value of enthalpy and entropy change refers to the type of interaction between Pb (II) and these chelators. 2Pb (II)-penicillamine complexes have negative ΔH^o, positive ΔS^o which indicate an enthalpy and entropy deriven and have a strongest complexes. Finally Pb (II)-quercetine complexes have negative ΔH^o and ΔS^o that means enthalpy deriven. The different in their behavior due to its different in their structures.

Interaction kinetics

In order to investigate the interaction kinetic of Pb (II) ion with chelators, the absorbance of complexes were followed with time at a certain wave length.

The first order rate equation and the second order rate equation were applied.

A+B→C+D

k : rate constant for the reaction which is independent of the concentration but depends on the

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TABLE 7 : Rate constant of the second order reaction for complex As (III) with chelators

Complex Title	Second order rate constant $k(M^{-1}.min^{-1})$
Pb (II) - Penicillamine	$9*10^{-2}$
Pb (II) - Quercetin	5.9*10^3

temperature.

First order reaction: The first order rate law for the consumptive of a reaction A:

$$\frac{dA}{dt} = -K[A] \quad (9)$$

$$ln\left(\frac{[A]}{[A]_o}\right) = -Kt \quad (10)$$

$$ln\,A - ln\,A_0 = -Kt \quad (11)$$

Second order reaction: The second-order rate law.

$$\frac{d[A]}{dt} = -K[A]^2 \quad (12)$$

$$\frac{1}{[A]} - \frac{1}{[A]_o} = Kt \quad (13)$$

A= Absorbance of complex (Pb (II)-chelator) with deferent time.

A' = Absorbance of complex (Pb (II)-chelator) in time zero.

TABLE (5 and 6) shows the absorption of complex Pb (II) with (penicillamine and quercetin) all of each with Time (0-30) min.

CONCLUSION

The complex of the chelating agents (penicillamine and qurcetin) with Lead (II) shows a high tendency of these antioxidants to Pb (II). The thermodynamic parameter shows that this complexation is a spontaneous and may be entropy or enthalpy driven or both, depending a chelator's structures.

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