Thermodynamic and kinetic study of the interaction of antioxidation with Ni(II),Cd(II) and Pb(II) ions

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By

Haider Nazar Hussein

B. Sc. in Chemistry
University of Al- Mustansiriya
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Under Supervisor

Prof.Dr. Ahmed Najem abd

Assist.prof.Dr. Elham Al-Rufaie

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بِسْمِ ٱللَّهِ ٱلرَّحْمَٰنِ ٱلرَّحِيمِ

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Title: Professor
Date: / / 2018

(Member)
Signature:
Name:Dr. Eman Talib Kareem
Title: Professor
Date: / / 2018

(Member)
Signature:
Name: Dr. Yehya Kamal Khaleel
Title: Assistant Professor
Date: / / 2018

(Member /Supervisor)
Signature:
Name: Dr. Ahmed Najem abd
Title: Professor
Date: / /2018

(Member /Supervisor)
Signature:
Name: Dr. Elham Majeed Ahmed
Title: Assistant Professor
Date: / / 2018

Approved by the deanery of the College of Science, University of Diyala.

(The Dean)

Signature:
Name: Dr. Tahseen H. Mubarak
Title: Professor
Date: / / 2018

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We certify that this thesis **(Thermodynamic and kinetic study of the interaction of antoxidation with Ni(II),Cd(II) and Pb(II) ions*)*** was carried out under our supervision in Chemistry Department, College of Science, Diyala University in partial fulfilment of the requirements for the degree of master of science in chemistry by the student (***HAIDER NAZAR HUSSEIN***).

Signature:
Name: Dr. Ahmed Najem Abd
Title: Professor
Date: / / 2018
(*Supervisor*)

Signature:
Name: Dr. Elham Majeed Ahmed
Title: Assistant Professor
Date: / / 2018
(*Supervisor*)

In view of the available recommendation, I forwarded this thesis for debate by the examination committee.

Signature:
Name: Dr. Ahmed Najem Abd
Title: Professor
Date: / / 2018
Head of Chemistry Department
College of Science
Diyala University

Scientific Amendment

I certify that the thesis entitle **(Thermodynamic and kinetic study of the interaction of antoxidation with Ni(II),Cd(II) and Pb(II) ions)**presented by"***HAIDER NAZAR HUSSEIN*** "** has been evaluated scientifically, therefore, it is suitable for debate by examining committee.

Signature

Name: Wadhah Naji Jassim

Title: Assistant Professor

Address: Baghdad University, College of Science

Date: / / 2018

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Signature:

Name: Dr. Arwa Abd El-Rasool

Title: Assistant Professor

Address: Diyala University, College of Education for Human Sciences

Date: / / 2018

Dedication

In the name of God the Merciful Say '' Do , and Allah will see your work , His Massanger , and the beliver s''

Great trust of God .

My God does not engoy the night except with your thanks . this day is good except for your obedience . And do not wait moments but your memory . and do not wait for the other except Afok . and do not pray paradise only to see you .

'' God almighty ''

To the one who reached the message valley of safety . And advised the nation .. To the prophct of mercy and light of the worlds.

'' propht Muhaimmad peace and blessings be upon him ''

To whom God has blessed and revered . who taught me tender without waiting . To whom shall I bear his name with all pride? Lask god to extend in your life time to see the fruit of the coming I will pick it up after alone wait and your words will remain stars toguide me today and tomorrow my dear faher .

Meaning of compassion and dedication to the smile of life and the secret of existence.

To the one who was the secret of my success and her tenderness surgical treatment to the most expensive. Habayeb my beloved mother.

To those who accom panied me since we carried small bags and with tou walked the path step and still accompanies me so far . To a candle burning illuminate the darkness of my life. My sister Nabaa. To brothers and sisters , to those who like fraternity and distinguished by loyalty and giring to springs . Honesty is pure to those with whom Iam pleased, and with their blessings in the paths of happy and sad life . To whom did you know how to find them and taught me not to waste my friends.

Thanks and appreciation

Be a scholar , if you can not be educated , if you can not love the scientists , if you can not annoyed them" After a journey of research , effort and diligence culminated in the conplation of this research , thank God Almightyfor the grace that has blessed us , the Almighty . we also can not expoess our thanks and appreciation to DR"AHMED NAJEM ABD" and DR" ELHAM MAJEED AL-RUFAIE" . For their sfforts , advice and knowledge through out this research . we aleo extendour Thanks and appreciation to all those who contributed in helping us to accomplish this research . we also mention to the Dean of the faculty of science. Diyala Unversity DR "TAHSEEN HUSSEIN MUBARAK" thanks and gratitude to the all friends , brothers and sister to those who helped us in our search and light that leads us in the injustice that some times stood in the way to ((MOUNIRA , SARAH , AISHA , HADEEL , HAIDER , HAMZA , MUSTAFA , AND AHMED)).

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Symbols and Abbreviations

Abbreviation	Meaning
A	Absorbance
Cm	Centimeter
$\Delta H°$	standard enthalpy change
$\Delta S°$	standard entropy change
$\Delta G°$	standard free energy change
ΔH	Change in Enthalpy
ΔS	Change in Entropy
ΔG	Change in free energy
K_{eq}	Equilibrium constant
HOMO	Highest occupied molecular orbital
I_o	Incident light
K	Kelvin
LUMO	Lowest unoccupied molecular orbital
M	Molar
ε	Molar absorptivity
X_{max}	Mole fraction
I	Transmitted light
α	Degree of dissociation
R	Gas constant
π	3.14
T	Temperature
t	Time
UV-Vis	Ultra Violet-Visible light
k	Rate constant
λ_{max}	Wave length at the maximum absorbance

Abstract

There is a wide variety of polyphenolic compounds named flavonoids. These are extensively distributed in plants, and they are considered to be dietary antioxidants. They occur naturally in a broad range of vegetables, fruits, and Green tea recognized as the pigments .

Many flavonoids have a metallic ion complexation capacity. The study of this capacity is important because it can be used in producing nutritional supplements, medicine, and heavy metal detoxification.

Chelation therapy is the use of chelating agents (complexing agents) to detoxify poisonous metal such as Nickel, Cadmium , and lead by converting them to chemically inert form that can be excreted without further interaction with the body.

Lead is considered as one of the most hazards and cumulative environmental pollutants that affect all biological systems through exposure to air, water and food sources. It is toxic a heavy metals which is known to induce a broad range of physiological, biochemical and behavioral dysfunction in humans. lead poisoning still remains an important health problem.

This prompted us to examine some known chelating agents such as (Curcumin, Quercetin, Vitamin C and Catechin) to interact with Ni II, Cd II and Pb II ions and formation of safe

complexes after that to calculate their physical thermodynamic functions, using spectrophotometric measurements.

The UV-Vis measurements were carried out in 40% ethanol/water for Quercetin, 60% ethanol/water for Curcumin and 0% ethanol/water for Vitamin C and Catechin as a best media for this work.

The electronic spectrum of free chelators in ethanol/water solutions were characterized by a single band for Curcumin, a single band for Catechin and a single band for Vitamin C, these are λ_{max}= 429nm, λ_{max}= 278nm, λ_{max}= 256nm respectively, while Quercetin shows double bands at λ_{max}(I)= 373nm and λ_{max} (II)= 256nm.

Addition of Ni II, Cd II and Pb II ions to the chelators solutions shows a increasing in absorbance with Catechin and Curcumin with little shift in λ_{max}. While with Vitamin C and Quercetin it shows a decreasing in absorbance and red shift in λ_{max} this change caused to form complexes but there is no reaction between Cd II and Quercetin.

The stoichiometry of the formed complexes were investigated by the method of continuous variation and they were found (1:1),The stability constants were calculated at four temperatures at the range of
(293 – 308) K which have a value at 293K with the order of:
Curcumin-Cd ($16.25x10^4$) > VitaminC-Cd ($1.46x10^4$) > Catechin-Cd ($0.79x10^4$)

and for Curcumin-Pb ($4.76x10^4$)> Quercetin-Pb ($4.52x10^4$) > VitaminC-Pb ($1.86x10^4$)> Catechin-Pb($0.69x10^4$).

and for Quercetin-Ni($9x10^4$)> Curcumin-Ni($2.37x10^4$)> VitaminC-Pb($1.69x10^4$)> Catechin-Ni($1.54x10^4$). That means the Curcumin was more effective than any of the other four chelators for both Cadmium and lead. And Quercetin was more effective than any of the other four chelators for Nickel

Thermodynamic parameters, ΔH^o and ΔS^o were determined at four different temperatures these are: The negative value of ΔG^o indicate that the indication will be favored and hence spontaneously happened to release energy as it was indicated by the negative value of ΔH^o, except Ni(II)-Curcumin, Ni(II)-Quercetin, Pb-(II)-Catechin, Cd(II)-Catechin, in which ΔH^o values were positive. ΔS^o be positive for all complexes , Expect Pb(II)-Quercetin

Chemical kinetics show, this effect subjects to the pseudo-first order chelation with Ni , Cd and Pb ions.

CHAPTER ONE

INTRODUCTION

1.1 Metal Toxicity

Metal Toxicity is the toxic effect of certain metals in certain forms and doses on life. Some metals are toxic when they form poisonous soluble compounds. Certain metals have no biological role . In the case of lead, any measurable amount may have negative health effects[1] . Many ordinary, everyday products have toxic metals in them. Toxic metals are in the foods we eat, water we drink, and the air we breathe. The human body requires extremely trace amounts of few metals, but too often the concern is with getting too much, rather than too little. Metal poisoning occurs as a result of the unhealthy accumulation of specific metals in the body. Metals become toxic when the quantity is too high. Mercury, lead and cadmium are three metals that can be especially harmful and aluminum has also presented concerns. These toxic metals enter the body through drinking, eating, inhaling, and skin and eye contact. Once in the body, they cause damage at the cellular level by initiating oxidative stress. This damage can contribute to the development of many diseases and health problems[2]. Some people have the ability to excrete these toxins out of their system, others, particularly those suffering from chronic conditions, are not so lucky and develop a build-up of metals called heavy metal toxicity. Further, heavy metals can accumulate in the body over time, causing symptoms you might not equate with heavy metals[3].

In many cases, the symptoms brought on by metal toxicity are often misdiagnosed for chronic conditions such as autism, chronic fatigue syndrome, depression and multiple sclerosis, There are two types of heavy metal toxicity: acute and chronic. Symptoms of acute toxicity are easy to recognize because they are usually quick and severe in onset. The symptoms include[4]:

1. Cramping, nausea, and vomiting
2. Pain
3. Sweating
4. Headache
5. Difficulty breathing
6. Impaired cognitive, motor, and language skills
7. Mania
8. Convulsions

Chronic exposure, on the other hand, produces different symptoms, which can be easily confused with symptoms of different illnesses. Some of the symptoms are impaired cognitive, motor, and language skills, learning difficulties, nervousness and emotional instability, insomnia and nausea.

In fact, because toxic metals block the absorption and utilization of essential minerals, this in itself can set up a whole cascade of symptoms that gradually get worse over time.

There a more specific checklist of symptoms of metal toxicity poisoning:

1. Chronic pain throughout the muscles and tendons or any soft tissue of the body
2. Chronic malaise -- general feeling of discomfort, fatigue, and illness
3. Brain fog -- state of forgetfulness and confusion
4. Chronic infections such as Candida
5. Gastrointestinal complaints, such as diarrhea, constipation, bloating, gas, heartburn, and indigestion
6. Food allergies
7. Migraines and/or headache
8. Visual disturbances

9. Mood swings, depression, and/or anxiety
10. Nervous system malfunctions - burning extremities, numbness, tingling, paralysis, and/or an electrifying feeling throughout the body .

Heavy metals are ubiquitous in the environment[5]. Humans risk overexposure from environmental concentrations that occur naturally eg, arsenic-rich mineral deposits) or human activities (eg, lead or mercury release as a result of industrial pollution)[6, 7].

It is not possible to completely avoid exposure to toxic metals [8]. Even people who are not occupationally exposed carry certain metals in their body as a result of exposure to other sources, such as food, beverages, or air [9, 10]. It is, however, possible to reduce metal toxicity risk through lifestyle choices that diminish the probability of harmful heavy metal uptake, such as dietary measures that may promote the safe metabolism or excretion of ingested heavy metals [11].

1.2 Heavy Metals

The phrase "heavy metals" points to mineral element that has a comparatively high density and is venomous, even at low concentration[12]. "Heavy metals" is a general plural term , which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3, or 5 times or more,[13]. greater than water[7, 14-18]. However being a heavy metal has little to do with density but concerns chemical properties. Heavy metals include lead (Pb), cadimum (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), and the platinum group elements[19]. Environment is defined as the totality of circumstances surrounding an organism or group of organisms especially, the blend of exterior physical conditions that have an effect and influence on the

growth, development and survival of organisms[20]. Several heavy metals such as Co, Cu, Fe, Mn, Mo, Ni, V, and Zn are required in minute quantities by organisms[21]. However, excessive sums of these elements can become harmful to organisms. Other heavy metals such as Pb, Cd, Hg, and As, (a metalloid but generally termed as a heavy metal) do not have any beneficial effect on organisms and are thus regarded as the "main threats" since they are very harmful to both plants and animals[22].

Table (1-1): Effect of heavy metal toxicity on plant

Heavy Metal	Plant	Toxic effect on plant	Reference
Cd	Wheat (*Triticum*sp.)	Reduction in seed germination; decrease in plant nutrient content; reduced shoot and root length.	[23, 24]
	Garlic(*Alliumsativum*)	Reduced shoot growth; Cd accumulation.	[25]
	Maize (*Zeamays*)	Reduced shoot growth; inhibition of root growth.	[26]
Ni	Pigeon pea	Decrease in chlorophyll content and stomatal conductance; decreased enzyme activity which affected Calvin cycle and CO_2 fixation	[27]
	Rye grass	Reduction in plant nutrient acquisition; decrease in shoot yield; chlorosis	[28]
	Wheat (*Triticum*sp.)	Reduction in plant nutrient acquisition	[29, 30]
	Rice	Inhibition of root growth	[31]
Pb	Maize	Reduction in germination percentage; suppressed growth; reduced plant biomass; decrease in plant protein content	[32]
	Portia tree	Reduction in number of leaves and leaf area; reduced plant height; decrease in plant biomass	[33]
	Oat (*Avena sativa*)	Inhibition of enzyme activity which affected CO_2 fixation	[34]

The most common heavy metals found at contaminated sites, in order of abundance are Pb, Cr, As, Zn, Cd, Ni, Cu, and Hg[35]. Those metals are important since they are capable of decreasing crop production due to the risk of bioaccumulation and biomagnification in the food chain. There is also the

risk of superficial and groundwater contamination. Knowledge of basic chemistry, environmental, and associated health effects of these heavy metals is necessary in understanding their speciation, bioavailability, and remedial options. The fate and transport of a heavy metal in soil depends significantly on the chemical form and speciation of the metal. Once in the soil, heavy metals are adsorbed by initial fast reactions (minutes, hours), followed by slow adsorption reactions (days, years) and are, therefore, redistributed into different chemical forms with varying bioavailability , mobility, and toxicity[36, 37]. This distribution is believed to be controlled by reactions of heavy metals in soils such as (i) mineral precipitation and dissolution, (ii) ion exchange, adsorption, and desorption, (iii) aqueous complexation, (iv) biological immobilization and mobilization, and (v) plant uptake[38].

1.2.1 Nickel

Is a transition element with atomic number 28 and atomic weight 58.69g/mol . Nickel is silvery white. It is hard, malleable, ductile, somewhat ferromagnetic, and a fair conductor of heat and electricity. It belongs to the iron-cobalt group of metals and is chiefly valuable for the alloys it forms. nickel is rarely found in its pure form on the Earth's surface, Nickel is an element that occurs in the environment only at very low levels and is essential in small doses, but it can be dangerous when the maximum tolerable amounts are exceeded. This can cause various kinds of cancer on different sites within the bodies of animals, mainly of those that live near refineries. The most common application of Ni is an ingredient of steel and other metal products. , both nickel in solution and the nickel in stainless steel are known to cause a skin irritation known as nickel itch, which is a form of dermatitis. Stainless steel watches, jewelry, and glasses frames have all been known to cause this irritation. More serious health hazards can come from

inhaling nickel dust. In nickel mining and other industrial environments where nickel is used, inhaling the dust has been linked to nasal and lung cancer[39]. The major sources of nickel contamination in the soil are metal plating industries, combustion of fossil fuels, and nickel mining and electroplating[40]. symptoms of poisoning Nickel are

1- Dizziness and headache.
2- Chest pain.
3- Vomiting
4- Mine workers are susceptible to nickel poisoning.
5- A urine sample may be collected to diagnose nickel poisoning.
6- Trouble sleeping[41].

1.2.2 Lead

Is a metal belonging to group IV and period 6 of the periodic table with atomic number 82, atomic weight 207.2g/mol , density 11.4 g /cm^3, melting point 327.4◦C, and boiling point 1725◦C. It is a naturally occurring, bluish gray It is very soft, highly malleable, ductile, and a poor conductor of electricity. It is very resistant to corrosion, It is usually found as a mineral combined with other elements, such as sulphur (i.e., PbS, $PbSO_4$) , or nitrate $Pb(NO_3)_2$[42].Inhalation and ingestion are the two routes of exposure, and the effects from both are the same. Pb accumulates in the body organs (i.e., brain), which may lead to poisoning (plumbism) or even death. The gastrointestinal tract, kidneys, and central nervous system are also affected by the presence of lead. Children exposed to lead are at risk of impaired development, lower IQ, shortened attention span, hyperactivity, and mental deterioration, with children under the age of six being at a more substantial risk. Adults usually experience decreased reaction time, loss of memory, nausea, insomnia, anorexia, and weakness of the joints when exposed to

lead[43]. Lead is not an essential element. It is well known to be toxic and its effects have been more extensively reviewed than the effects of other trace metals. Lead can cause serious injury to the brain, nervous system, red blood cells, and kidneys[44]. Exposure to lead can result in a wide range of biological effects depending on the level and duration two words of exposure. Various effects occur over a broad range of doses, with the developing young and infants being more sensitive than adults. Lead poisoning, which is so severe as to cause evident illness, is now very rare. Lead performs no known essential function in the human body, it can merely do harm after an uptake from food, air, or water. Lead is a particularly dangerous chemical, as it can accumulate in individual organisms, but also in entire food chains.

Studies have shown that lead does not readily accumulate in the fruiting parts of vegetable and fruit crops (e.g., corn, beans, squash, tomatoes, strawberries, and apples). Higher concentrations are more likely to be found in leafy vegetables (e.g., lettuce) and on the surface of root crops (e.g.,carrots)[45]. symptoms of poisoning Lead are

1- High blood pressure
2- Joint and muscle pain
3- Difficulties with memory or concentration
4- Headache
5- Abdominal pain
6- Mood disorders
7- Reduced sperm count and abnormal sperm
8- Miscarriage, stillbirth or premature birth in pregnant women[46].

1.2.3 Cadmium

Cadmium is located at the end of the second row of transition elements with atomic number 48, atomic weight 112.4g/mol , density 8.65 g/cm^3,

melting point 320.9 ◦C, and boiling point 765◦C. Together with Hg and Pb, Cd is one of the big three heavy metal poisons and is not known for any essential biological function.

In its compounds, Cd occurs as the divalent Cd(II) ion. Cadmium is directly below Zn in the periodic table and has a chemical similarity to that of Zn, an essential micronutrient for plants and animals. This may account in part for Cd's toxicity; because Zn is being an essential trace element, its substitution by Cd may cause the malfunctioning of metabolic processes[47]. The most significant use of Cd is in Ni/Cd batteries, as rechargeable or secondary power sources exhibiting high output, long life, low maintenance, and high tolerance to physical and electrical stress. Cadmium coatings provide good corrosion resistance coating to vessels and other vehicles, particularly in high-stress environments such as marine and aerospace. Other uses of cadmium are as pigments, stabilizers for polyvinyl chloride (PVC), in alloys and electronic compounds. The application of agricultural inputs such as fertilizers, pesticides, and bio solids (sewage sludge), the disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in soils, and the bioavailability of this Cd determines whether plant Cd uptake occurs to a significant degree[48]. Cadmium is very bio persistent but has few toxicological properties and, once absorbed by an organism, remains resident for many years. Cadmium in the body is known to affect several enzymes. It is believed that the renal damage that results in proteinuria is the result of Cd adversely affecting enzymes responsible for re-absorption of proteins in kidney tubules. Cadmium poisoning in the Jintsu River Valley was attributed to irrigated rice contaminated from an upstream mine producing Pb, Zn, and Cd. The major threat to human health is chronic accumulation in the kidneys leading to kidney dysfunction. Food intake and tobacco smoking are the main routes by which Cd enters the body[49]. symptoms of poisoning Cadmium are

1- Nausea and Vomiting
2- Lung Hemorrhage
3- Kidney Damage
4- Cancer
5- bone disease,
6- loss of the sense of smell and anemia[50].

1.3 Heavy Metal Detoxification

Detoxification is the removal of metallic toxic substances from the body. In conventional medicine, detoxification can also be achieved artificially using techniques such as dialysis and chelation therapy. There is a firm scientific base in evidence-based medicine for this type of detoxification. Many alternative medicine practitioners promote various other types of detoxification such as diet detoxification. The detox is performed to make the body avoid toxic metals.

Figure (1.1): Detox Diet Plants[51]

Toxic metals are individual metals and metal compounds that negatively affect people's health. Arsenic and selenium are toxic semi-metallic elements. In very small amounts, many of these are essential. In larger amounts, they become toxic. They may build up in biological systems and become a significant health hazard. Heavy metals, such as Hg, Pb and Al, accumulate in the body over time and are suspected of triggering dangerous conditions like heart disease, dementia, autism, thyroid problems, neurological conditions, infertility and birth defects. The good news is that a heavy metal detox can remove these contaminants from human and minimize their impact on health. Chelation, controversial metal detox procedure in which metals are purged from the body, usually by the way of intravenous administration of certain drugs, has been touted as a miracle cure for many sicknesses. Its effectiveness as a treatment however has come under much scrutiny. It may be harmful. There are more dietary steps we can take to get rid not only of heavy metals but other toxins as well. Detox diets and detox recipes are more popular than ever [52].

1.4 Chelation Therapy

A chelate is a chemical compound is composed of a metal ion and a chelating agent. A chelating agent is a substance whose molecules can form several bonds to a single metal ion. Chelation therapy is a medical procedure that involves the administration of chelating agents to eliminate heavy metals from the body. Chelation therapy has long history of use in clinical toxicology and remains in use for some very specific medical treatments, although it is administered under very careful medical supervision due to more inherent risk[53] .

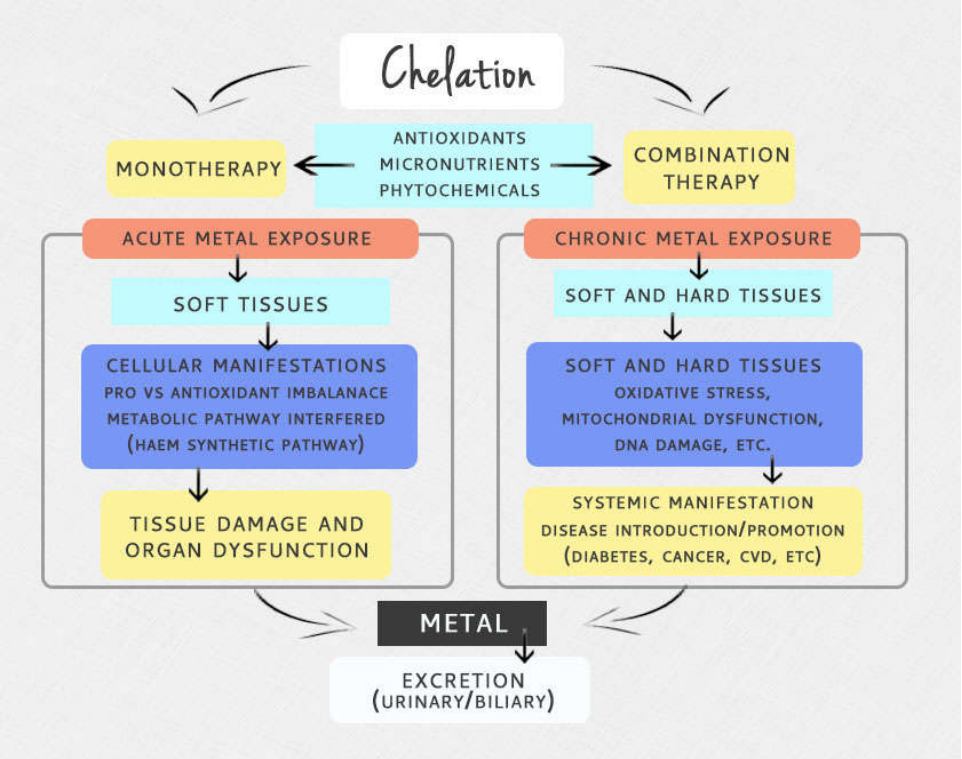


Figure (1.2): Chelation[54].

Chelation therapy should be administered with care as it has a number of possible side effects, including death. In response to the increasing use of chelation therapy as alternative medicine, and in circumstances in which the therapy should not be used in conventional medicine, various health organizations have confirmed that medical evidence does not support the effectiveness of chelation therapy for any purpose other than the treatment of heavy metal poisoning[55] .

When used properly in response to a diagnosis of harm from metal toxicity, side effects of chelation therapy include low blood calcium, harm to kidneys, lowered levels of dietary elements, increased enzymes as would be detected in liver function tests, allergic reactions, and dehydration [56] . When administered inappropriately, chelation therapy brings risk of cancer, neurodevelopment disorder from toxicity, and death[57] .

1.5 Antioxidants

Antioxidants may be molecules that can neutralize free radicals by accepting or donating electron(s) to eliminate the unpaired condition of the radical. The antioxidant molecules may directly react with the reactive radicals and destroy them, while they may become new free radicals which are less active, longer-lived and less dangerous than those radicals they have neutralized. They may be neutralized by other antioxidants or other mechanisms to terminate their radical status. For example, many antioxidants have aromatic ring structures and are able to delocalize the unpaired electron.

Most of these natural antioxidants come from fruits, vegetables, spices, grains and herbs such as ginseng, curcuman , ginkgo, rosemary, green tea, grape, ginger and garlic. They contain a wide variety of antioxidant compounds, such as phenolics (phenol and polyphenols), flavonoids, carotenoids, steroids and thiol compounds [58]. These antioxidants may help to protect cellular damages from oxidative stress and also decrease the risk of chronic diseases .The change of optical absorbance of either antioxidant or oxidant is measured for the quantitation for antioxidant capability[59]. The chemical approaches are simple and easy to study the total antioxidant activity, which includes the radical scavenging ability and reductive activity [60];

1. Slower signs of aging, including of the skin, eyes, tissue, joints, heart and brain
2. Healthier, more youthful, glowing skin
3. Reduced cancer risk
4. Detoxification support
5. Longer life span
6. Protection against heart disease and stroke
7. Less risk for cognitive problems, such as dementia

8. Reduced risk for vision loss or disorders like macular degeneration and cataracts
9. Antioxidants are also added to food or household products to prevent oxidation and spoilage

1.5.1 Dietary antioxidant

Vitamin C, Vitamin E, and beta carotene are among the most widely studied dietary antioxidants . Vitamin C is considered the most important water – soluble antioxidant in extracellular fluids. It is capable of neutralizing in the aqueous phase before lipid per oxidation is initiated.

Vitamin E, a major Lipid – soluble antioxidant, is the most effective chain – breaking antioxidant within the cell membrane where it protects membrane fatty acids from Lipid per oxidation. Vitamin C has been cited as being capable of regenerating vitamin E [61, 62]

1.5.2 phytonutrients

A number of the dietry antioxidant substances exist beyond the traditional vitamins discussed above. Many plants – derived substances, collectively termed, phytonutrients, are becoming increasingly known for their antioxidant activity. Phenolic compounds such as flavonoids are ubiquitous within the plant kingdom. Flavonoids serve as protectors against a wide variety of environmental stress, while in humans; flavonoids appear to function as, biological response modifiers. Flavonoids have been demonstrated to have anti - inflammatory, anti - allergenic, anti - viral, anti - aging, and anti - carcinogenic activity [63, 64].

The broad therapeutic effects of flavonoids can be largely attributed to their antioxidant properties [65-67].

1.5.3.Endogenous antioxidants

In addition to dietry antioxidants, the body relies on several endogenous defense mechanisms to help protect against free radical – induced cell damage.

The antioxidant enzymes; glutathione peroxidase, catalase, and superoxide dismutase (SOD) metabolism oxidative toxic intermediates and require micronutrient cofactors such as selenium, iron, copper, zinc, and manganese for optimum catalytic activity [68].

1.6 Flavonoids

The flavonoids are a diverse group of low – molecular - mass poly phenolic substances, ubiquitous in all vascular plants, They occur naturally in broad range of fruits, vegetables, nuts, seeds, herbs, spices, stems, flowers, and beverages such as green tea and red wine[69-71].

There are more than 6000 different compounds[72]. Flavonoids contribute to the flavor of the fruits and vegetables, and primarily recognized as the pigments responsible for autumnal brush of hues and many shades of yellow, orange, and red in flowers and foods [73, 74]. They also have important roles in plant growth, reproduction and pathogen and predator resistance[75].

In the plant kingdom, flavonoids appear most often as β – o – glycoside derivatives. In leaves, flowers and fruits, flavonoids occur in the form of glycosides and esters with organic acids, whereas lignified tissues contain mainly free forms of flavonoids. Seed may contain both the glycoside forms and a glycons. With reference to polarity, plant flavonoids may be divided into lipophylic and hydrophilic ones [76, 77].

1.6.1 classification of flavonoids

Flavonoids occur as a glycones, glycosides and methylated derivatives. In plants all contain fifteen carbon atoms in their basic nucleus: two six - membred rings linked with a three carbon unit which may not apart of a third ring.For convenience, the rings are labeled A, B, and C . The individual carbon C and "primed" numerals for B - ring. Primed modified numbering system is not used for chalcones[78, 79].

Flavonoids are phenyl benzo - pyrones (Phenyl chromenes) with an assortment of structure based on common three - ring nucleus. They are usually subdivided according to their substituents into eight different classes: (Flavones, Flavonols, Flavanones, Dihydroflavonol, Flavanol, Chalcone, Isoflavone, Anthocyanidine) [80, 81].

1.6.2.Antioxidant and anti-free radical activities of flavonoids

The most described property of flavonoids is their capacity to protect the organism against free radicals and oxygenated reactive species during the metabolism of oxygen .The protective effect of flavonoids is due to several mechanisms such as free radicals trapping, enzymes inhibition and metallic ions chelation. These properties depend on the structure of the flavonoids and the degree of substitution and saturation[82].

1.7 Quercetin

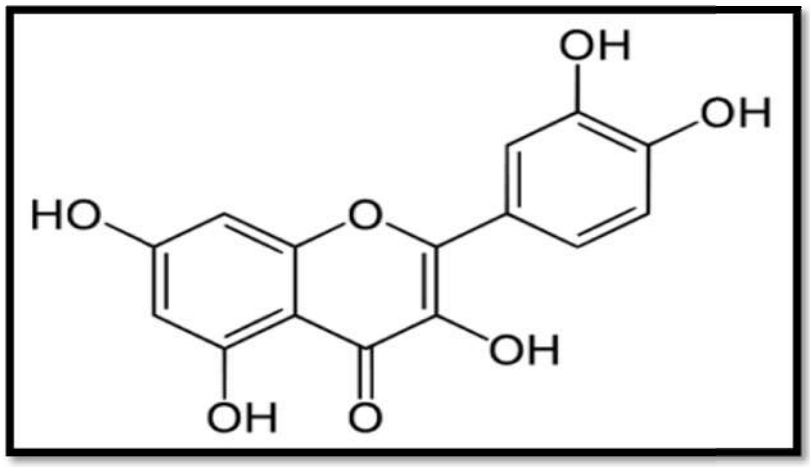


Figure (1.3): Chemical structure of Quercetin

Quercetin is a flavonol 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 quercetum[83].It is a naturally occurring polar auxin transport inhibitor [84].

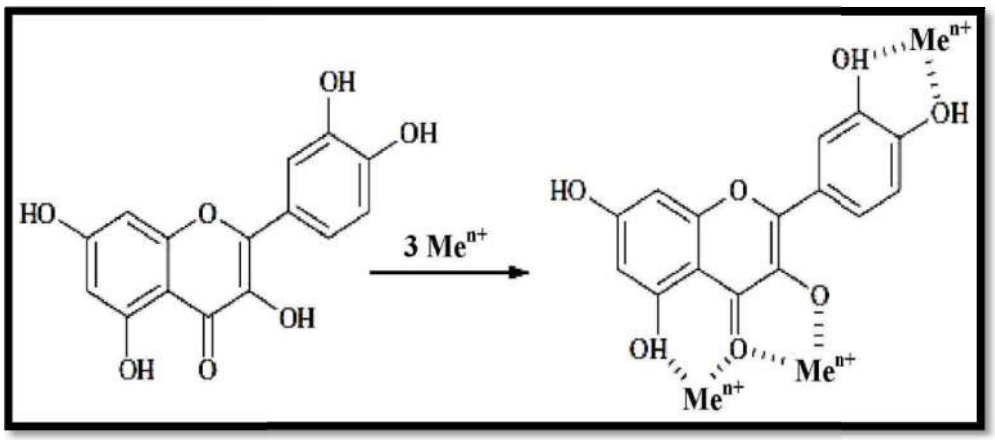


Figure (1.4): Position of chelating agents

Quercetin in higher concentration occur in the outermost rings in red onions and in the part closest to the root. The latest being the part of the plant with the highest concentration[85]. Quercetin had 79% organically grown tomatoes more than chemically grown fruit[86]. Quercetin is present in various kinds of honey from different plant sources[87].

The best described property of Quercetin is its ability to act as antioxidant. Quercetin seems to be the most powerful flavonoids for protecting the body against reactive oxygen species, produced during the normal oxygen metabolism or are induced by exogenous damage [88].

The most important mechanisms and the sequence of proceedings by which free radicals interfere with the cellular functions appear to be the lipid peroxidation leading lastly the cell death. Living organisms have developed antioxidant line of defense systems to protect this cellular death to happen from reactive oxygen species [89].

In general, Quercetin is poorly absorbed, absorbed 25% of it from small intestine in human. the humans absorb appreciable amount of quercetin, contradicts the assumption [90].

Quercetin is found as couples form with glucuronic acid, sulfate or methyl groups in human plasma, with no significant amounts of free quercetin.

Research shows that anti-inflammatory foods containing quercetin can help manage a number of

1. inflammatory health problems,
2. including heart disease
3. blood vessel problems,
4. allergies,
5. infections,
6. chronic fatigue,
7. symptoms related to autoimmune disorders like arthritis.

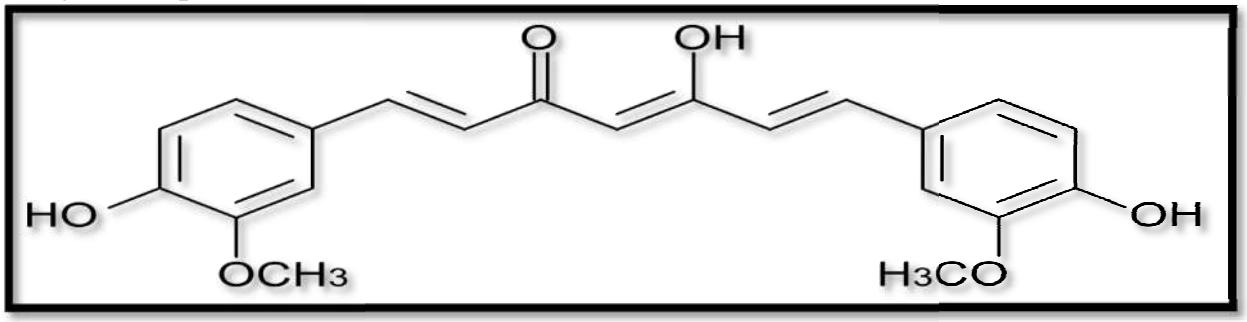
It all come down to high-antioxidant foods‘ ability to be “scavenge free radicals.” As a major bioflavonoid in our diets, quercetin (a type of “polyphenolic antioxidant”) helps slow the aging progress because it lessens the effects of oxidative stress on the body[91]. Oxidative stress takes place in

all of us but is increased by things like a poor diet, high levels of stress, a lack of sleep and exposure to chemical toxins. Quercetin plays a role in regulating the immune system's response to outside stressors through cell signaling pathways called kinases and phosphatases, two types of enzyme and membrane proteins needed for proper cellular function[91].

1.8 Curcumin

Another example of natural material with some antibacterial activities is curcumin. It is an orange–yellow crystalline powder practically insoluble in water and ether but soluble in ethanol, dimethylsulfoxide, and acetone.

Curcumin was first isolated in 1815 by Vogel[92]; in 1870 it was isolated in crystalline form and identified as (1E,6E) -1,7-bis(4-hydroxy-3-methoxyphenyl)- 1,6-heptadiene-3,5-dione or diferuloylmethane[93]. The feruloylmethane skeleton of curcumin was confirmed in 1910 by the initial work and synthesis by Lampe[94]. Curcumin has a melting point of 183°C, its molecular formula is $C_{21}H_{20}O_6$ and molecular weight 368.37 Besides curcumin, turmeric contains other chemical constituents known as the curcuminoids (figure1.5) [94] The curcuminoids impart the characteristic yellow color to turmeric. The major curcuminoids present in turmeric are demethoxycurcumin, bisdemethoxycurcumin, and the recently identifiedCyclocurcumin[95]. Commercial curcumin contains about 77% curcumin, 17% demethoxycurcumin, and 3% bis-demethoxycurcumin as its major components.



Figure(1.5): Structure of various curcumins[96]

Curcumin is the major constituent of the yellow pigments isolated from rhizome of Curcuma longa(turmeric). The root of this plant has been used in India as preservative, colorant, flavoring in meals (curry) and as a traditional medicine. Several studies in recent years have shown that curcumin has antioxidant, anti-microbial, anti-parasitic, anti-mutagen ,anticancer properties[97, 98], and anti-inflammatory[99].

Curcumin acts as a superoxide radical scavenger[100], A recent report describes the H-atom donation from the β-diketone moiety to a lipid alkyl or a lipid peroxyl radical as a potentially more important antioxidant action of curcumin[101].

Curcumin anti-inflammatory activity was attributed to the hydroxyl and phenol groups in the molecule and these groups are also essential for the inhibition of prostaglandins PG synthetase and leucotrienessynthesis(LT)[101].

Also it was suggested that the anti-inflammatory action is associated with the β-dicarbonylic system, which has conjugated double bonds (dienes). This system seems to be responsible, not only for anti-inflammatory power, but also for antiparasitic activity[102].

The presence of a dieneketone system provides a lipophilicity to the compounds and thus probably better skin penetration. Structure–activityrelationship studies suggest that a hydroxy group at the para-position is most critical for the expression of biological activity[102].

1.9 Catechins

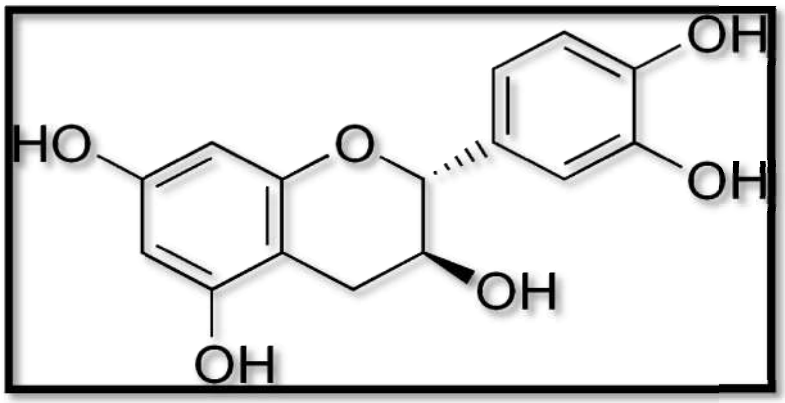


Figure (1.6): Chemical structure of Catechins[103]

(2R,3S)-2-(3,4-dihydroxyphenyl)-3,4-dihydro-2H-chromene-3,5,7-triol are members of the flavan-3-ols (also referred to as flavanols) which is a class of flavonoid. Afzelechin, catechins and gallocatechin are three subgroupings of the flavanols which representing varying degrees of B-ring hydroxylation [104]. The epi-isomers of the catechins and gallocatechins are the dominant forms in tea. The "tea catechins" is a term commonly used to refer to both catechins and gallocatechins make up as much as 30% wt/wt of dissolved solids. A large percentage of the catechins present in tea exist as gallic acid esters. Gallation is found to be occured mainly at the 3-position[105].

Other than tea, catechins have also been found in chocolate, cocoa, apples, beer, black, red and white currants, blueberries, cacao liquor , gooseberries, grape seeds (Vitisvinifera), kiwi fruit, strawberry, red wine, etc. [106]. The major catechins in tea are (-)-epigallocatechingallate (EGCG), (-)-epigallocatechin (EGC), (-)-epicatechingallate (ECG), (-)-epicatechin (EC) and (+)-catechin (C)[107].Catechin biosynthesis is also environmentally dependent , The catechins' role in plants is to provide protection from the damage from UV rays in sunlight, and catechin production is strongly affected by photosynthesis[108-110].

Catechins have antioxidant activity by chelating redox active transition-metal ions, scavenging free radicals, inhibiting pro-oxidant enzymes,

inhibiting redox active transcription factors, and inducing antioxidant enzymes, The (+)-catechin electron/proton donating capacity and its radical scavenging antioxidant activity impacts the deprotonation of the catechol group [111].

1.10 Vitamin C

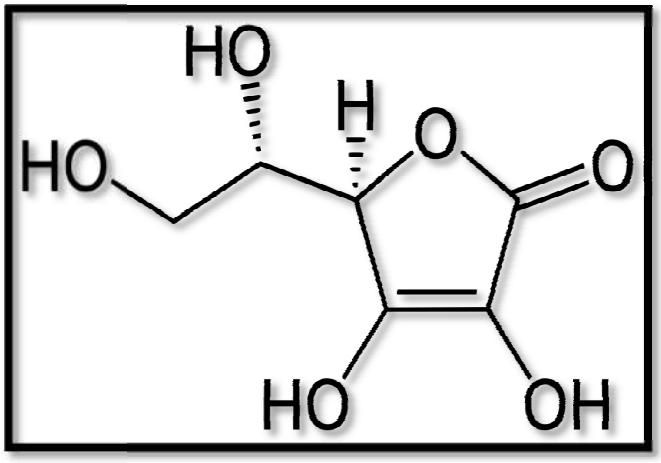


Figure (1.7): Chemical structure of Vitamin C[112]

Is the term frequently used to refer to L-ascorbic acid in a nutritional context and it also encompasses its oxidation product, dehydroascorbic acid. L-ascorbic acid is found naturally in a wide variety of plants and animals. The chemical formula $C_6H_8O_6$ and a molecular weight of 176.12 . its water-soluble vitamin C is important in forming collagen, The human body does not produce it and its only source is from diet[113].

A fundamental feature of the chemistry of L-ascorbic acid is its redox behavior. In an excellent paper on the complex redoxbehaviour of L-ascorbic acid, Creutz[114] pointed out that the oxidation and reduction reactions of L-ascorbic acid and its redox companions are complicated by the intervention of simultaneous proton transfer reactions. Of particular interest in the context of transition metal chemistry is the fact that L-ascorbic acid will form chelate complexes with transition metal ions[115]. In most cases, the structures of these species have been deduced from spectroscopic studies of one sort or

another and it is generally believed that such complexes are formed to produce a five-member ring with the enediol part of the molecule[116].

Ascorbic acid is a powerful antioxidant because it can donate a hydrogen atom and form a relatively stable ascorbyl free radical. As a scavenger of reactive oxygen and nitrogen oxide species, ascorbic acid has been shown to be effective against the superoxide radical ion, hydrogen peroxide, the hydroxyl radical and singlet oxygen [117].

1.11 Chelation of metal ions

The ions of Nickel (Ni^{+2}),and Cadmium (Cd^{+2}) are essential for certain physiological functions of living cells . They can be, either as components of hemoprotiens, or of cofactors of various enzymes implicated in antioxidant defense system of cells. Besides their beneficial role, they are also responsible for the production of the sulfhydryl radical by the reduction of hydrogen peroxide ($^{\bullet}OH$), according to the following reaction.

$$H_2O_2 + Pb^{+2} \longrightarrow {}^{\bullet}OH + {}^{-}OH + Pb^{+2}$$

The flavonoid form a stable complex with transition metals (Fe^{+3}, Al^{+3}, Cd^{+2}, Ni^{+2} Pb^{+2}); the stiochiometry of the complex and the site of chelation depend on the nature of the flavonoid mainly the presence of the catechol part and the pH. Moreover, this phenomenon of chelation is accompanied by the oxidation of the flavonoid (Cd^{+2}, Ni^{+2} Pb^{+2}) . The chelation is occurred generally on the hydroxyl groups in position 3' and 4' of the B ring, on the position 5 of hydroxyl group of A ring and on the positions 3 and 4 of carbonyl of C ring[118-120].

1.12 Molecular Complex

The term molecular complex is used to describe a variety of types of association products of two or more molecules. In the past two decades or so extensive experimental attention has been given to a large group of complexes formed by the weak interaction of certain classes of organic substances, functioning as electron donors, with other substances which act as electron acceptors [121,122]

The substances which serve as donor components can be divided in two groups. The first group includes alkenes, alkynes, aromatic hydro carbons , and their substitution products. These are classed as π complexes. The second group of donors encompasses a large group of substances in which there are non- bonded electrons available for coordination. Typical example of these so – called n donors are alcohols, organic sulfides, organic iodides, and nitrogen bases in which the lone pairs are located in atomic orbital of oxygen, sulfur, nitrogen and iodine atoms. There are many types of acceptors such as, inorganic acceptors (halogens, silver salts, salt of copper (I) and mercury (II), metal halides, …) hydroxylic substance and haloforms, π acids and organic acceptors[123,124].

Donor – acceptor complexes, the compositions of which can be represented by integral mole ratios of the components, are in many instances so unstable that they cannot be isolated in the pure state at ordinary temperatures but exist only in solutions in equilibrium with their components, usually be detected readily because of differences in their physical properties (e.g., absorption spectra) from those of the pure[125].

It was recognized some time ago that certain types of molecular complex should be regarded as products of electron donor – acceptor interactions[126,127].

The exact nature of the coordinate link between the complex components however has been the subject of extensive and controversial discussion over the past several decades.

Keefer , in attempting to account for the weakness of the coordinate link between the components of certain complexes, considered the possibility that ″residual valence forces″were saturated by the interaction [128].

Bennet and Willis, took the opposite view and proposed that covalent bonds, were established between the donors and acceptors.

Rossoti , proposed that they are formed through electrostatic attraction between molecules with permanent dipoles or permanent partial moments and non-polar substance which can be polarized by induction [129].

Gibson and Loeffler suggested that these changes spectrum, which are frequently observed when complexes are formed, are associated with a transfer of electrons from one component to the other[130].

1.13 Thermodynamics and Biological Systems

All living organisms have an unrelenting requirement for energy. The flow of energy that sustains life on earth originates on the sun, a small percentage of the solar energy that reaches the earth is captured by plants and certain microorganisms, photoautotrophs, can utilize solar energy during photo synthesis .The study of energy transformations in living organisms is called bioenergetics, it is useful in determining the direction and extent to which specific biochemical reactions will proceed .Thermodynamics is concerned with heat and energy transformations, such transformations are considered to take place in a "Universe" that is composed of a system and its surroundings[131, 132].

A biological system may be an entire organism or a cell or a reaction occurring in living organism, which consume nutrients from their surroundings and release waste products to it, are open systems.

Chemical reactions are determined by three factors:

I- Enthalpy (H): a measure of heat contents.

II- Entropy (S): a measure of disorder are derived from the first and second law of thermodynamics.

III- Free energy (G): a measure of the tendey of a process to take place, is derived from a mathematical relationship enthalpy and entropy.

$$\Delta G = \Delta H - T\Delta S \text{----------(1-1)}$$

T: is in absolute temperature

ΔS: has a positive sign when entropy increases

and ΔH: has a negative sign when heat is released, either of these conditions, typical of spontaneous process, will make ΔG negative (spontaneous process)[133, 134].

The standard free energy (ΔG°), which is a constant for each individual reaction, defined under the standard conditions of 25°C and 1atm pressure.

For the reaction

$$aA + bB \rightleftharpoons cC + dD$$

The change in free energy is related to the reaction's equilibrium constant:

$$\Delta G = \Delta G^{\circ} + 2.303RT \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \text{----------(1-2)}$$

If the reaction at equilibrium, the ΔG=0 and the expression reduced

$$\Delta G^{\circ} = -2.303RT \log K_{eq} \text{----------(1-3)}$$

1.14Stability of complex in solution

A metal ion in solution does not exist isolated, but in combination with ligands (such as solvent molecules or simple ions) or chelating groups, giving rise to complex ions or coordination compounds. These complexes contain a central atom or ion, often a transition metal, and a cluster of ions or neutral molecules surrounding it.

All metals form complexes, although the extent of formation and nature of these depend very largely on the electronic structure of the metal. Stability of a complex in solution" refers to the degree of association between the two species involved in the state of equilibrium. Qualitatively, the greater association, the greater stability of the compound. The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability[135]. Thus, if we have a reaction of the type:-

$M + nL \rightarrow ML_n$

then the larger stability constant, the higher proportion of ML_4 that exists in the solution. Free metal ions rarely exist in solution so that M, will usually be surrounded by solvent molecules which will compete with the ligand molecules, L, and be successively replaced by them.

1.15 Thermodynamics and equilibrium chemistry

Thermodynamics is the study of thermal, electrical, chemical, and mechanical forms of energy. The study of thermodynamics crosses many disciplines, including physics, engineering, and chemistry. the various branches of thermodynamics, the most important to chemistry is the study of the changes in energy occurring during a chemical reaction. Chemical systems spontaneously react in a fashion that lowers their overall free energy[136] in equation (1-1).

At a constant temperature and pressure, typical of many bench-top chemical reactions, the free energy of a chemical reaction is given by the Gibb's free energy function equation (1-1) [138]

Reactions in which heat is produced have a negative ΔH and are called exothermic. Endothermic reactions absorb heat from their surroundings and have a positive ΔH. Entropy is a measure of randomness, or disorder. The entropy of an individual species is always positive and tends to be larger for gases than for solids and for more complex rather than simpler molecules. Reactions that result in a large number of simple, gaseous products usually have a positive ΔS. The sign of ΔG can be used to predict the direction in which a reaction moves to reach its equilibrium position. A reaction is always thermodynamically favored when enthalpy decreases and entropy increases. Substituting the inequalities $\Delta H < 0$ and $\Delta S > 0$ into equation (1-1) shows that ΔG is negative when a reaction is thermodynamically favored. When ΔG is positive, the reaction is unfavorable as written (although the reverse reaction is favorable). Systems at equilibrium have a ΔG of zero. At equilibrium the Gibb's free energy is zero, and equation below

$$\Delta G^\circ = -RT \ln K_{eq} \text{ ----------(1-4)}$$

where K_{eq} is an equilibrium constant that defines the reaction's equilibrium position[136].

1.16 Spectrophotometer

Spectroscopy is the quantitative and qualitative measurement of the reflection or transmission properties of a material as a function of wavelength.

The use of spectrophotometers spans various scientific fields, such as physics, materials science, chemistry, biochemistry and molecular biology. Ultraviolet–Visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis) refers to the absorbance or reflectance in the ultraviolet- Visible spectral region. This means it uses light in the visible and adjacent area (near-UV and near-infrared [NIR]) ranges.

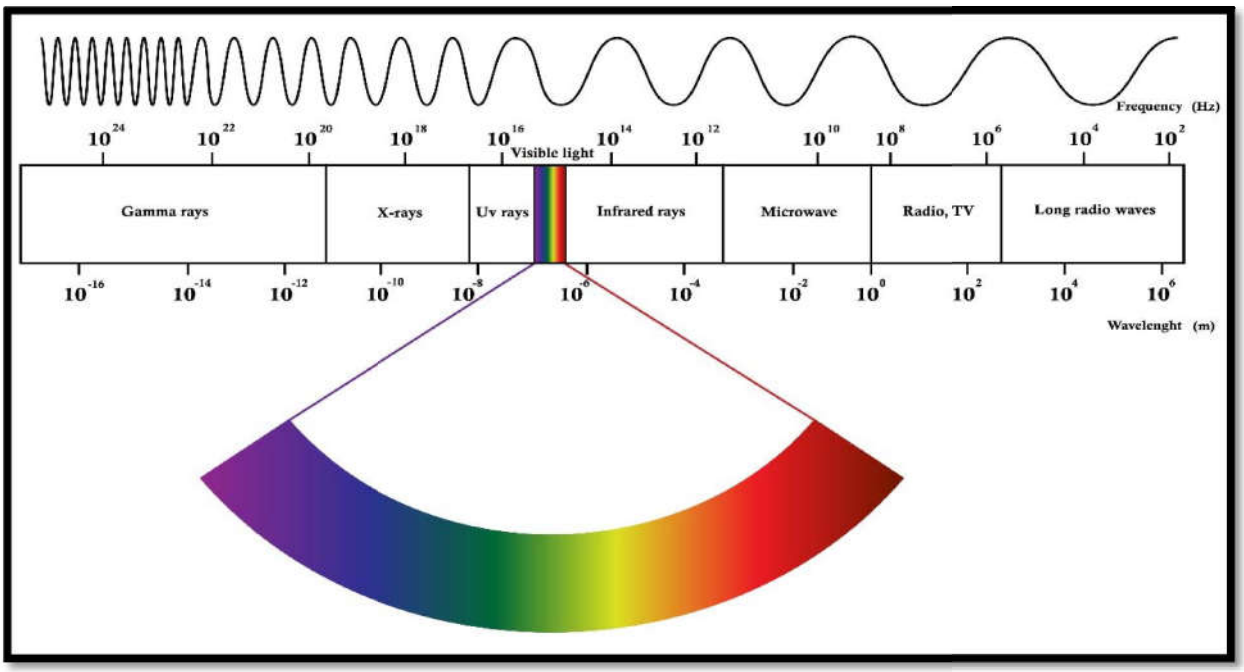


Figure (1.8): The regions of the electromagnetic spectrum [138]

The absorbance or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state[138].

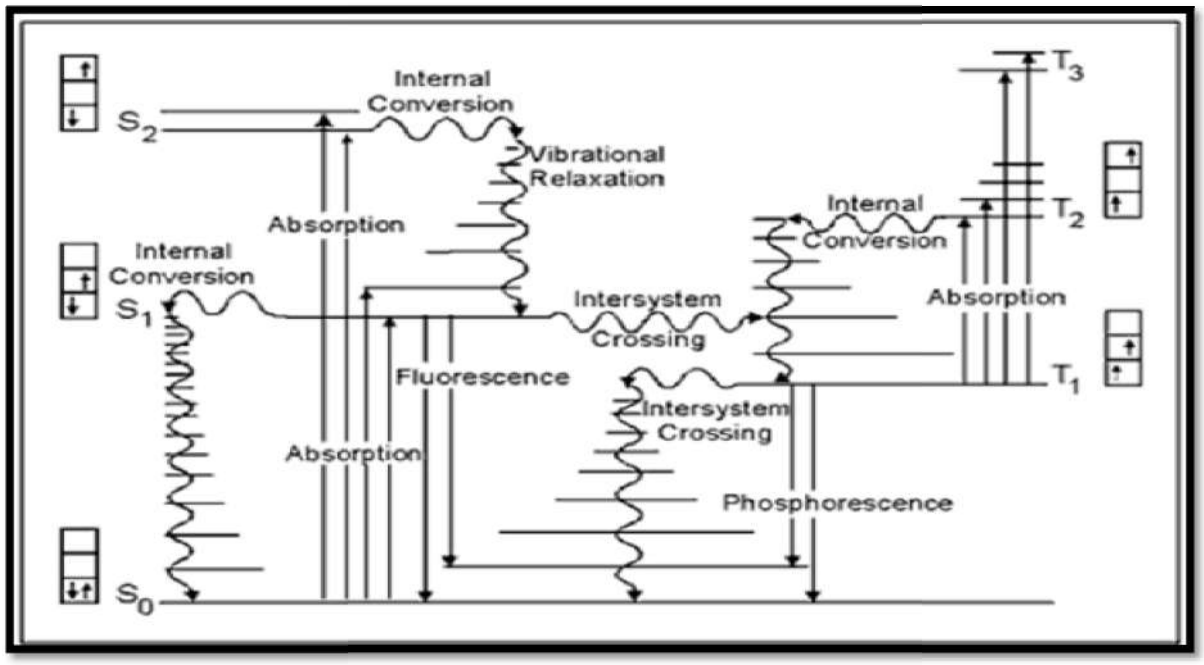


Figure (1.9): Physical basis of Absorbance, Fluorescence and phosphorescence[193]

Molecules that capable of absorbing light are called chromophores. In absorption spectroscopy the particular frequencies at which light is absorbed are affected by the structure and environment of chromophore. Light energy is used to promote electrons from the ground state to variation excited state. Different chemical structure absorb different frequencies of light since each has a different characteristic electronic structure (pattern of electron distribution). Molecules containing π-electrons or non-bonding electrons (n-electrons) may absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbital's.

The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO) the longer wavelength of light is absorbed[139].

The instrument used in ultraviolet-visible spectroscopy is called a UV/Vis spectrometer. It measures the intensity of light(I) passing through the sample, then compare it to the intensity of light before it passes through the same sample (I_o). The ratio I/I_o is called the transmittance, and is usually expressed as a percentage of (T %). The absorbance may be quantified by the Beer – Lambert low:

A= log (100 / T %)…….(1-5)

Log I_o/I = ε.c.l …….(1-6)

I_o : intensity of incident light

I : intensity of transmitted light

C : molar concentration

L : length of the light path in cm

T% : Transmittance light percentage

ε: the molar extinction coefficient

Log I_o/I : the absorbance A_λ at the particular wavelength or frequency. A plot of A or ε versus wavelength or frequency is known as absorption spectrum. Wavelengths corresponding to maxima in such spectra are denoted by λ_{max}. This spectrum is a fixed property of a pure chromophore and it is used in identification of previously-characterized molecules. Since absorbance is directly depending on molar concentration, it could be used to measure the concentration provided a standard curve for that chromophoreis also available

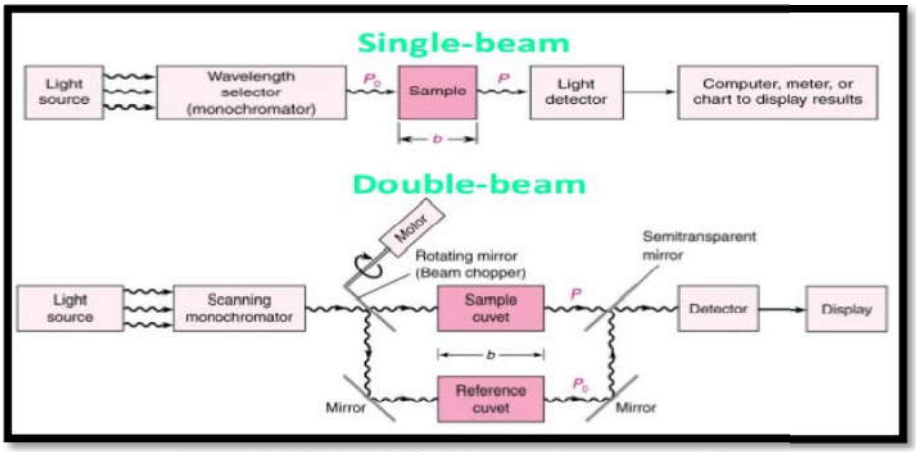


Figure (1.10): Uv-Visible Spectrophotometer [140]

The basic outline of the absorption spectra that measured in a spectro photometer are shown in Figure (1.10). Electromagnetic radiation is generated by a lamp which contains a metal filament through which an electric current flows. For a wavelength in a visible range a tungsten-halogen lamp (290-900nm) is used while deuterium lamps provide both ultraviolet and visible radiation (210-370nm). The light emitted from these sources consist of a wide

range of wavelengths. It is necessary to select a single wavelength by passing the light through a mono chromator of some sort. In modern instruments, this is usually a diffraction grating which achieves the same effect as the prism used by Newton.

This monochromatic light is then used as incident light in the absorption experiment. Many designs are available for spectrophotometer including single beam, split (double) beam and dual beam instrument (see Figure 1.10). A cuvette is a sample container, which is constructed from different materials, such as glass, plastic and quartz. Because the cuvette (and the solvent) may have its own absorption spectrum, it is essential to determine a blank spectrum of cuvette plus solvent and then subtract this from that of the solvent containing the chromophore (analyte), in order to obtain the real spectrum for the chromophore solely. In a duel beam instrument, this could be with one beam passing through the blank cuvette and the other through the analyte[140]

The applications of Absorption Spectroscopy are:

1. Advantage is frequently taken of the Beer-Lambert law to carry out quantitative measurements. If the absorptivity is known, it is possible to calculate concentrations directly from the absorbance readings at specific wavelength.
2. In enzyme assays the concentration of either substrate or product may be measured to allow calculation of rates of enzyme-catalyzed reactions.
3. Structural studies for biopolymers such as proteins and DNA.
4. Absorption spectra are characteristic for specific bio molecules.

1.17 Literature survey

Middleton & Kandaswami(1994)[141]: The earliest presented complexing reaction of flavonoids with aluminum as the central ions and flavone as the ligand. It was observed that complex formation causes a batho chromic shift in both absorption bands, I and II.

Pietta(2000)[142]: found that, the chelating properties of flavonoids towards metal ions have been attributed to the presence of the 3-or5-hydroxyl pyran-4-one, rather than the ortho-hydroxyl in the B-ring

Mira, Viswanathan(2002)[143, 144]: proposing that catechol moiety is the major site for metal chelating The results of Bodini et al indicate that coordination to the catechol group of quercetin is the strongest for iron, even in acidic media [145]

Cornard and Merlin(2002)[120]: assert the opposite, that in acidic media the ortho - dihydroxy groups of quercetin are never involved in complexation with Al (III). The same authors found two binding sites in the Al (III) – quercetin complex formation is the 3 - hydroxy groups, which are strongly depends on the medium and pH.

Torreggani et al(2005)[146]: also found that two chelating processes occurred consecutively, implicating two binding sites in the Cu (II) – Quercetin complex.

Swaran J.S. Flora and Vidhu Pachauri (2010)[54]: provide an update of the existing chelating agents and the various strategies available for the treatment of heavy metals and metalloid intoxication. 2,3-Dimercaprol haslong been the mainstay of chelation therapy for lead or arsenic poisoning ,however its serious side effects have led researchers to develop less toxic analogues.

Hydrophilic meso-2,3-dimercaptosuccinic acid effectively promote renal metal excretion, but their ability to access intracellular metals is weak .

LetiziaDa Sacco and Andrea Masotti (2010)[147]: Chitin and chitosan arenatural polysaccharide polymers. they have been used in few studies dealingwith arsenic (As) removal from the groundwater and no evidence of the use of these natural polymers for arsenic trioxide (As_2O_3) delivery in tumor therapy. They suggest that chitin and/or chitosan might have the right properties to be employed as efficient polymers for such applications.

Gholamreza Dehghan and Zahra Khoshkam (2011)[148]: They studied the ability of quercetin to chelating the toxic tin in an organic stannous chloride ($SnCl_2.2H_2O$) form. To access the more information about chelation, 1H-NMR,IR and UV-visible spectroscopic measurements have been carried out .

Guangliang Liu, Aymara Fernandez, and Yong Cai (2012)[149]: Dissolved organic matter (DOM) binding with arsenic (III) in presence of iron (Fe) and formation of Fe-bridged As-Fe-DOM complexes. Were investigated using a size exclusion chromatography (SEC) and UV-inductively coupled plasma massspectrometry (ICP-MS) technique. The kinetic data of As(III)-Fe-DOM complexation were well described by a pseudo-first order rate equation (R^2 =0.95), with the rate constant (k′) being 0.17±0.04 h-1. and stability constant (Ks) derived from two-site ligand binding model, with (log Ks) ranging from 4.4±0.2to 5.6±0.4 .

C.Montoliu, J. Pungercar, J.-M. Sabatier, F. Th´evenod, and A.Yasutake (2013)[150]: Toxic metals such as arsenic, cadmium, lead, and mercury are ubiquitous, have no beneficial role in human homeostasis, and contribute to

non communic able chronic diseases. Novel drug targets for chronic disease are eagerly sought, potentially helpful agents that aid in detoxification of toxic elements, chelators, have largely been restricted to overt acute poisoning. Peptides glutathione and metal othionein chelate both essential and toxic elements as they are sequestered, transported and excreted .

Al-Rufaie E. M. and Al-Khafaji N. R. (2014)[151]: Study the interaction of lead (II) ion with a poly hydroxyllated flavonoids, the quercetin molecule, was investigated electrochemically in acidic media. The differential pulspolarographic technique were used to determine the kinetic parameters of $K°_{th}$, α_n using meites. also thermodynamic parameters such as ΔH, ΔG and ΔS of Pb^{+2}-complexes with quercetin at (293-313) K

The Aims of the present work:

The aim of the present work is to study the complexation of Pb(II),Ni(II),Cd(II) ions by four of the flavonoid compound (Curcumin , Quercetin , Vitamin C , Catechin) as follows:

1. Optimizing of all the chemical and physical conditions for the complexation.

2. Determining λ_{max} and the absorbance for each compound alone in their optimized condition.

3. Measuring of the spectrum for the mixtures of these compounds with Pb (II),Ni(II) and Cd(II) ions.

4. Determining the stoichiometric ratio of the complexes by the Job method

5. Determining the equilibrium constant and the other thermodynamic parameters ($\Delta H°$, $\Delta G°$ and $\Delta S°$) for the complexation.

6. Conducting kinetic studies for the rate constants and the reaction order determinations.

CHAPTER TWO

EXPERIMENTAL

2.1 Materials: The following grade chemicals with their supplies and purity were listed in Table (2-1).

Table (2-1): The chemical compound used

No.	Compound	Chemicl formula	M.wt ($g.mol^{-1}$)	Company	Purity %
1	Nickel nitrate	$Ni(NO_3)_2$	290.8	Sigma Aldrich	99
2	Lead nitrate	$Pb(NO_3)_2$	331.23	Hopkin & Williams LTD (CHADWELL HEAT ESSEX ENGLAND)	99
3	Cadmium sulfate octahydrate	$3CdSO_4.8H_2O$	769.54	Fluka	98
4	Curcumin	$C_{21}H_{20}O_8$	468.38	Santa Cruz Biotechnology	98
5	Quercetin dihydrate	$C_{15}H_{10}O_7 \cdot 2H_2O$	338.26	Sigma Aldrich	99
6	Vitamin C	$C_6H_8O_6$	176.12	Labo Chemia	99
7	Catechins	$C_{15}H_{14}O_6$	290.27	Sigma Aldrich	99.8
8	Absolute ethanol	C_2H_5OH	46.07	Fluka AG/Switzerlad	99.9

2.2 Instruments:

Table (2-2): The used instruments.

No	Instrument's Name	Instrument's type and company
1	UV-Vis spectrophotometer	(Shimadzu UV-1800) Germany
2	Water bath	Electrothermal-England
3	Distilled water apparatus	GFL-Germany
4	Oven	Gallenkamp-England
5	Sensitive digital balance	Sartorius AG Göttingen BL210S-Germany

2.3 Solutions:

1. Absolute Ethanol as a solvent
2. **Nickel nitrate solutions:** (10^{-2} M) stock solution of Ni (II) was prepared by dissolving (0.2908g) of Nickel nitrate [$Ni(NO_3)_2$] in (100 ml) volumetric flask using water as a solvent.
3. **Lead nitrate solutions:** (10^{-2} M) stock solution of lead (II) was prepared by dissolving (0.3312g) of lead nitrate [$Pb(NO_3)_2$] in (100 ml) volumetric flask using water as a solvent.
4. **Cadmium sulfate octahydrate solutions:** (10^{-2} M) stock solution of Cadimum(II) was prepared by dissolving (0.7699g) of Cadmium sulfate octahydrate ($3CdSO_4.8H_2O$) in (100 ml) volumetric flask using water as a solvent.

5. **Quercetin solutions:** (10^{-2} M) stock solution of quercetin was prepared by dissolving (0.3382 g) of quercetin in (100 ml) volumetric flask using ethanol / water as a solvent (40%ethanol / 60%water)
6. **Curcumin solutions:** (10^{-2} M) stock solution of Curcumin was prepared by dissolving (0.4683g) of Curcumin in (100 ml) volumetric flask using ethanol/water as a solvent (60%ethanol / 40%water)
7. **Vitamin C solutions :** (10^{-2}M) stock solution of Vitamin C was prepared by dissolving (0.1761g) of Vitamin C in (100 ml) volumetric flask using distilled water as a solvent.
8. **Catechin solutions:** (10^{-2}M) stock solution of Catechin was prepared by dissolving (0.2902g) of Catechin in (100 ml) volumetric flask using distilled water as a solvent.

2.4 Methods:

Spectrophotometric Measurements

Absorption spectra were measured with the UV-Vis spectrophotometer using a quartz cell of 1 cm path length. The absorbance of metals ions and antioxidant solutions were measured in a wave length of (190-800) nm; by the use the same solvent as a references.

2.4.1 Applicability of Beer's Law (calibration Curve):

After fixing the optimum conditions, calibration graphs of the complexing agents (curcumin ,vitamin c quercetin, and catechin) were constructed. Into a series of solutions differ in concentration ranging from ($9x10^{-5}$ to $1x10^{-4}$ M) were prepared by dilution from their stock solutions for curcumin ,vitamin c quercetin, and catechin. The absorption spectrum were measured at their λ_{max}.

2.4.2 Determination of the Stoichiometric Ratio(Job Method):

A series of solutions have a mole fraction between (0.1 to 0.9), were prepared by mixing different volumes of equi molar of Ni(II),Pb(II),Cd(II) and antioxidants stock solutions of a concentration ($4x10^{-4}$M) for vitamin c and catechin , and stock solutions of a concentration ($4x10^{-5}$M) for curcumin and quercetin.

The principle of this method involves the preparation of a series of equimolar solutions with the summation of total volume of compound 1 and compound 2 is constant:

$V_{total} = V_1 + V_2$ …… (2.1)

The mole fraction of compound 1 and 2 is varied between 0 to 1 and the absorbance of the solution was measured versus the blank.

The absorbance was plotted against mole fraction X, then (n) can be calculated from the abscissa of the maximum of the curve (X_{max}):

$n = X_{max} / 1 – X_{max}$ …….. (2.2)

n: coordination number of the complex

X_{max} = mole fraction corresponds to the maximum absorbance.

2.4.3 Determination of Rate Constant and Order of Interaction:

The rate constant for the interaction of chelators with (lead , Nickel and Cadimum) ions were done for the stoichiometric ratio by measuring the absorbance with time at constant temperatures in a time interval of zero to 60 min., at four different temperatures (293K, 298K, 303K, 308K).

The principle of preparation and calculate is complex were evaluated by the preparation of two sets of solutions, the first one of solutions were communicated to contain stoichiometric amount of the metal (Pb^{+2}or Ni^{+2}or

Cd^{+2}) to the ligand (curcumin, Quercetin, Vitamin C, Catechin). The second one was formulated to contain fivefold excess of the ligand [152].

The interaction between metal ions (M) and the ligand (L) proceeds according to the equation:

$$M + L \rightleftharpoons ML$$
$$\alpha \quad \alpha \qquad 1-\alpha$$

And $K=\frac{[ML]}{[M][L]}$ ----------(2.3)

Were K = stability constant.

If α is the degree of dissociation and c is the molar concentration, then the above equation (2.3) may be written as follows:

$K=\frac{(1-\alpha)C}{(\alpha C)(\alpha C)}$ ----------(2.4)

$K=1-\boldsymbol{\alpha} / \boldsymbol{\alpha}^2 c$ ----------(2.5)

Given that $\boldsymbol{\alpha} = \mathbf{A_m - A_s/A_m}$; where Am and As are the absorbance of the solution containing an excess and stoichiometric amount of reagent, respectively.

2.4.4 Determination of the Molar Absorptivity of the Complex:

A series of solutions of Nickel-antioxidants, lead-antioxidants and Cadmium-antioxidants complexes were prepared by mixing ($4*10^{-4}$M) lead, Nickel, and Cadmium solutions with ($4*10^{-4}$M) Curcumin and Catechin solutions, and mixing($4*10^{-5}$M) lead, Nickel, Cadmium solutions with ($4*10^{-5}$M) Vitamin C and Quercetin. Then recording the absorption spectrum for them.

2.4.5 Determination of thermodynamic parameters for metal ions chelators Interaction

Thermodynamic parameters; the standard enthalpy change ΔH^o, standard entropy change ΔS^o, and standard free energy change ΔG^o, and their relation to equilibrium of studied systems were calculated as follows:

K_{eq} were calculated from the concentration of all component at the equilibrium as in section (3.5) which allows us to calculate ΔG^o at different temperatures[153]

$\Delta G^o = - RT \ln K_{eq}$ …….. (2.6)

$\ln K_{eq} = -\Delta G^o / RT$ …… (2.7)

Both K_{eq} and ΔG^o are temperature dependent amounts

Differentiating equation (2.7) versus (1/T) gives

$\ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$ ……(2.8)

The enthalpy of communication can be determined by measuring the equilibrium constant for a system at different temperature. The enthalpy of the system can then be calculated from the slope ($-\Delta H^o/R$) of the resulting linear van't Hoff plot of ($\ln K_{eq}$) versus (1/T)[154].

Entropy change for the system can then be calculated from the intercept by equation (2.8) :

Intercept $= \Delta S^\circ / R$ ……. (2.9)

CHAPTER THREE

RESULT & DISCUSSION

3.1 Absorption Spectrum

UV VIS. Spectrometry has become a major technique for the structural analysis of flavonoids because of these two reasons. The first is that only small amount of compounds is required. The second is that the amount of structural information gained from UV VIS. Spectrum can be enhanced by the use of reagent which reacts with one or more functional group on the flavonoids skeleton[155].

3.1.1 Optimization of the Experimental Conditions spectrum of chelators in ethanol/water mixtures:

The kind of solvent may influence the position of the spectral band and the maximum absorbance, these slightly affects the values of λ_{max}, ε and the shape of the spectrum. Optimized solvent mixtures (ethanol/water) were obtained by measuring the UV-vis absorption spectra for the studied chelators in various mixtures, table (3.1).

Table (3.1) shows the data for Quercetin , Curcumin , Vitanin C and Catechin in various ethanol-water mixture, Note the bands do not exhibit any significant changes in λ_{max} with the variation of solvent composition, whereas the absorbance does, see figure (3.1).

The UV-vis absorption spectrum for Curcumin shows one absorption band at λ_{max} = 429nm $\pi \longrightarrow \pi^*$, Vitamin C shows one band at λ_{max} = 257nm, Catechin shows one band at λ_{max} = 278nm. These bands are all due to $n \longrightarrow \pi^*$ transition[156].

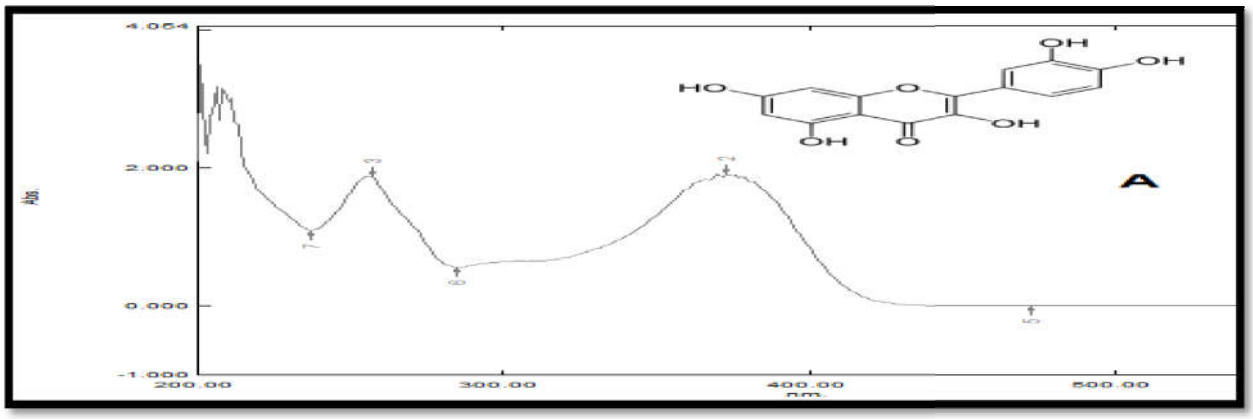
Quercetin illustrate the presence of two bands, the first at λ_{max} = 373nm (the right part of the molecule - cinnamoyl) and the second at λ_{max} = 256nm (for the left part of the molecule - benzyl band). According to these measurements which have been conducted in different solvent mixtures, it is possible to choose water

as a solvent for Catechin and Vitamin C (0% ethanol), (60% - 40%) ethanol-water for quercetin ,(40% - 60%) ethanol-water for Curcumin as a best medium in all subsequent measuremen.

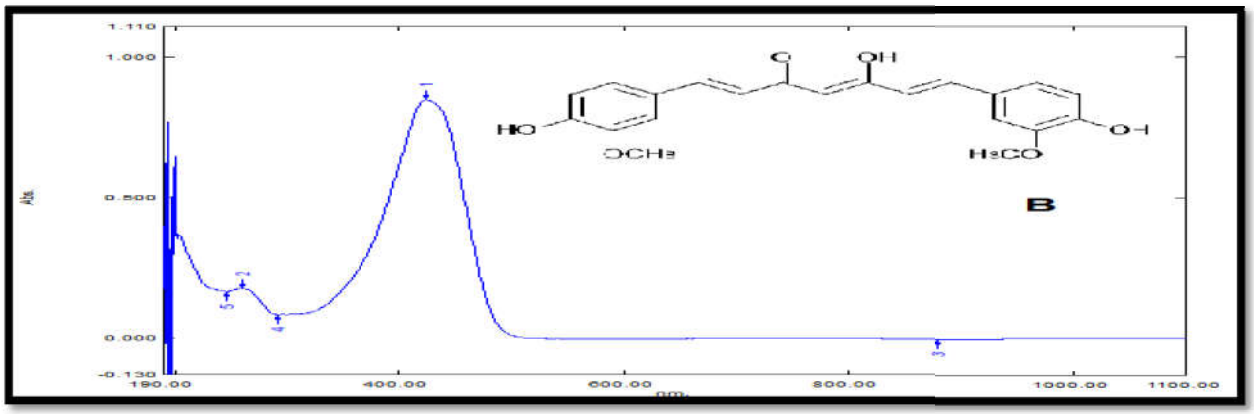
Table (3.1): The absorbance of Quercetin,Curcumin,Catechin,Vitamin C in a avarious Ethanol – Water mixtures.

No.	Chelators and its concentration	Water %	Wave length λ / nm		Absorbance	
			λ_I	λ_{II}	I	II
1	(10^{-4}M) Querctin	10%	374	256	0.476	0.442
		40%	374	256	0.465	0.443
		50%	375	256	0.482	0.465
		60%	373	257	1.905	1.879
		70%	372	255	1.207	1.224
		80%	371	255	0.682	0.704
2	(10^{-5}M) Curcumin	10%	428	-	0.082	-
		40%	429	-	0.087	-
		50%	429	-	0.085	-
		60%	429	-	0.075	-
		70%	432	-	0.071	-
		80%	425	-	0.058	-
3	(10^{-4}M) Catechin	0%	-	-	-	-
		40%	-	-	-	-
		50%	-	-	-	-
		60%	-	-	-	-
		70%	-	-	-	-
		80%	-	-	-	-
		100%	278	-	0.371	-
4	(10^{-4}M) Vitamin C	40%	-	-	-	-
		50%	-	-	-	-
		60%	-	-	-	-
		70%	-	-	-	-
		80%	-	-	-	-
		100%	257	-	1.095	-

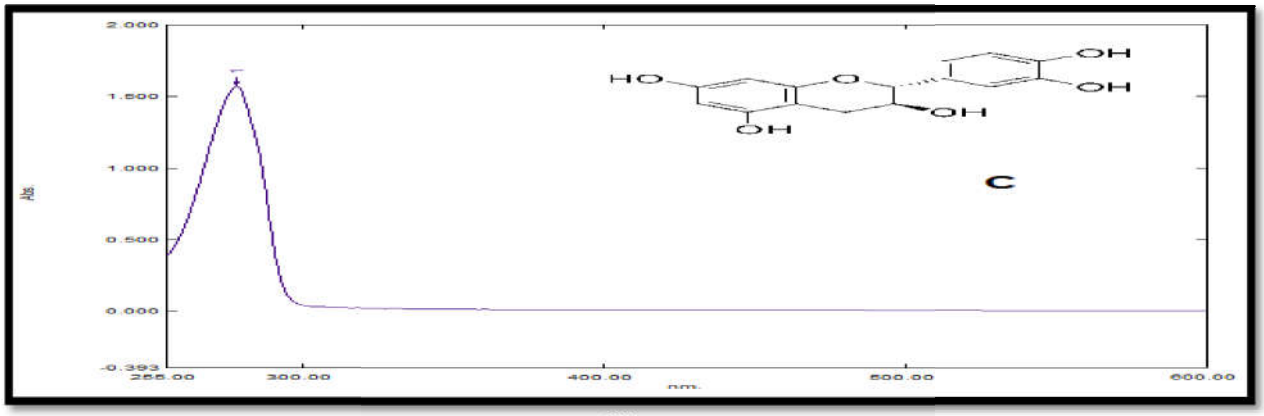
1- The absorbance measurements were done in 40% water/ ethanol solution due to the solubility of Quercetin in ethanol.
2- The absorbance measurements were done in 60% water/ ethanol solution due to the solubility of Curcumin in ethanol.
3- The absorbance measurements were done 100% Water due to the solubility of Catechin and Vitamin C in water



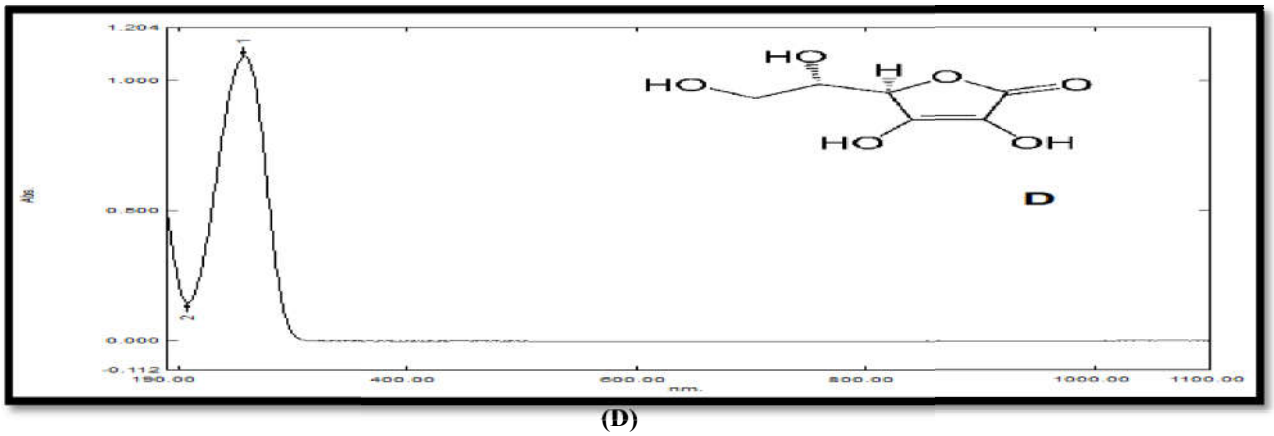
(A)



(B)



(C)



(D)

Figure (3.1) : UV-Visible absorption spectra of (10^{-5}M) solutions
A) Quercetin in 40%:60% (water:ethanol) B) Curcumin in60%:40% (water:ethanol) C) Catechin in water D) Vitamin C in water

3.2 Calibration Curve and the Applicability of Beer-Lambert Law

For the applicability of beer's law, the absorbance of solution was plotted against the concentration, a straight line is passing through the origin shows beer's law to be obeyed, the slope equal to (εl) when l=1cm

$A=\text{Log}\ (I_o/I) = \varepsilon C\ l$…….. (3.1)

Calibration curve of chelating agents were constructed between different concentration ranging from ($1x10^{-4}$ to $9x10^{-5}$ M) were prepared as in section (2.4.1) and the absorbance were recorded, the results were listed in table (3.2a,b) and figure (3.2).

Table (3.2)a : The Absorbance of different concentration of Catechin and Vitamin C in their solvents.

No	Conc (M)	Abs	
		Catechin	Vitamin C
1	$1x10^{-4}$	0.371	0.985
2	$2x10^{-4}$	0.752	1.223
3	$3x10^{-4}$	1.191	1.446
4	$4x10^{-4}$	1.575	1.875
5	$5x10^{-4}$	1.810	2.168
6	$6x10^{-4}$	2.092	2.256
7	$7x10^{-4}$	2.434	2.890
8	$8x10^{-4}$	2.792	3.353
9	$1x10^{-5}$	3.251	0.124
10	$9x10^{-5}$	3.720	0.311

Table (3.2)b : The Absorbance of different concentration of Curcumin and Quercetin in their solvents.

No	Conc (M)	Abs	
		Curcumin	Quercetin
1	$1x10^{-5}$	0.591	0.131
2	$2x10^{-5}$	1.253	0.52
3	$3x10^{-5}$	1.884	0.764
4	$4x10^{-5}$	2.461	0.954
5	$5x10^{-5}$	2.833	1.230
6	$6x10^{-5}$	3.500	1.432
7	$8x10^{-5}$	4.100	1.789

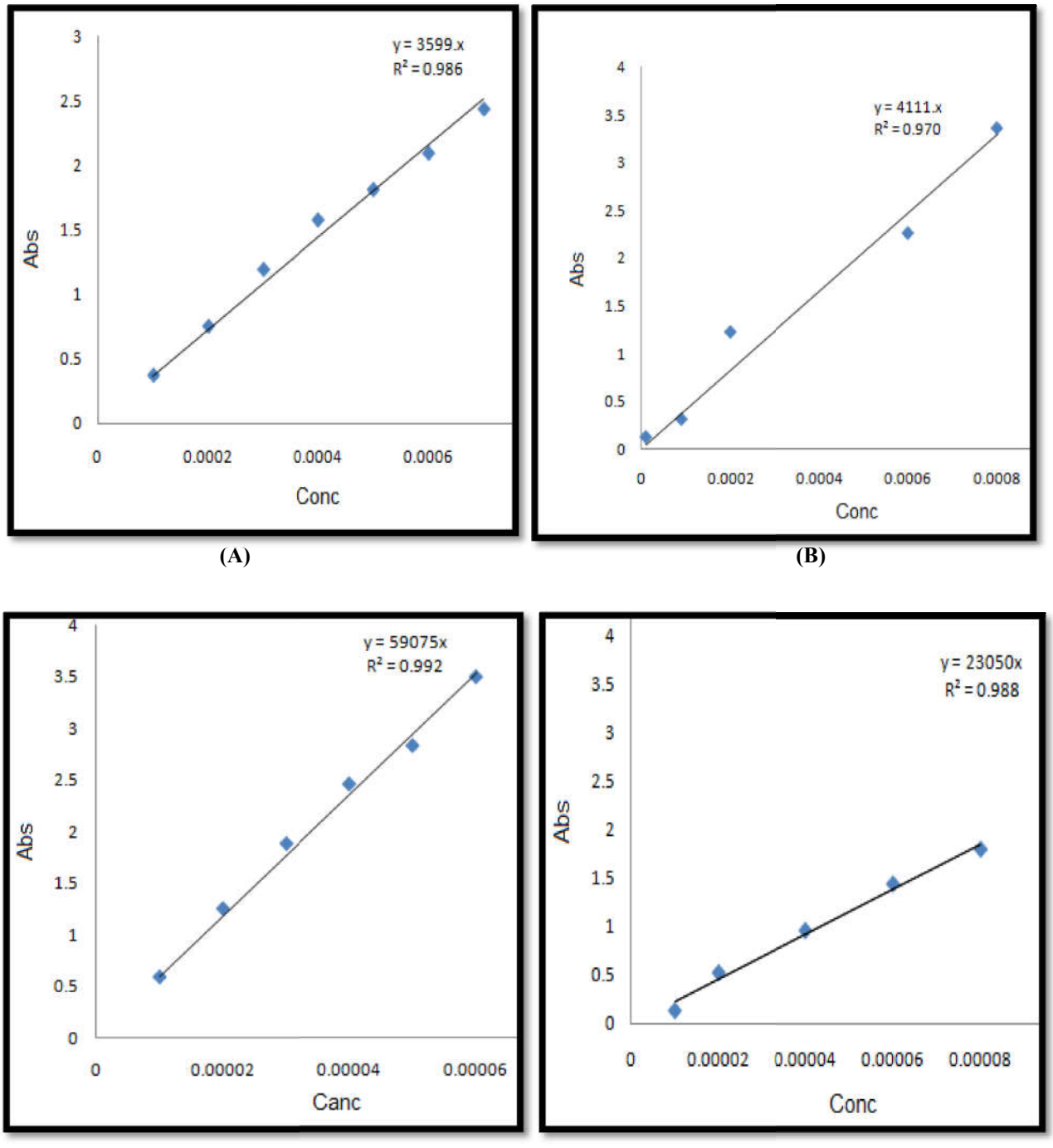


Figure (3.2): The calibration curve of (A)Catechin , (B)Vitamin C , (C)Curcumin (D)Quercetin

As a result, a straight line in Figure (3.2) shows that (Catechin , Vitamin C , Curcumin , Quercetin) solutions obey Beers law, and their slope equal to the molar absorptivity (ε).Figure (3.2) shows the calibration graphs of chelators. The analytical values of statistical treatment for the calibration graphs are summarized in table (3.3).

Table (3.3): Values of the molar absorptivity of antioxidants.

No	chelators	Linear equation	Molar absorptivity(ε) ($L.mol^{-1}.cm^{-1}$)	Correlation coefficient (R^2)	λ_{max}(nm)
A	**Catechin**	y=35990x	35990	0.986	278
B	**Vitamin C**	y=41111x	41111	0.970	257
C	**Curcumin**	y=59075x	59075	0.992	424
D	**Quercetin**	y=23050x	23050	0.988	373

3.3 The interaction between chelators and metal ion

The chelating agents in different media were studied first to choose the best solvent in which chelating agents have a maximum absorbance (section 3.1.1). The spectrum of the mixture of chelating agents with Nickel (II), Lead (II) and Cadimum (II) shows a shoft in λ_{max} (red shift) [130] and a change in the absorbance due to a complex formation between the chelators and metals ion, and the existence of the equilibriums as:

Ni II + chelators ⇋ [Ni-chelators]complex

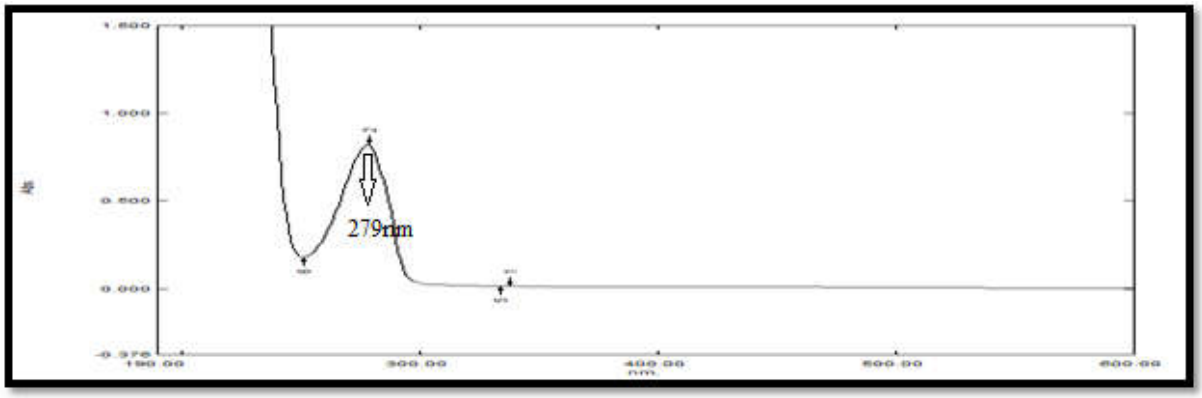
Pb II + chelators ⇋ [Pb-chelators]complex

Cd II + chelators ⇋ [Cd-chelators]complex

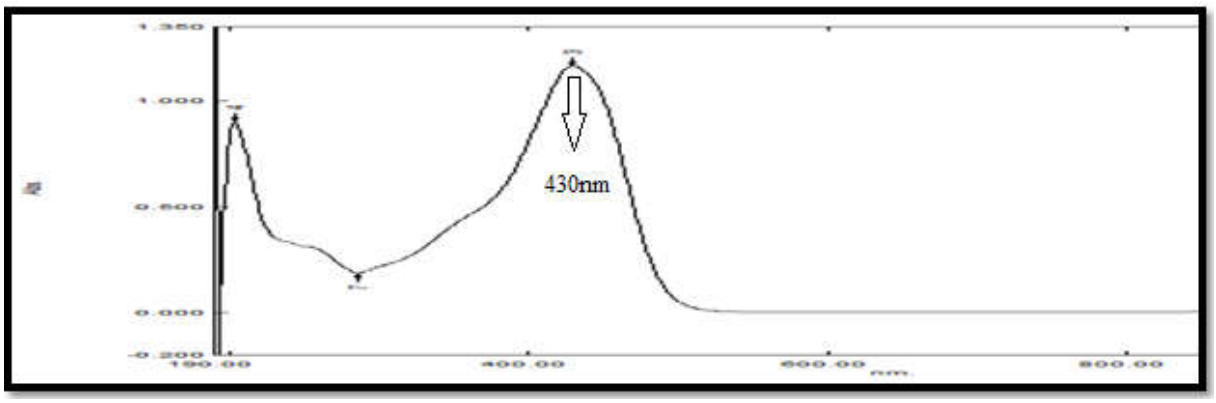
The electronic spectrum of the chelators (Catechin, Curcumin, Vitamin C and Quercetin) in their solvents are mainly characterized by an important absorption bands, see Table (3.4). Upon the addition of Nickel(II), Lead (II) and Cadimum (II) to the chelators solutions, a significant change is observed in their absorbance and wavelength.

3.3.1 Nickel (II) ion complexes:

The absorption spectrum of Nickel (II)–chelators were illustrated in Figures (3.3) to (3.6) in their solutions.

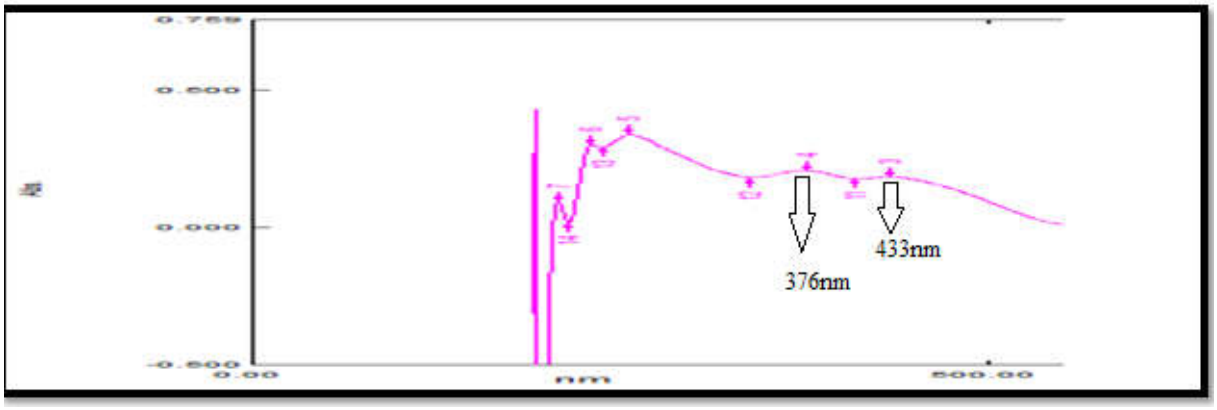


Figure(3.3) Ni(II) – Catechin complex in water solution λ_{max}=279nm



Figure(3.4) Ni(II) – Curcumin complex in 60%water : 40% ethanol solution λ_{max} =430nm

Figure(3.5) Ni(II) –Vitamin C complex in water solution λ_{max}=261nm



Figure(3.6) Ni(II) – Quercetin complex in 40%water : 60% ethanol solution new λ_{max} =433nm , λ_{max} =376nm

Table (3.4): Absorbance of Ni (II) with the antioxidants.

Compound	λmax (nm)	Absorbance
Catechin	278	0.371
Ni(II) – Catechin	279	0.823
Curcumin	429	0.087
Ni(II) – Curcumin	430	1.165
Vitamin C	257	1.905
Ni(II) – Vitamin C	261	1.879
Quercetin	373	1.905
Ni(II) – Quercetin	433 376	0.185 0.209

Table (3.4) shows that the interaction between Ni (II) ion with Catechin and Curcumin increasing their absorbance with a little shift in λ_{max}. For Vitamin C it shows a shift in λ_{max} to a longer wavelength and an decrease in absorbance. (Quercetin-Ni II) complex shows a bathochromic shift (red shift) in band I with the formation of new band at 433nm.

3.3.1.2 Cd(II) ion complexes:

The absorption spectrum of Cadimum (II)–chelators were illustrated in Figures (3.7) to (3.9) in their solutions.

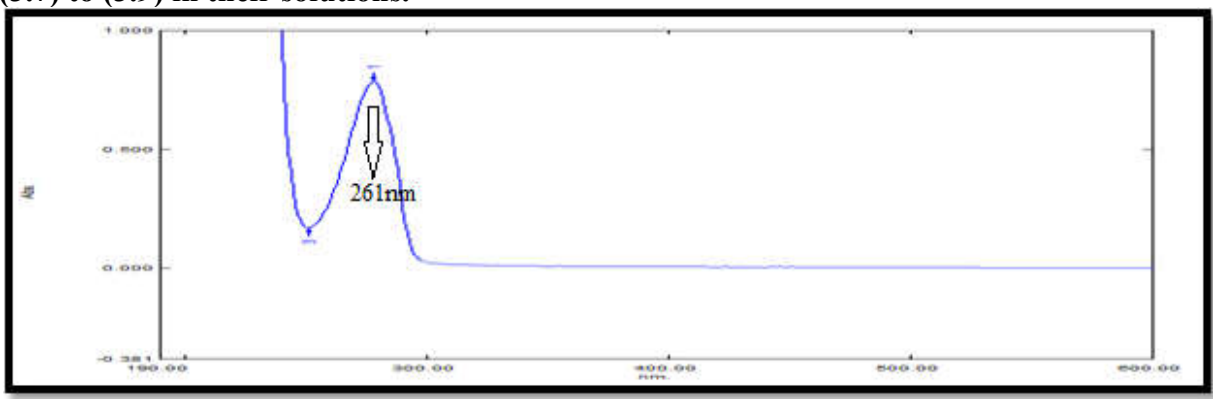


Figure (3.7): Cd (II)-Catechin complex in water and λ_{max}=278nm

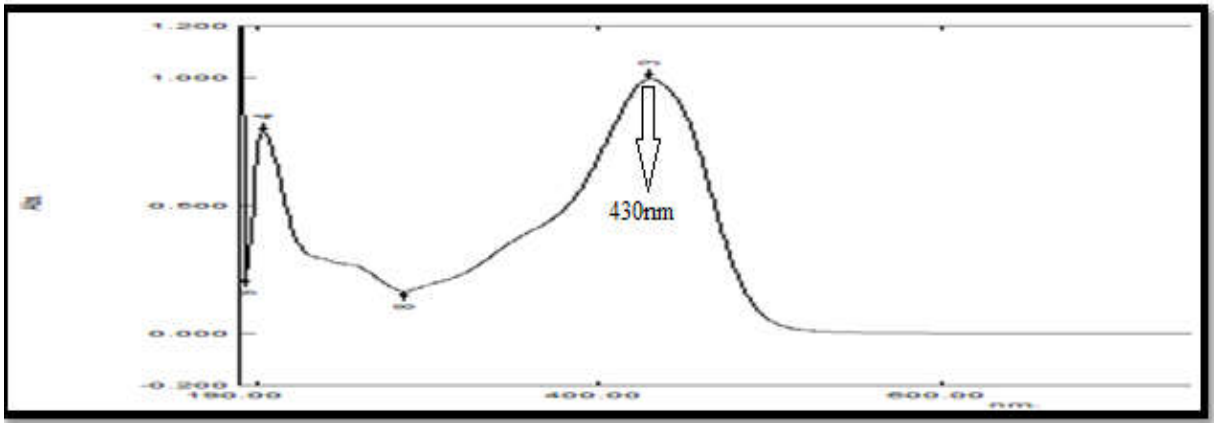


Figure (3.8): Cd (II)- Curcumin complex in 60%water:40%ethanol solution λ_{max} =430nm

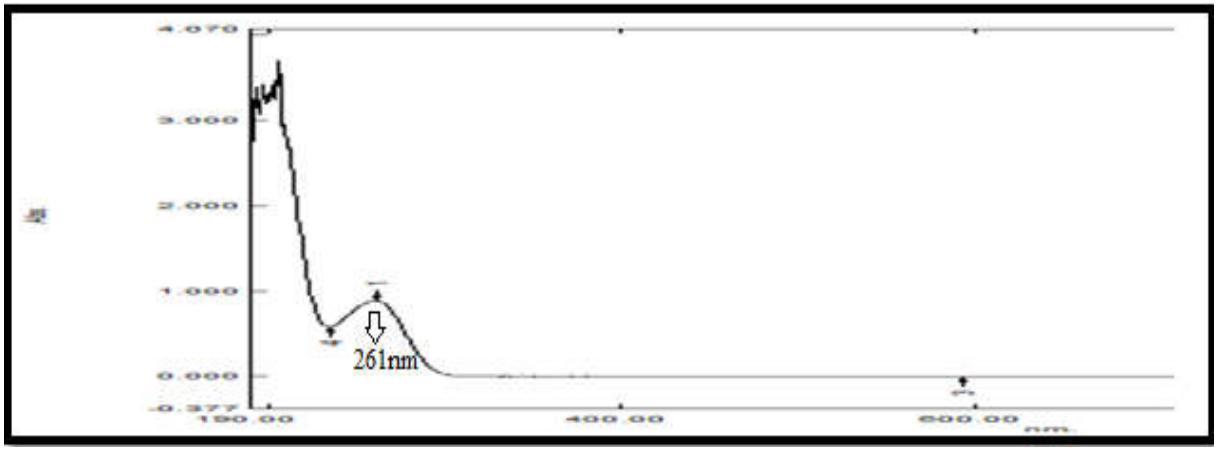


Figure (3.9): Cd (II)-Vitamin C complex in water and λ_{max}=261nm

Table (3.5): Absorbance of Cd(II) with the antioxidants.

Compound	λmax (nm)	Absorbance
Catechin	278	0.371
Cd(II) – Catechin	278	0.788
Curcumin	429	0.087
Cd(II) – Curcumin	430	0.994
Vitamin C	257	1.095
Cd(II) – Vitamin C	261	0.889
Quercetin	373	1.905
Cd(II) – Quercetin	No change	No change

Table (3.5) shows that the interaction between Cd (II) ion with Catechin and Curcumin increasing their absorbance with no effect on the λ_{max}. For Vitamin C it shows a shift in λ_{max} to a longer wavelength and an decrease in absorbance. Quercetin-Cd(II) mixture has no change in both λ_{max} and absorbance, yhat means there is no interact between Cd(II) and Quercetin.

3.3.2 Pb(II) ion complexes:

The absorption spectrum of Lead (II)–chelators were illustrated in Figures (3.10) to (3.13) in their solutions.

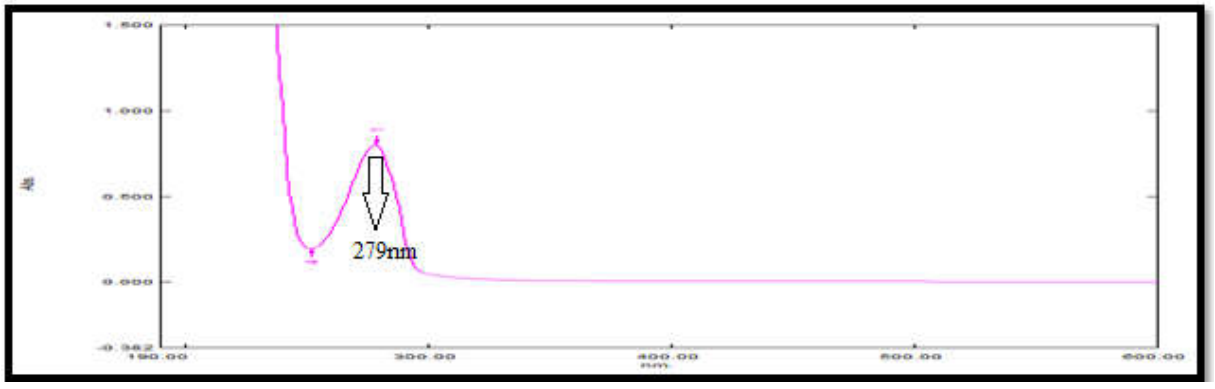


Figure (3.10): Pb (II)-Catechin complex in water and λ_{max}=279nm

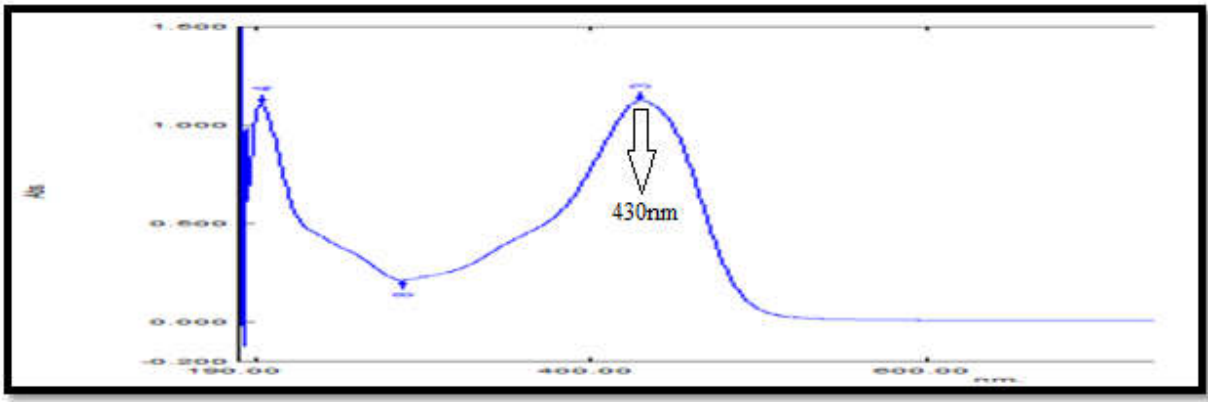


Figure (3.11): Pb (II)- Curcumin complex in 60%water : 40% ethanol solution λ_{max} = 430nm

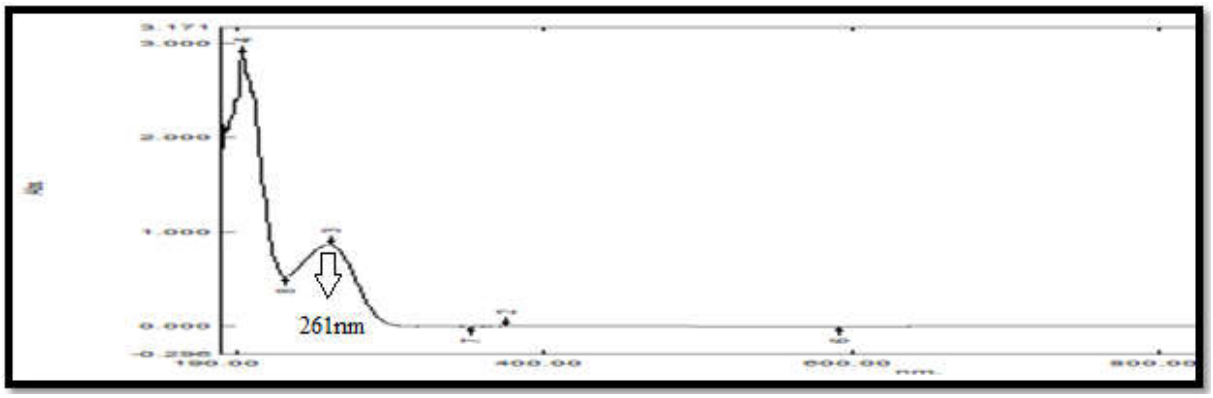
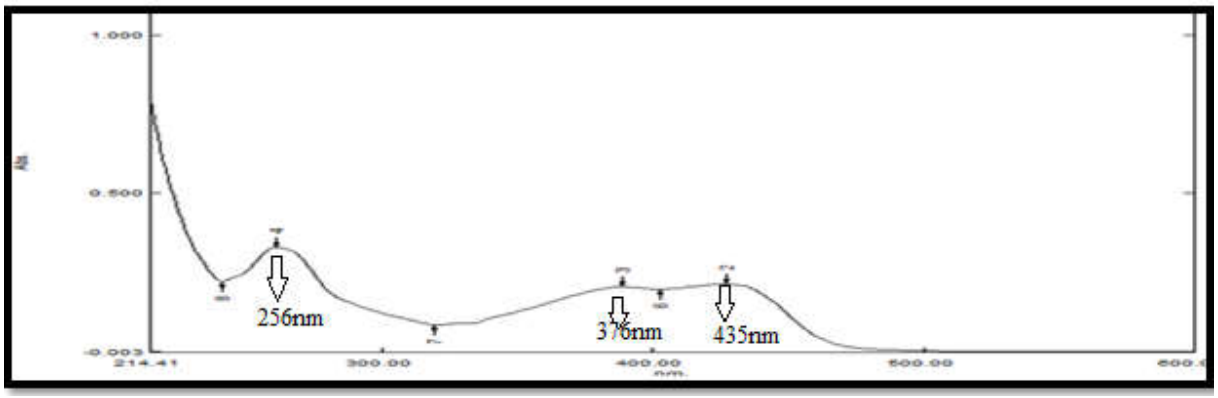


Figure (3.12): Cd (II)-Vitamin C complex in water and λ_{max}=261nm



Figure(3.13) Cd(II) – Quercetin complex in 40%water : 60% ethanol solution new λ_{max} =435nm and λ_{max} =371nm

Table (3.6): Absorbance of Pb (II) with the antioxidants.

Compound	λmax (nm)	Absorbance
Catechin	278	0.371
Pb(II) – Catechin	279	0.806
Curcumin	429	0.087
Pb(II) – Curcumin	430	1.125
Vitamin C	257	1.095
Pb(II) – Vitamin C	261	0.865
Quercetin	373	1.905
Pb(II) – Quercetin	435 376	0.137 0.151

Table (3.6) shows that the interaction between Pb(II) ion with Catechin and Curcumin increasing their absorbance with no effect on the λ_{max} . For Vitamin C it shows a shift in λ_{max} to a longer wavelength and an decrease in absorbance.(Quercetin-Pb II) complex shows a bathochromic shift (red shift) in band I with the formation of new band at 435nm.

3.4 Stoichiometric analysis

The stoichiometry of the solution complexes formed by the interaction of the metal ion with chelators were investigated by the method of continuous variation, this method is sometimes known as Job's method in section (2.4.2).

3.4.1. Stoichiometry of Nickel (II) – chelators complexe

By the use of continuous variation method, the stoichiometry of the complex between Nickel (II) and chelators were obtained by preparing a series of solutions of Nickel (II) and chelators with total concentration of ($4x10^{-4}$M with Catechin and Vitamin C) and ($4x10^{-5}$M with Curcumin and Quercetin) then recording the absorbance of each solution, the result obtained were presented in table (3.7) to (3.10)

Table (3.7): Absorbance of a mixture of Catechin – Ni (II) at 298K and λ_{max} = 279 nm.

No.	X_{Ni}	Abs
1	0.1	0.166
2	0.2	0.293
3	0.3	0.455
4	0.4	0.601
5	0.5	0.735
6	0.6	0.685
7	0.7	0.609
8	0.8	0.513
9	0.9	0.330

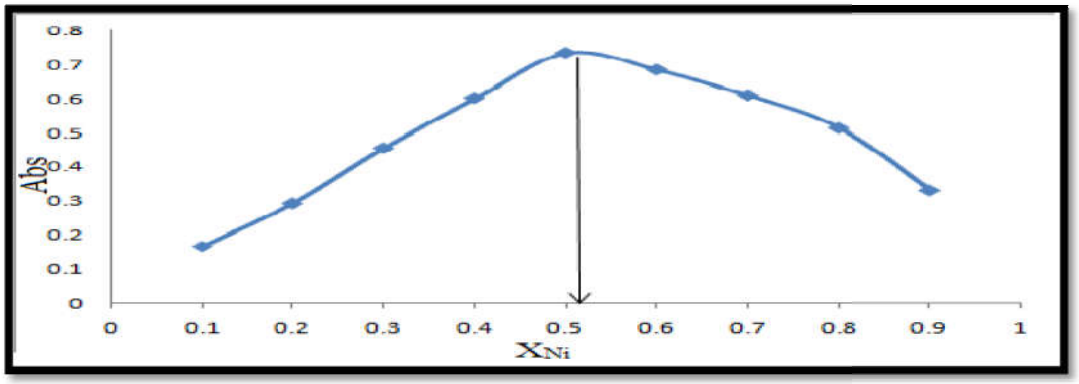


Figure (3.14): Job's plot for the composition of Ni (II) - Catechin complex at λ_{max} = 279nm.

Table (3.8): Absorbance of a mixture of Curcumin – Ni (II) at 298K and λ_{max} = 430 nm

No.	X_{Ni}	Abs
1	0.1	0.058
2	0.2	0.133
3	0.3	0.376
4	0.4	0.705
5	0.5	1.009
6	0.6	0.934
7	0.7	0.777
8	0.8	0.540
9	0.9	0.220

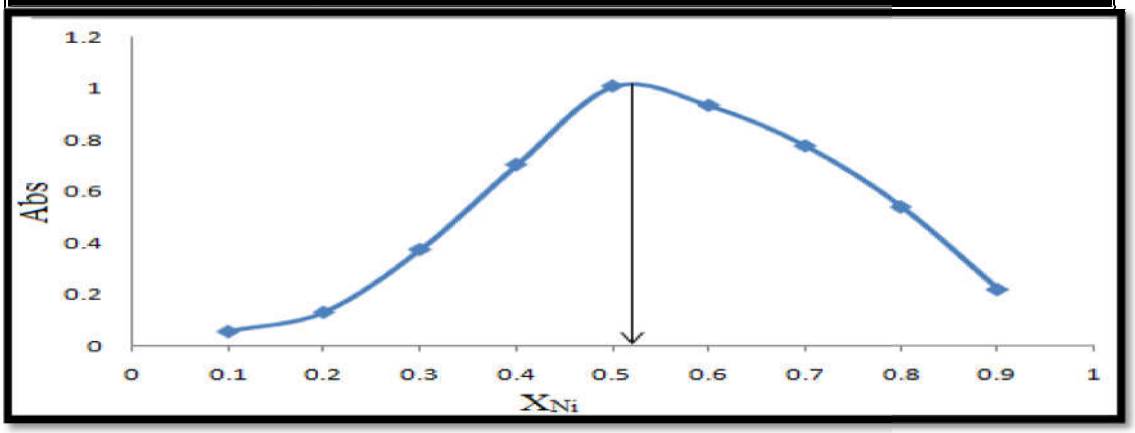


Figure (3.15): Job's plot for the composition of Ni (II) - Curcumin complex at λ_{max} = 430nm.

Table (3.9): Absorbance of a mixture of Vitamin C – Ni (II) at 298K and λmax = 261 nm

No.	X_{Ni}	Abs
1	0.1	0.498
2	0.2	0.808
3	0.3	1.130
4	0.4	1.470
5	0.5	1.640
6	0.6	1.930
7	0.7	1.530
8	0.8	0.910
9	0.9	0.770

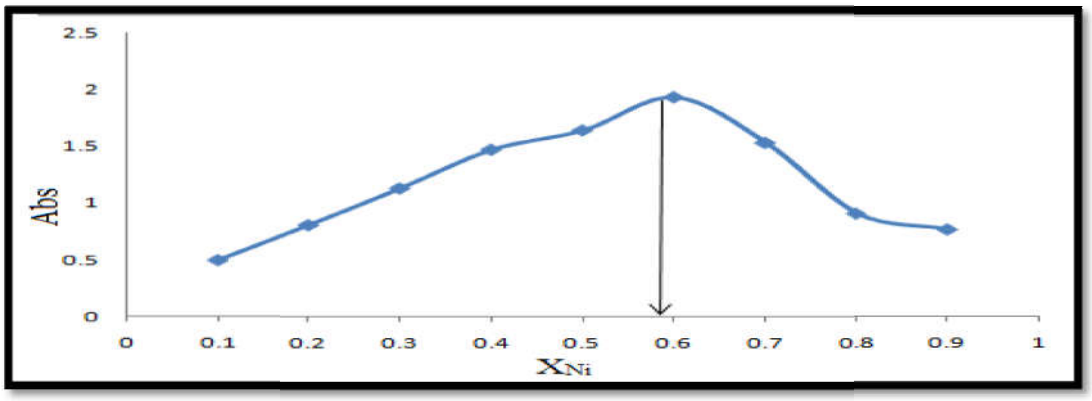


Figure (3.16): Job's plot for the composition of Ni (II) - VitaminC complex at λ_{max} = 261nm.

Table (3.10): Absorbance of a mixture of Quercetin – Ni (II) at 298K and λmax =433 nm

No.	X_{Ni}	Abs
1	0.1	0.107
2	0.2	0.135
3	0.3	0.161
4	0.4	0.178
5	0.5	0.200
6	0.6	0.170
7	0.7	0.145
8	0.8	0.121
9	0.9	0.113

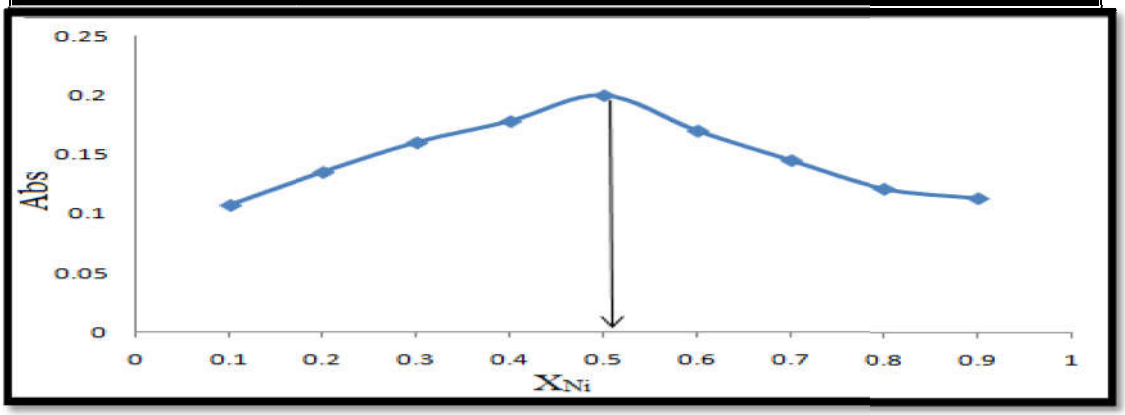


Figure (3.17): Job's plot for the composition of Ni (II) - Quercetin complex at λ_{max} = 433nm.

As it is evident from Figure (3.14) to (3.17), Job's plot implies that the stoichiometric ratio of Nickel (II) – chelators complexes were (1:1) for: Ni(II) – Catechin , Ni (II) - Curcumin , Ni (II) - Vitamin C and Ni (II) – Quercetin.

3.4.2. Stoichiometry of Cadimum (II) – chelators complexes

By the use of continuous variation method, the stoichiometry of the complex between Cadimum (II) and chelators were obtained by preparing a series of solutions of Cadimum (II) and chelators with total concentration of ($4x10^{-4}$M with Catechin and Vitamin C),($4x10^{-5}$M with Curcumin) and recording the absorbance of each solution, the result obtained were presented in table (3.11) to (3.13)

Table (3.11): Absorbance of a mixture of Catechin–Cd (II) at 298K and λ_{max} = 279 nm

No.	X_{Cd}	Abs
1	0.1	0.146
2	0.2	0.302
3	0.3	0.445
4	0.4	0.634
5	0.5	0.790
6	0.6	0.747
7	0.7	0.531
8	0.8	0.418
9	0.9	0.288

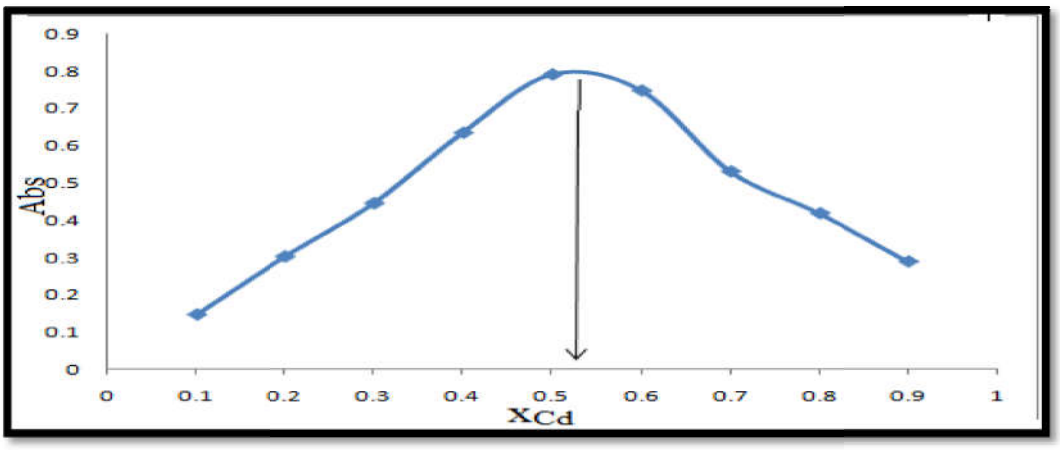


Figure (3.18): Job's plot for the composition of Cd (II) - Catechin complex at λ_{max} = 279nm.

Table (3.12): Absorbance of a mixture of Curcumin –Cd (II) at 298K and λ_{max} = 430 nm

No.	X_{Cd}	Abs
1	0.1	0.300
2	0.2	0.454
3	0.3	0.583
4	0.4	0.744
5	0.5	0.812
6	0.6	0.716
7	0.7	0.585
8	0.8	0.439
9	0.9	0.408

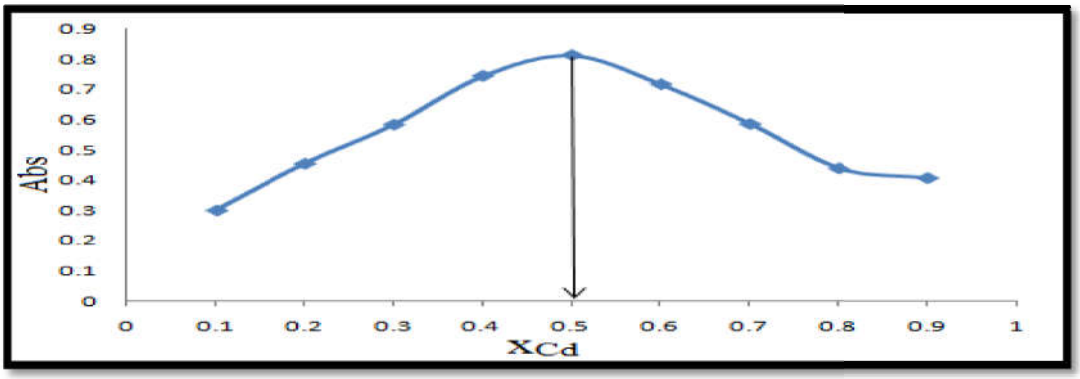


Figure (3.19): Job's plot for the composition of Cd (II) – Curcumin complex at λ_{max} = 430nm.

Table (3.13): Absorbance of a mixture of Vitamin C – Cd (II) at 298K and λ_{max} = 261 nm

No.	X_{Cd}	Abs
1	0.1	0.371
2	0.2	0.723
3	0.3	0.971
4	0.4	1.233
5	0.5	1.499
6	0.6	1.700
7	0.7	1.370
8	0.8	1.100
9	0.9	1.030

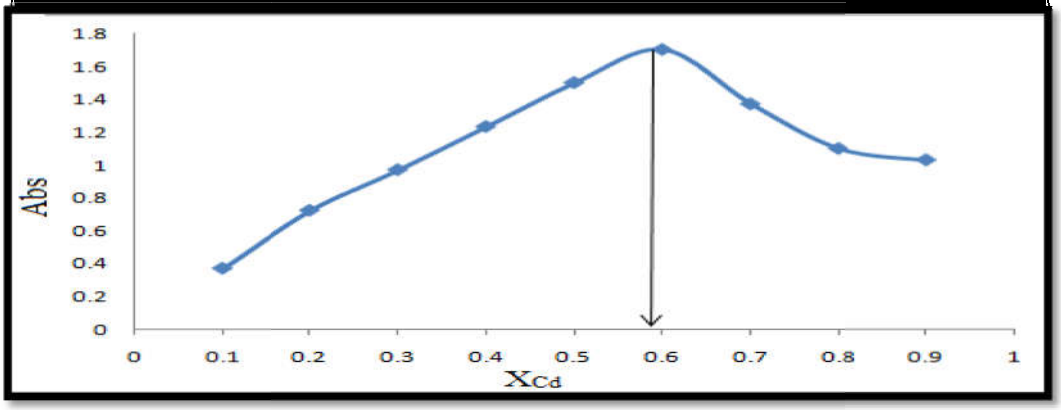


Figure (3.20): Job's plot for the composition of Cd (II) –Vitamin C complex at λ_{max} = 261nm.

As it is evident from Figure (3.18) to (3.20), Job's plot implies that the stoichiometric ratio of Cadimum (II) – chelators complexes were(1:1)for : Cd (II) – Catechin , Cd (II) - Curcumin and Cd (II) - Vitamin C .

3.4.3. Stoichiometry of Lead (II) – chelators complexes

By the use of continuous variation method, the stoichiometry of the complex between Lead (II) and chelators were obtained by preparing a series of solutions of Lead (II) and chelators with total concentration of ($4x10^{-4}$M with Catechin and Vitamin C),($4x10^{-5}$M with Curcumin and Quercetin) and recording the absorbance of each solution, the result obtained were presented in table (3.14) to (3.17)

Table (3.14): Absorbance of a mixture of Catechin – Pb (II) at 298K and λ_{max} = 279 nm

No.	X_{Pb}	Abs
1	0.1	0.174
2	0.2	0.301
3	0.3	0.458
4	0.4	0.609
5	0.5	0.733
6	0.6	0.721
7	0.7	0.531
8	0.8	0.275
9	0.9	0.198

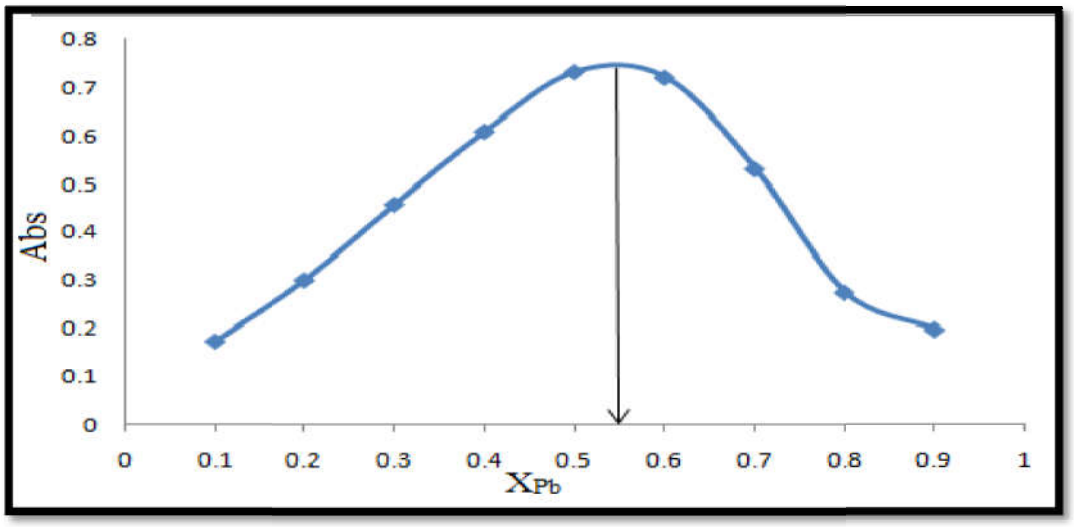


Figure (3.21): Job's plot for the composition of Pb (II) – Catechin complex at λ_{max} = 279nm.

Table (3.15): Absorbance of a mixture of Curcumin– Pb (II) at 298K and λ_{max} = 430 nm

No.	X_{Pb}	Abs
1	0.1	0.187
2	0.2	0.304
3	0.3	0.540
4	0.4	0.785
5	0.5	1.061
6	0.6	1.197
7	0.7	1.041
8	0.8	1.020
9	0.9	0.769

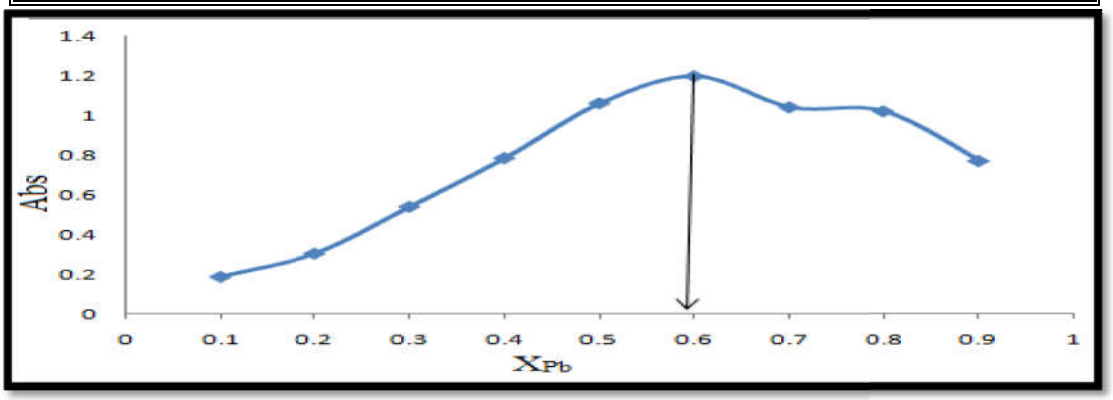


Figure (3.22): Job's plot for the composition of Pb (II) – Curcumin complex at λ_{max} = 430nm.

Table (3.16): Absorbance of a mixture of Vitamin C– Pb (II) at 298K and λ_{max} = 261nm

No.	X_{Pb}	Abs
1	0.1	0.36
2	0.2	0.68
3	0.3	1.14
4	0.4	1.42
5	0.5	2.28
6	0.6	2.58
7	0.7	2.29
8	0.8	2.01
9	0.9	1.36

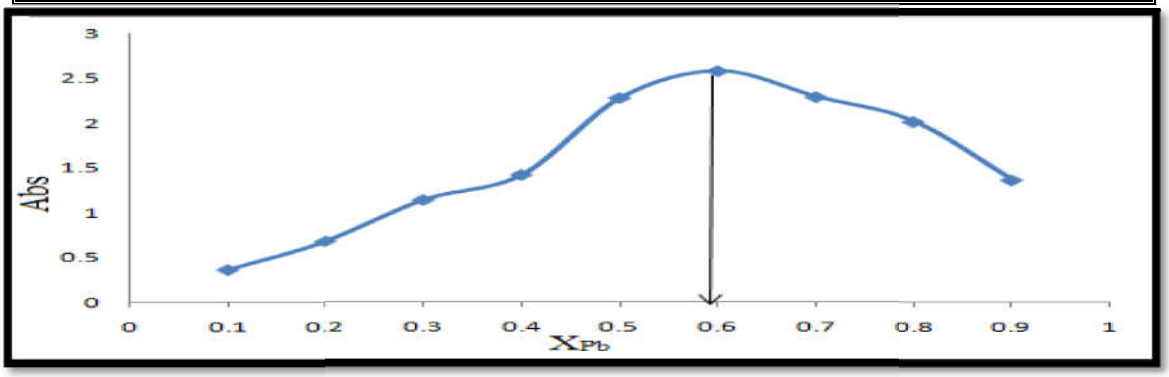


Figure (3.23): Job's plot for the composition of Pb (II) – Vitamin C complex at λ_{max} = 261nm

Table (3.17): Absorbance of a mixture of Quercetin – Pb (II) at 298K and λ_{max} =435 nm

No.	X_{Pb}	Abs
1	0.1	0.015
2	0.2	0.032
3	0.3	0.066
4	0.4	0.089
5	0.5	0.098
6	0.6	0.133
7	0.7	0.105
8	0.8	0.102
9	0.9	0.049

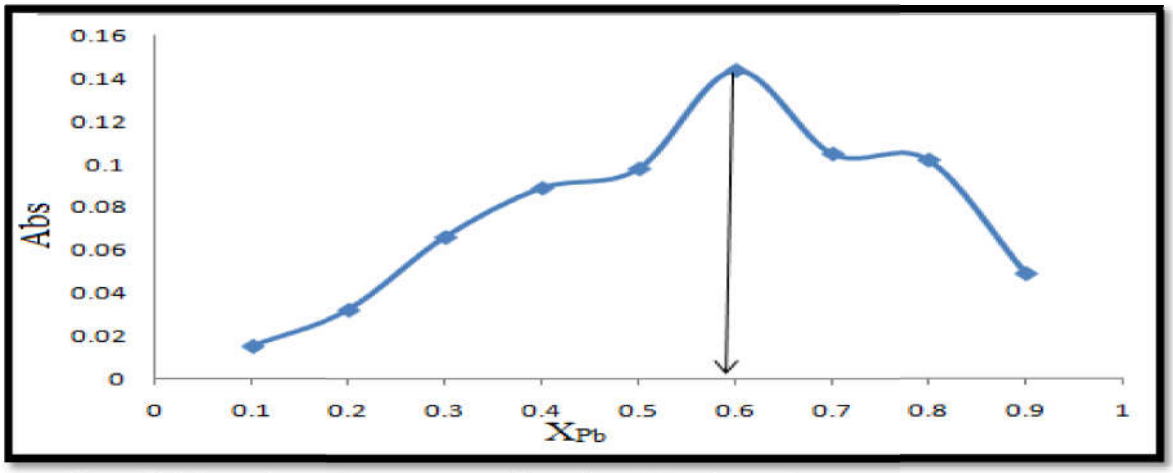


Figure (3.24): Job's plot for the composition of Pb (II) – Quercetin complex at λ_{max} = 435nm

As it is evident from Figure (3.21) to (3.24), Job's plot implies that the stoichiometric ratio of Lead (II) – chelators complexes were(1:1)for: Pb (II) – Catechin , Pb (II) - Curcumin , Pb (II) - Vitamin C and Pb (II) – Quercetin .

3.5. Determination of the stability constant (K_{eq})

The effect of temperature on the stability constant was studied and the results were tabulated in table (3.18)-(3.21).

Table (3.18): Stability constant at 293 K.

No	Metal-ligand	Am	As	α	$K_{eq}x10^4$
1	Ni-Catechin	1.209	0.811	0.3291	1.54
2	Ni-Curcumin	2.426	0.905	0.6269	2.37
3	Ni-Vitamin C	1.326	0.905	0.3174	1.69
4	Ni-Quercetin	0.155	0.261	-0.6838	9.00
5	Cd –Catechin	1.255	0.722	0.4247	0.79
6	Cd –Curcumin	2.259	1.530	0.3227	16.25
7	Cd -Vitamin C	2.457	1.630	0.3365	1.46
8	Cd-Quercetin				
9	Pb –Catechin	1.375	0.761	0.4465	0.69
10	Pb –Curcumin	2.094	1.030	0.5081	4.76
11	Pb -Vitamin C	2.290	1.591	0.3052	1.86
12	Pb –Quercetin	0.043	0.089	-1.0697	4.52

Table (3.19): Stability constant at 298 K.

No	Metal-ligand	Am	As	α	$K_{eq}x10^4$
1	Ni-Catechin	0.797	0.335	0.1127	1.47
2	Ni-Curcumin	2.422	1.430	0.4095	8.79
3	Ni-Vitamin C	2.462	1.621	0.3419	1.40
4	Ni-Quercetin	0.177	0.281	-0.5875	11.49
5	Cd -Catechin	1.218	0.767	0.3702	1.14
6	Cd -Curcumin	2.416	1.624	0.3294	15.54
7	Cd -Vitamin C	2.355	1.524	0.3528	1.29
8	Cd-Quercetin				
9	Pb -Catechin	1.294	0.824	0.3632	1.20
10	Pb -Curcumin	2.009	0.971	0.5171	4.51
11	Pb -Vitamin C	2.281	1.422	0.3765	1.09
12	Pb -Quercetin	0.051	0.108	-1.1176	4.23

Table (3.20): Stability constant at 303 K.

No	Metal-ligand	Am	As	α	$K_{eq}x10^4$
1	Ni-Catechin	0.788	0.368	0.1358	1.16
2	Ni-Curcumin	2.461	1.566	0.3636	1.20
3	Ni-Vitamin C	2.261	1.451	0.3586	1.24
4	Ni-Quercetin	0.186	0.281	-0.5107	14.44
5	Cd -Catechin	1.241	0.808	0.3483	1.34
6	Cd -Curcumin	2.412	1.591	0.3407	14.18
7	Cd -Vitamin C	2.397	1.511	0.3696	1.15
8	Cd-Quercetin				
9	Pb -Catechin	1.263	0.861	0.3190	1.67
10	Pb -Curcumin	1.937	0.929	0.5203	4.42
11	Pb -Vitamin C	2.145	1.062	0.5048	0.55
12	Pb -Quercetin	0.059	0.128	-1.1694	3.96

Table (3.21): Stability constant at 308 K.

No	Metal-ligand	Am	As	α	$K_{eq}x10^4$
1	Ni-Catechin	1.212	0.744	0.3861	1.02
2	Ni-Curcumin	2.389	1.565	0.3449	13.76
3	Ni-Vitamin C	2.389	1.522	0.3629	1.20
4	Ni-Quercetin	0.193	0.278	-0.4404	18.56
5	Cd –Catechin	1.181	0.787	0.3330	1.50
6	Cd –Curcumin	2.355	1.525	0.3524	13.03
7	Cd -Vitamin C	2.419	1.521	0.3716	1.13
8	Cd – Quercetin				
9	Pb -Catechin	1.216	0.858	0.2944	2.03
10	Pb -Curcumin	1.902	0.905	0.5241	4.32
11	Pb -Vitamin C	2.222	1.044	0.5301	0.41
12	Pb -Quercetin	0.078	0.172	-1.2051	3.79

Table(3:22) Equilibrium constant for Ni II with the four antioxidants at four temperature

Temp (K)	$K_{eq}(mol^{-1}.L)x10^4$			
	(1:1) Ni-Catechin	(1:1) Ni-Curcumin	(1:1) Ni-Vitamin C	(1:1) Ni-Quercetin
293	1.50	2.3	1.69	9.0
298	1.47	8.8	1.40	11.5
303	1.16	12.0	1.25	14.4
308	1.03	13.7	1.21	18.5

Table(3:23) Equilibrium constant for Cd II with the four antioxidants at four temperature

Temp (K)	$K_{eq}(mol^{-1}.L)x10^4$			
	(1:1) Cd-Catechin	(1:1) Cd-Curcumin	(1:1) Cd-Vitamin C	(1:1) Cd-Quercetin
293	0.79	16.25	1.46	
298	1.14	15.54	1.29	
303	1.34	14.18	1.15	
308	1.50	13.03	1.13	

Table(3:24) Equilibrium constant for Pb II with the four antioxidants at four temperature

Temp (K)	$K_{eq}(mol^{-1}.L)x10^4$			
	(1:1) pb-Catechin	(1:1) pb-Curcumin	(1:1) pb-Vitamin C	(1:1) pb-Quercetin
293	0.69	4.76	1.86	4.52
298	1.20	4.51	1.09	4.23
303	1.67	4.42	0.55	3.96
308	2.03	4.32	0.41	3.79

The equilibrium constant for the interaction of Ni II, Cd II and Pb II with four antioxidants were calculated by the application of equation (3.6) at four different degrees of temperature (293,298,303 and 308K) and the results were present in tables(3:22) , (3:23) and (3:24)

Table (3:22) shows an increase in the value of K_{eq} for Ni-Curcumin and Ni-Quercetin complexes with increase temperature that's means the complexes formed in higher concentration with the rise in temperature and the complexes formed were more stable, At the same time Ni-Catechin and Ni-Vitamin C be reversely, this may be due to a dissociation of the complex formed with increase in temperature. It is evident for the result that the stability of this antioxidant complexes with Ni were in this following order

Ni-Quercetin > Ni-Curcumin > Ni-VitaminC > Ni-Catechin

Table (3:23) shows an increase in the value of K_{eq} for Cd-Catechin complex with increase temperature that's means the complexes formed in higher concentration with the rise in temperature and the complexes formed were more stable, At the same time Cd-Curcumin and Cd-Vitamin C be reversed, this may be due to a dissociation of the complex formed with increase in temperature. It is evident for the result that the stability of this antioxidant complexes with Cd were in this following order

Cd-Curcumin > Cd -VitaminC > Cd –Catechin

Table (3:24) shows an increase in the value of K_{eq} for Pb-Catechin complex with increase temperature that's means the complexes formed in higher concentration with the rise in temperature and the complexes formed were more stable, At the same time Pb-Curcumin, Pb-Vitamin C and Pb-Quercetin be reversed, this may be due to a dissociation of the complex formed with increase in temperature. It is evident for the result that the stability of this antioxidant complexes with Pb were in this following order

Pb-Curcumin > Pb-Quercetin > Pb-Catechin > Pb VitaminC

3.6 Thermodynamic parameters

3.6.1. Thermodynamic parameters for Nickel(II) chelators' complexes

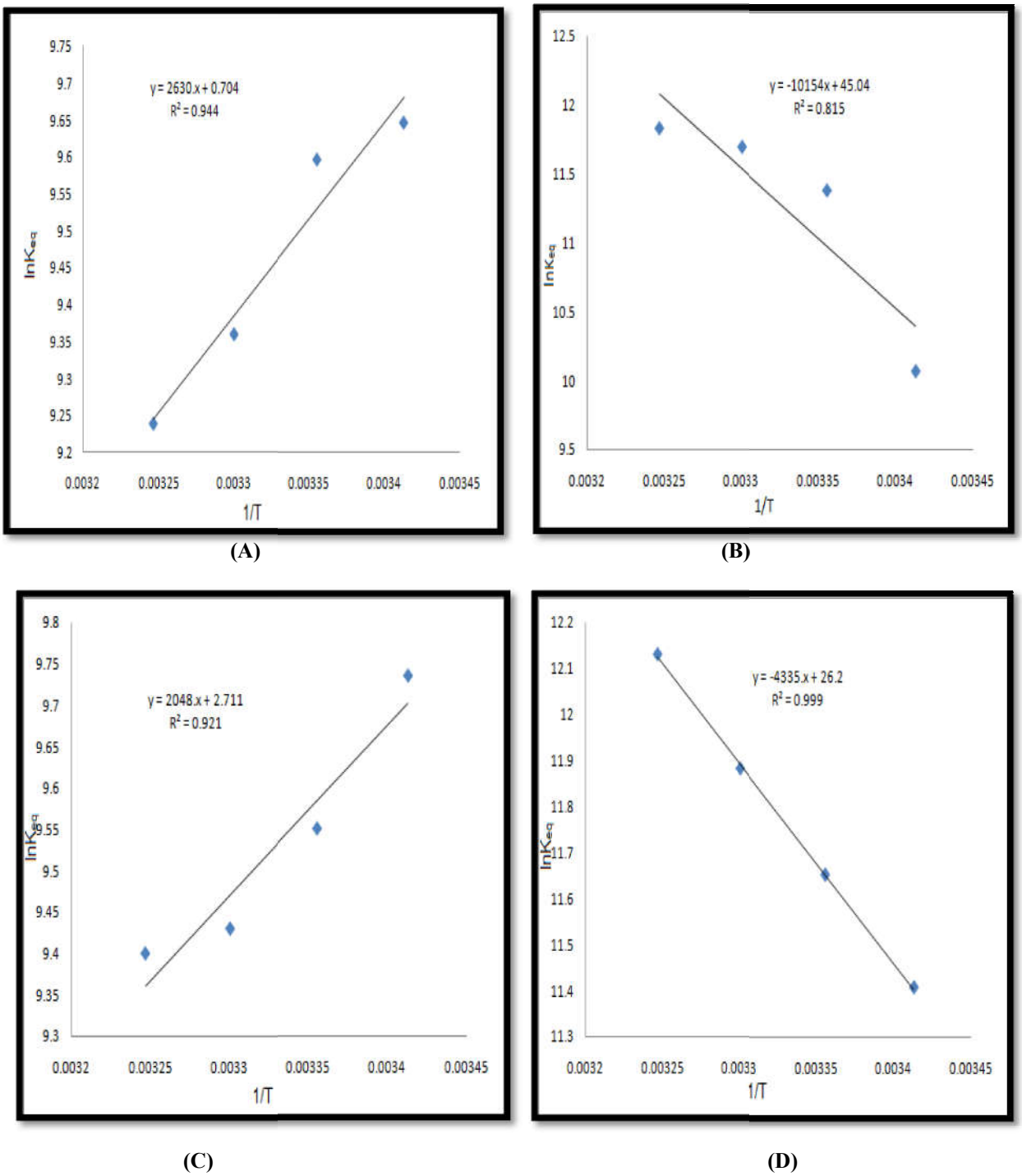


Figure (3.25): Vant Hoff plot for interaction of A) Catechin - Ni (II) complex at 279nm B)Curcumin - Ni (II) complex at 430nm, C) Vitamin C - Ni (II) complex at 261nm D) Quercetin - Ni (II) complex at 433nm.

Table (3.25): Thermodynamic parameters for Ni (II) - Catechin complex.

T(K)	$k_{eq}x10^4$	$\Delta G°$ (J.mole^{-1})	$\Delta H°$(J.mole^{-1})	$\Delta S°$ (J.mole^{-1}.K^{-1})
293	1.50	-23500.0	-21865.82	5.853056
298	1.47	-23777.5		
303	1.16	-23580.1		
308	1.10	-23658.9		

Table (3.26): Thermodynamic parameters for Ni (II) – Curcumin complex

T(K)	$k_{eq}x10^4$	$\Delta G°$ (J.mole^{-1})	$\Delta H°$(J.mole^{-1})	$\Delta S°$ (J.mole^{-1}.K^{-1})
293	2.3	-24541.1	84420.356	374.46256
298	8.8	-28207.1		
303	12.0	-29467.9		
308	13.7	-30299.8		

Table (3.27): Thermodynamic parameters for Ni (II) – Vitamin C complex

T(K)	$k_{eq}x10^4$	$\Delta G°$ (J.mole^{-1})	$\Delta H°$(J.mole^{-1})	$\Delta S°$ (J.mole^{-1}.K^{-1})
293	1.69	-23718.5	-17027.072	22.539254
298	1.40	-23664.3		
303	1.25	-23756.5		
308	1.21	-24071.7		

Table (3.28): Thermodynamic parameters for Ni (II) - Quercetin complex.

T(K)	$k_{eq}x10^4$	$\Delta G°$ (J.mole^{-1})	$\Delta H°$(J.mole^{-1})	$\Delta S°$ (J.mole^{-1}.K^{-1})
293	9.0	-27789.2	36041.19	217.8268
298	11.5	-28869.5		
303	14.4	-29934.9		
308	18.5	-31065.6		

3.6.2. Thermodynamic parameters for Cadimum(II) chelators' complexes

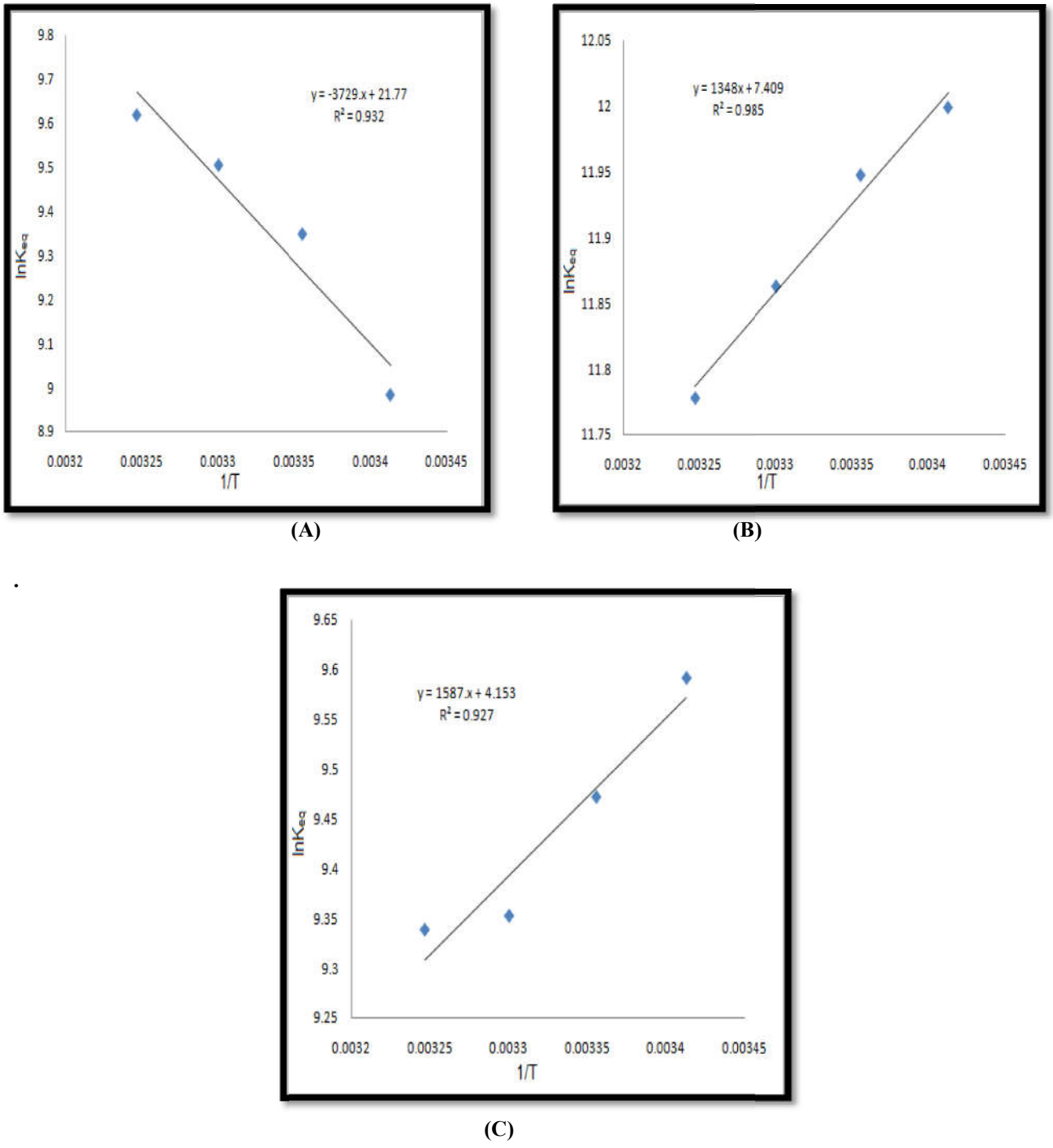


Figure (3.26): Vant Hoff plot for interaction of A) Catechin - Cd (II) complex at 279nm \B) Curcumin - Cd (II) complex at 430nm and C) Vitamin C - Cd (II) complex at 261nm

Table (3.29): Thermodynamic parameters for Cd (II) - Catechin complex.

T(K)	$k_{eq}x10^4$	$\Delta G°$ (J.mole^{-1})	$\Delta H°$(J.mole^{-1})	$\Delta S°$ (J.mole^{-1}.K^{-1})
293	0.79	-21884.8	31002.906	180.99578
298	1.14	-23161.7		
303	1.34	-23943.5		
308	1.50	-24628.7		

Table (3.30): Thermodynamic parameters for Cd (II) – Curcumin complex

T(K)	$k_{eq}x10^4$	$\Delta G°$ (J.mole^{-1})	$\Delta H°$(J.mole^{-1})	$\Delta S°$ (J.mole^{-1}.K^{-1})
293	16.25	-29229.5	-11207.272	61.598426
298	15.54	-29600.7		
303	14.18	-29884.2		
308	13.03	-30159.6		

Table (3.31): Thermodynamic parameters for Cd (II) – Vitamin C complex.

T(K)	$k_{eq}x10^4$	$\Delta G°$ (J.mole^{-1})	$\Delta H°$(J.mole^{-1})	$\Delta S°$ (J.mole^{-1}.K^{-1})
293	1.46	-23364.8	-13194.318	34.528042
298	1.29	-23468.0		
303	1.15	-23561.8		
308	1.13	-23914.6		

3.6.3. Thermodynamic parameters for Lead(II) chelators' complexes

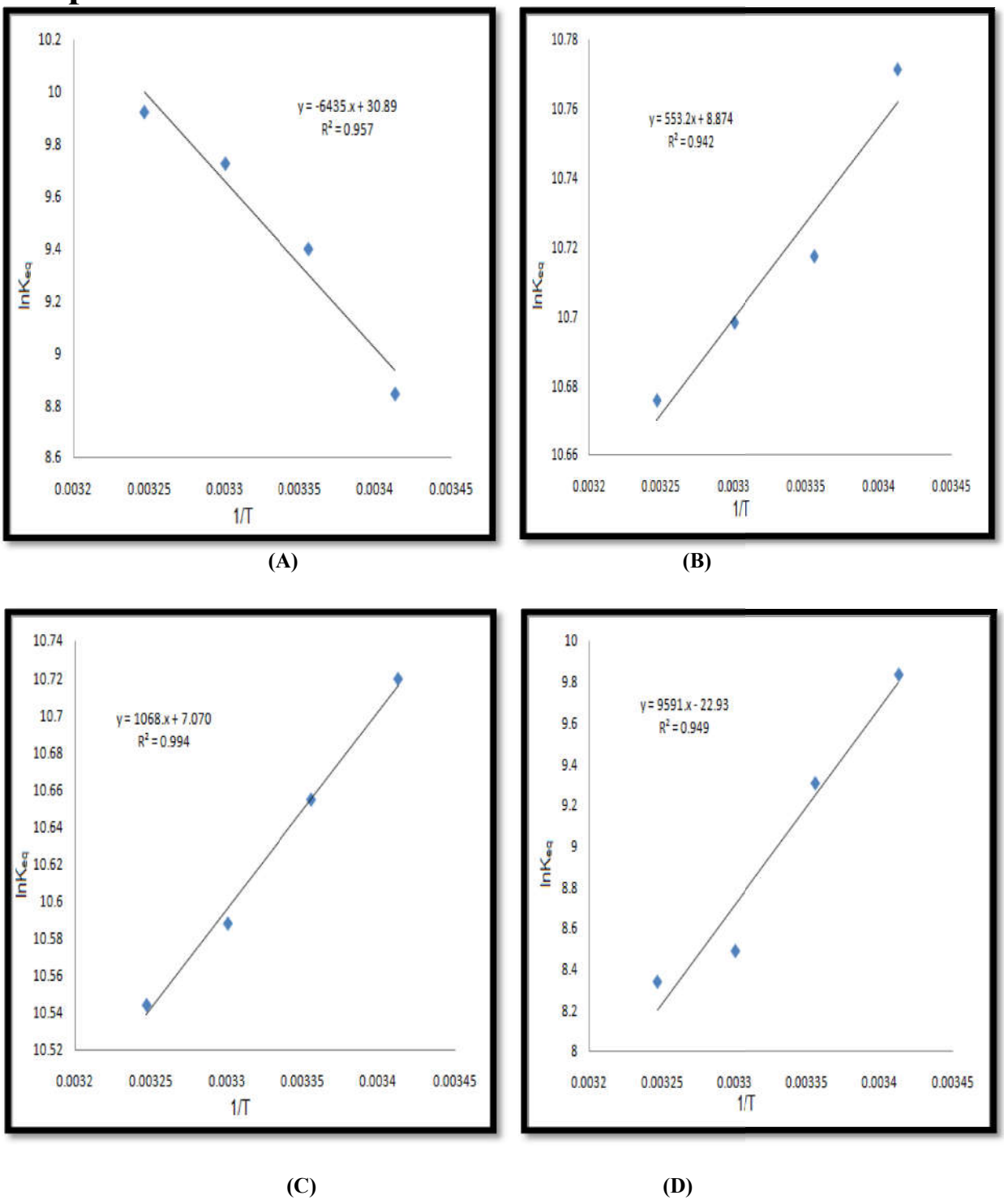


Figure (3.27): Vant Hoff plot for interaction of A) Catechin - Pb (II) complex at 279nm B) Curcumin - Pb(II) complex at 430nm , C) Vitamin C - Pb (II) complex at 261nm D) Quercetin - Pb (II) complex at 435nm.

Table (3.32): Thermodynamic parameters for Pb (II) – Catechin complex.

T(K)	$k_{eq}x10^4$	$\Delta G°$ (J.mole^{-1})	$\Delta H°$(J.mole^{-1})	$\Delta S°$ (J.mole^{-1}.K^{-1})
293	0.69	-21546.2	53500.59	256.81946
298	1.20	-23284.8		
303	1.67	-24497.0		
308	2.03	-25404.6		

Table (3.33): Thermodynamic parameters for Pb (II) – Curcumin complex.

T(K)	$k_{eq}x10^4$	$\Delta G°$ (J.mole^{-1})	$\Delta H°$(J.mole^{-1})	$\Delta S°$ (J.mole^{-1}.K^{-1})
293	4.76	-26238.7	-4599.3048	73.778436
298	4.51	-26552.9		
303	4.42	-26950.3		
308	4.32	-27337.5		

Table (3.34): Thermodynamic parameters for Pb (II) – Vitamin C complex.

T(K)	$k_{eq}x10^4$	$\Delta G°$ (J.mole^{-1})	$\Delta H°$(J.mole^{-1})	$\Delta S°$ (J.mole^{-1}.K^{-1})
293	1.86	-26112.0	-8879.352	58.77998
298	1.09	-26397.3		
303	0.55	-26672.6		
308	0.41	-27000.8		

Table (3.35): Thermodynamic parameters for Pb (II) - Quercetin complex.

T(K)	$k_{eq}x10^4$	$\Delta G°$ (J.mole^{-1})	$\Delta H°$(J.mole^{-1})	$\Delta S°$ (J.mole^{-1}.K^{-1})
293	4.52	-23953.6	-79739.574	-190.64002
298	4.23	-23053.1		
303	3.96	-21382.1		
308	3.79	-21350.9		

To explain the thermodynamic properties for the prepared complexes one can classified thats complexes to three groups depended on the similarity in thermodynamic parameters.

Table(3.36)classification of ligind-metal depend on similarity of thmodynamic parameter

Group I	Group II	Group III
VitaminC-Ni	Catechin-Pb	Quercetin-Pb
VitaminC-Cd	Catechin-Cd	
VitaminC-Pb	Quercetin-Ni	
Catecin-Ni	Curcumin-Ni	
Quercetin-Pb		
Curcumin-Pb		
Curcumin-Cd		

The values of their equilibrium constant (K_{eq}) were decrease with an increase in temperature that's mean the complexes are less stable in higher temperature ,and the values increase with increases temperature that means the complexes be more stable at higher temperature.

Gibbs free energy were negative for all groups. Negative values mean that the reaction would be favored and would release energy (spontaneous interaction). And it increases or decreases with the increase in temperature depending on the ligand type and the change in the enthalpy and entropy.

Enthalpy change and entropy change were the binding energy components during the complex formation, for group (I,III), shows that $\Delta H°$ were negative (exothermic process) which refers to an increase in binding interaction, increase binding produces a more negative enthalpy change. And in group(II) $\Delta H°$ were positive (endothermic process) which refers to an decrease in binding interaction.

Entropy change increases ΔS° positive for groups(I,II), confirming that the complex formation is entropically favourable. Expect group (III) ΔS° negative confirming that the complex formation is non entropically favourable.

3.7 Interaction kinetics

These include the investigation of how different experimental condition can influence the speed of a chemical reaction to yield information about the reaction mechanism, as well as the construction of a mathematical models that can characterizes of a chemical reaction.

In order to investigate the interaction kinetic of metal ion with chelators, the absorbance of complexes were recorded with time at a certain wave length, temperature and its stoichiometric ratio.

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

$$A+B \longrightarrow C+D$$

$$\mathbf{r = k\,[A]^a[B]^b}$$

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

3.7.1 First order reaction:

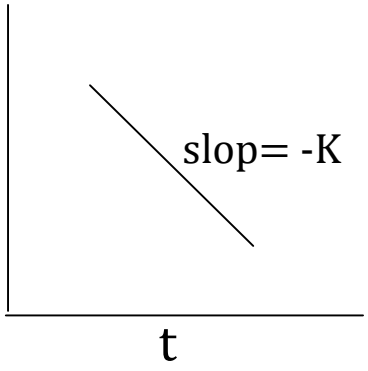
The first order rate law for the consumptive of a reactant A:

$$\frac{dA}{dt} = -K[c] \text{.....(3:10)}$$

$$ln\frac{[A]}{[A°]} = -Kt \text{ .....(3:11)}$$

$$ln\ A - ln\ A° = -Kt \text{ .....(3:12)}$$

$$ln\ A = -Kt + ln\ A° \text{ .....(3:13)}$$



A straight line is obtained when Ln A is plotted against t, the slop gives the rate constant –k and half-life; $t_{1/2} = \frac{0.693}{K}$

3.7.2 Second order reaction:

The second order rate law

$\frac{d[A]}{dt} = -K[c]^2$ .....(3:14)

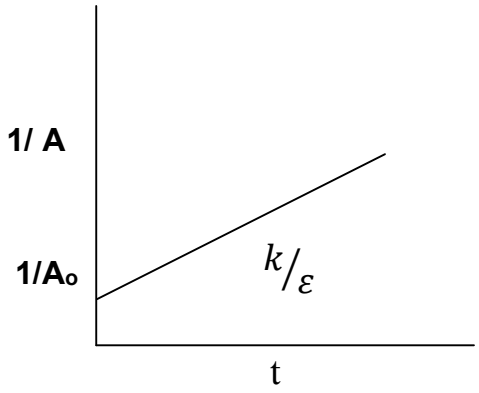
Of the integration

Abs $= \varepsilon cl$ [c] = [conc]

$C = \frac{Abs}{\varepsilon\, l}$

$\frac{1}{[A/\varepsilon l]} - \frac{1}{[A°/\varepsilon l]} = kt$

$\frac{1}{[A]} - \frac{1}{[A°]} = \frac{k}{\varepsilon}$ t .....(3:15)



A plot of $\frac{1}{[c]}$ against t gives a straight line and the slope of this line give $\frac{k}{\varepsilon}$

A= Absorbance of complex at time. **A°** = Absorbance of complex in time zero.

3.8 Reaction order and rate constant

In order to determine the order of the interaction of metal ions with antioxidants, the first order rate equation (3.13) and the second order rate equation (3.15) were applied for the interaction between Ni ,Cd and Pb ions with the four antioxidants.

3.8.1 First order Ni-antioxidants interaction at four temperature

Table (3-37): Absorbance at time t for Ni(II)-chelator complexes at 293K.

Time(min)	Catechin		Curcumin		Vitamin C		Quercetin	
	A	LnA	A	LnA	A	LnA	A	LnA
5	0.732	-0.31197	0.867	-0.14272	1.53	0.425268	0.271	-1.3356
10	0.728	-0.31745	0.856	-0.15548	1.522	0.420025	0.263	-1.34323
15	0.726	-0.32021	0.853	-0.15911	1.515	0.415415	0.261	-1.36258
20	0.725	-0.32158	0.851	-0.16134	1.503	0.407463	0.256	-1.4065
25	0.722	-0.32573	0.844	-0.16961	1.495	0.402126	0.245	-1.43129
30	0.720	-0.32850	0.842	-0.17198	1.488	0.397433	0.239	-1.46534
35	0.715	-0.33547	0.841	-0.17316	1.479	0.391366	0.231	-1.49611
40	0.714	-0.33687	0.840	-0.17435	1.465	0.381855	0.224	-1.51413
45	0.713	-0.33827	0.835	-0.18032	1.457	0.376380	0.22	-1.56065
50	0.712	-0.33968	0.831	-0.18633	1.448	0.370183	0.21	-1.57022
55	0.711	-0.34249	0.825	-0.19237	1.435	0.361165	0.208	-1.57022
60	0.711	-0.34249	0.821	-0.19723	1.43	0.357674	0.208	-1.57022

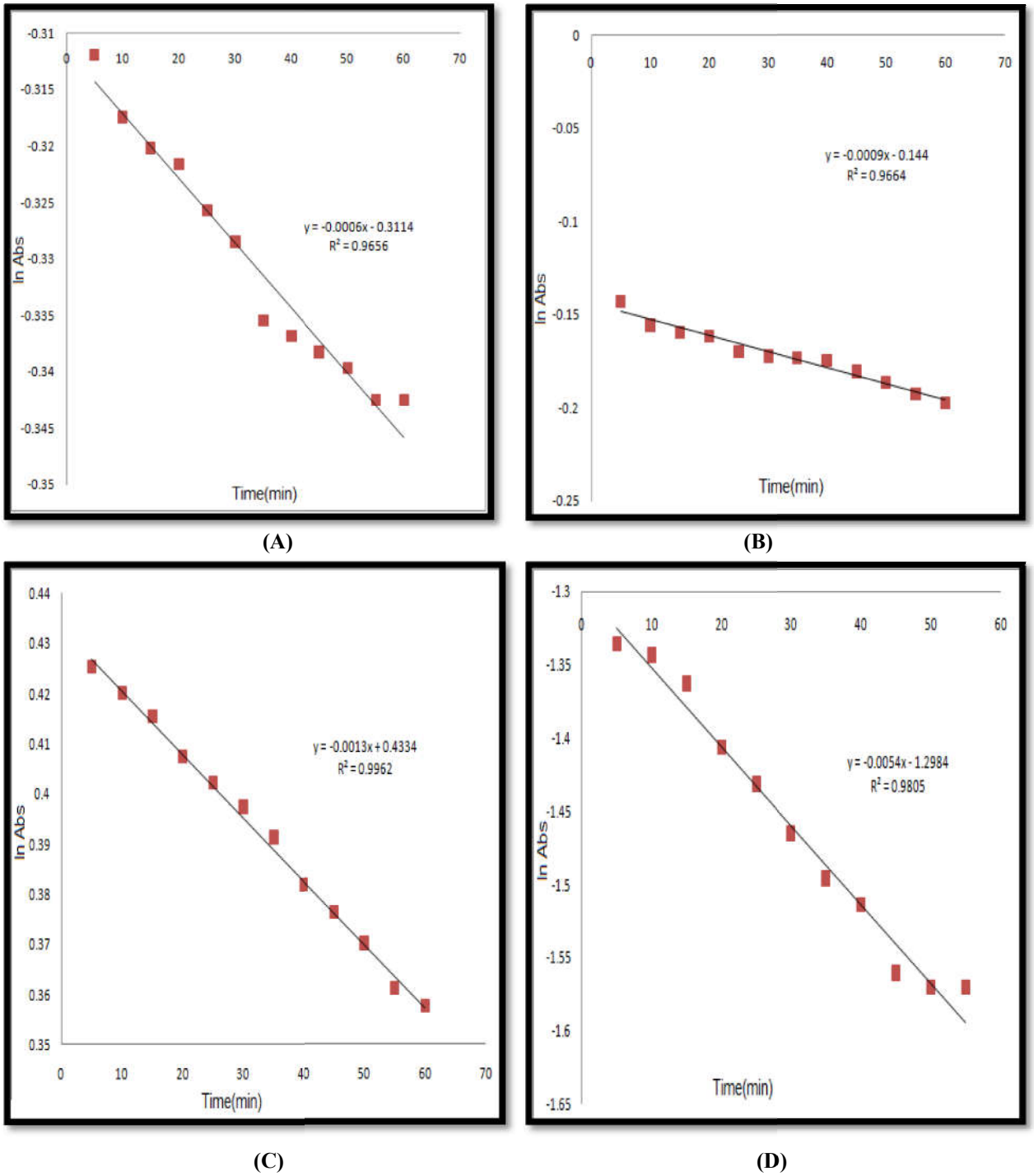


Figure (3.28): The application of the first order reaction equation for complex of Ni (II)-chelator at 293K temperatures: A) Catechin B) Curcumin C) Vitamin C D) Quercetin

Table (3.38): Absorbance at time t for Ni(II)-chelator complexes at 298K.

Time(min)	Catechin		Curcumin		Vitamin C		Quercetin	
	A	LnA	A	lnA	A	lnA	A	lnA
5	0.716	-0.33408	0.818	-0.20089	1.918	0.651283	0.172	-1.76026
10	0.714	-0.33687	0.817	-0.20212	1.885	0.633928	0.168	-1.78379
15	0.713	-0.33827	0.812	-0.20825	1.879	0.63074	0.16	-1.83258
20	0.711	-0.34249	0.810	-0.21072	1.853	0.616806	0.159	-1.83885
25	0.708	-0.34531	0.807	-0.21443	1.85	0.615186	0.157	-1.85151
30	0.707	-0.34672	0.796	-0.22816	1.841	0.610309	0.155	-1.86433
35	0.705	-0.34956	0.793	-0.23193	1.828	0.603222	0.152	-1.88387
40	0.704	-0.35098	0.791	-0.23446	1.822	0.599935	0.151	-1.89048
45	0.703	-0.3524	0.788	-0.23826	1.79	0.582216	0.147	-1.91732
50	0.701	-0.35525	0.785	-0.24207	1.788	0.581098	0.130	-2.04022
55	0.699	-0.3581	0.781	-0.24718	1.782	0.577736	0.127	-2.06357
60	0.698	-0.35954	0.779	-0.24974	1.779	0.576051	0.125	-2.07944

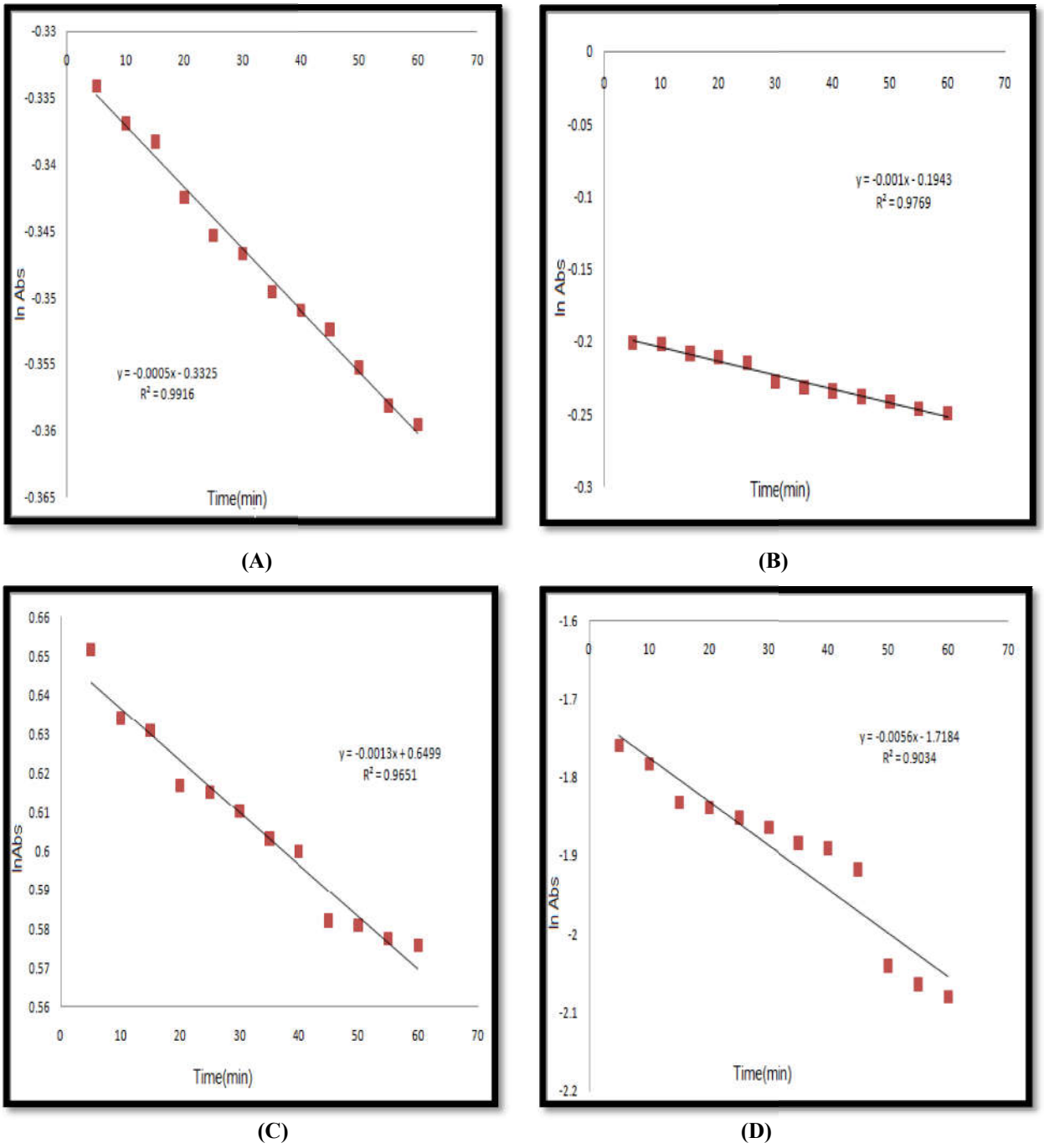


Figure (3.29): The application of the first order reaction equation for complex of Ni (II)-chelator at 298K temperatures: A) **Catechin B) Curcumin C) Vitamin C D) Quercetin**

Table (3.39): Absorbance at time t for Ni(II)-chelator complexes at 303K

Time(min)	Catechin		Curcumin		Vitamin C		Quercetin	
	A	LnA	A	LnA	A	LnA	A	LnA
5	0.715	-0.33547	0.985	-0.01511	1.552	0.439544	0.257	-1.36258
10	0.715	-0.33547	0.971	-0.02943	1.545	0.435024	0.256	-1.39837
15	0.713	-0.33827	0.965	-0.03563	1.544	0.434376	0.247	-1.41882
20	0.712	-0.33968	0.959	-0.04186	1.537	0.429832	0.242	-1.41882
25	0.711	-0.34108	0.946	-0.05551	1.535	0.42853	0.242	-1.42712
30	0.710	-0.34249	0.939	-0.06294	1.533	0.427227	0.24	-1.45672
35	0.709	-0.3439	0.929	-0.07365	1.524	0.421338	0.233	-1.50959
40	0.709	-0.3439	0.921	-0.0823	1.51	0.41211	0.221	-1.56065
45	0.708	-0.34531	0.918	-0.08556	1.502	0.406798	0.211	-1.58475
50	0.707	-0.34672	0.915	-0.08883	1.494	0.401457	0.205	-1.6874
55	0.706	-0.34814	0.902	-0.10314	1.487	0.396761	0.185	-1.6874
60	0.705	-0.34956	0.881	-0.1267	1.477	0.390013	0.185	-1.6874

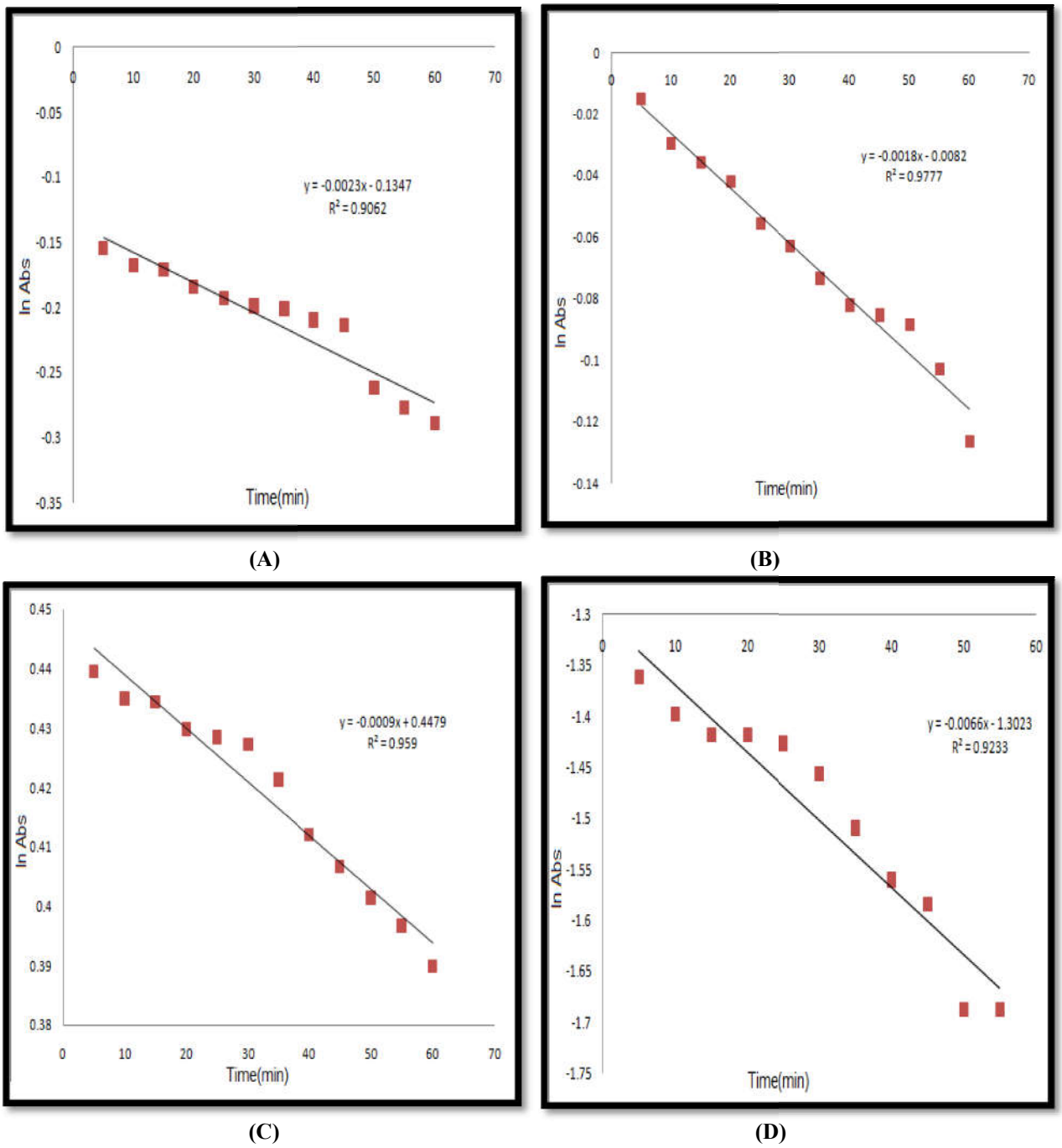


Figure (3.30): The application of the first order reaction equation for complex of Ni (II)-chelator at 303K temperatures: A) Catechin B) Curcumin C) Vitamin C D)Quercetin

Table (3.40): Absorbance at time t for Ni(II)-chelator complexes at 308K

Time(min)	Catechin		Curcumin		Vitamin C		Quercetin	
	A	LnA	A	LnA	A	LnA	A	LnA
5	0.707	-0.34672	0.857	-0.15432	1.882	0.632335	0.261	-1.34323
10	0.706	-0.34814	0.846	-0.16724	1.879	0.63074	0.258	-1.3548
15	0.706	-0.34814	0.843	-0.17079	1.875	0.628609	0.249	-1.3903
20	0.705	-0.34956	0.832	-0.18392	1.87	0.625938	0.235	-1.44817
25	0.705	-0.34956	0.825	-0.19237	1.868	0.624868	0.231	-1.46968
30	0.705	-0.34956	0.82	-0.19845	1.867	0.624333	0.217	-1.52786
35	0.704	-0.35098	0.818	-0.20089	1.865	0.623261	0.215	-1.53712
40	0.703	-0.3524	0.811	-0.20949	1.865	0.623261	0.213	-1.54646
45	0.701	-0.35525	0.808	-0.21319	1.862	0.621651	0.194	-1.6399
50	0.701	-0.35525	0.77	-0.26136	1.859	0.620039	0.181	-1.70926
55	0.700	-0.35667	0.758	-0.27707	1.855	0.617885	0.179	-1.72037
60	0.700	-0.35667	0.749	-0.28902	1.854	0.617345	0.171	-1.77196

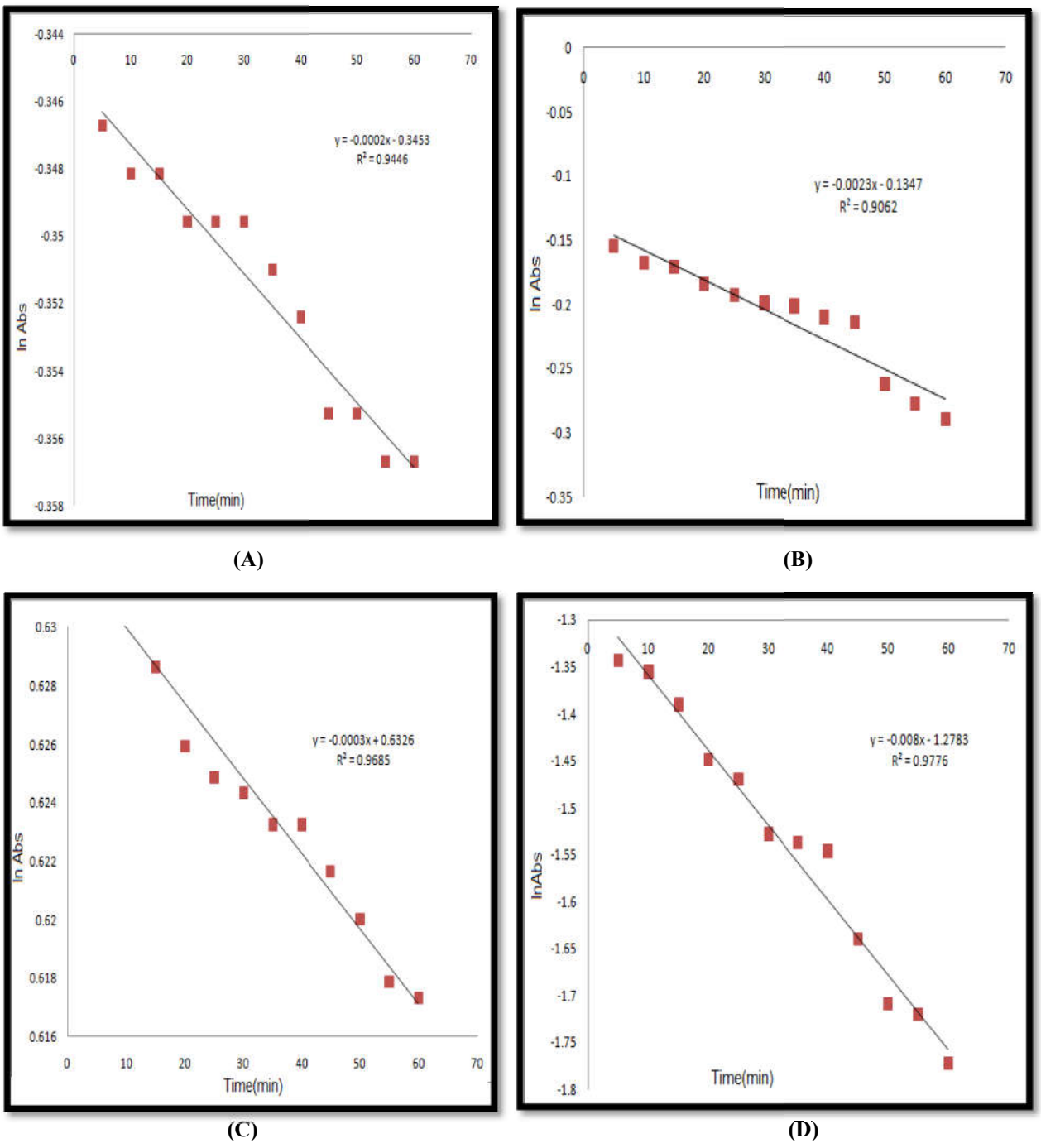


Figure (3.31): The application of the first order reaction equation for complex of Ni (II)-chelator at 308K temperatures: A) Catechin B) Curcumin C) Vitamin C D) Quercetin

Table (3-41): Rate constant and R^2 of the first order reaction for complex [Ni (II) – Catechin] at 293,298,303,308K temperature.

Complex	*temp*	*k (min^{-1})*	*R^2*
Cat-Ni	293	$6x10^{-4}$	0.9656
Cat-Ni	298	$5x10^{-4}$	0.9916
Cat-Ni	303	$3x10^{-4}$	0.9851
Cat-Ni	308	$2x10^{-4}$	0.9446

Table (3.42): Rate constant and R^2 of the first order reaction for complex [Ni (II) – Curcumin] at 293,298,303,308K temperature.

Complex	*temp*	*k(min^{-1})*	*R^2*
Cur-Ni	293	$0.9x10^{-3}$	0.9664
Cur-Ni	298	$1.0x10^{-3}$	0.9769
Cur-Ni	303	$1.8x10^{-3}$	0.9777
Cur-Ni	308	$2.3x10^{-3}$	0.9062

Table (3.43): Rate constant and R^2 of the first order reaction for complex [Ni (II) – Vitamin C] at 293,298,303,308K temperature.

Complex	*temp*	*k(min^{-1})*	*R^2*
VitC-Ni	293	$13x10^{-4}$	0.9962
VitC-Ni	298	$13x10^{-4}$	0.9651
VitC-Ni	303	$9.0x10^{-4}$	0.9590
VitC-Ni	308	$3.0x10^{-4}$	0.9685

Table (3-44): Rate constant and R^2 of the first order reaction for complex [Ni (II) – Quercetin] at93,298,303,308K temperature.

complex	*temp*	*k(min^{-1})*	*R^2*
Qur-Ni	293	$5.4x10^{-3}$	0.9805
Qur-Ni	298	$5.6x10^{-3}$	0.9034
Qur-Ni	303	$6.6x10^{-3}$	0.9233
Qur-Ni	308	$8.0x10^{-3}$	0.9776

3.8.2 First order Cd-antioxidants interaction at four temperature

Table (3.45): Absorbance at time t for Cd(II)-chelator complexes at 293K

Time(min)	Catechin		Curcumin		Vitamin C	
	A	lnA	A	lnA	A	lnA
5	0.731	-0.31334	0.733	-0.31061	1.659	0.506215
10	0.730	-0.31471	0.731	-0.31334	1.657	0.505009
15	0.729	-0.31608	0.729	-0.31608	1.653	0.502592
20	0.727	-0.31883	0.727	-0.31883	1.651	0.501381
25	0.726	-0.32021	0.726	-0.32021	1.65	0.500775
30	0.726	-0.32021	0.720	-0.3285	1.649	0.500169
35	0.726	-0.32021	0.716	-0.33408	1.648	0.499562
40	0.725	-0.32158	0.712	-0.33968	1.646	0.498348
45	0.724	-0.32296	0.709	-0.3439	1.645	0.49774
50	0.723	-0.32435	0.702	-0.35382	1.642	0.495915
55	0.722	-0.32573	0.697	-0.36097	1.639	0.494086
60	0.722	-0.32573	0.691	-0.36962	1.638	0.493476

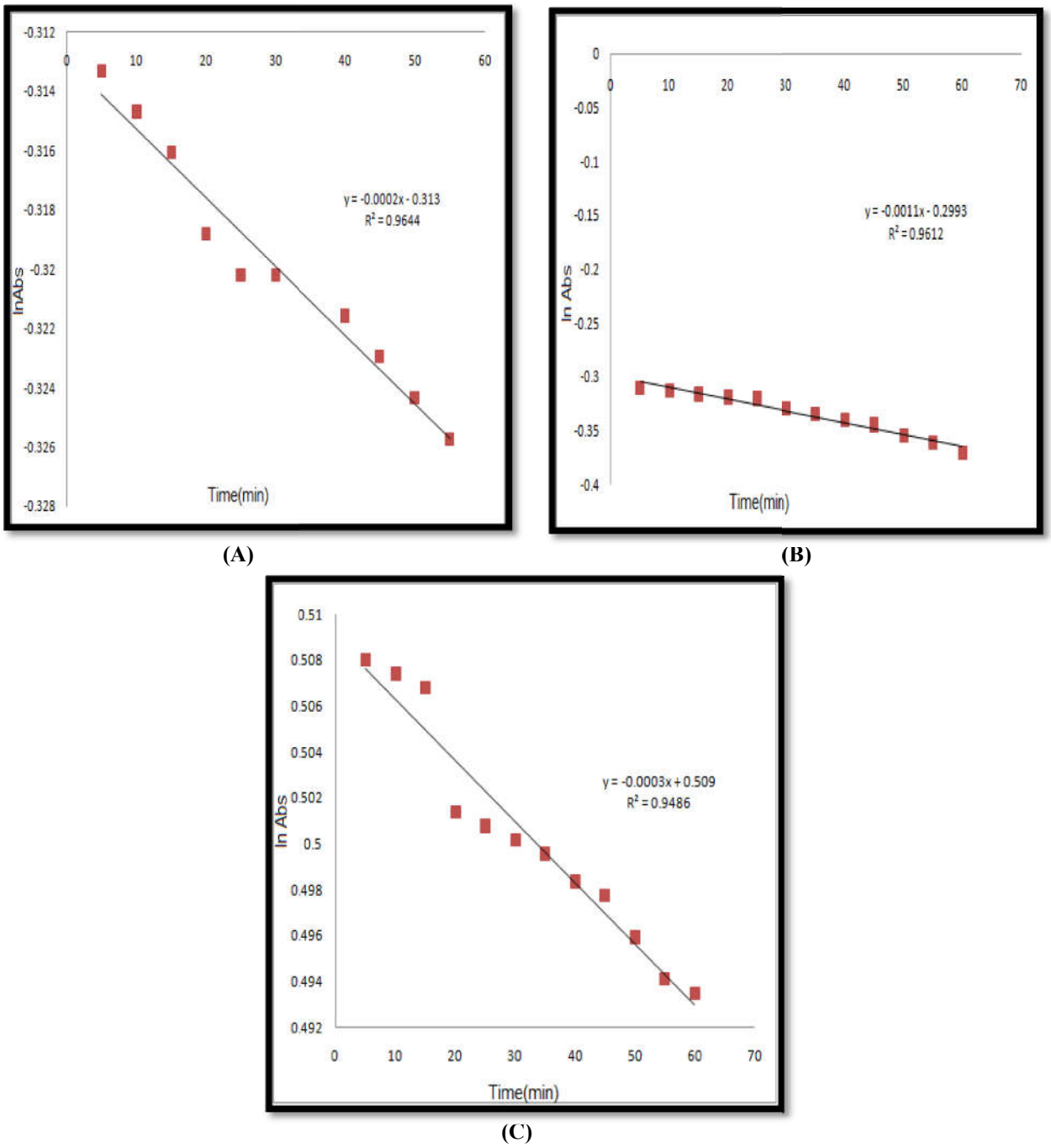
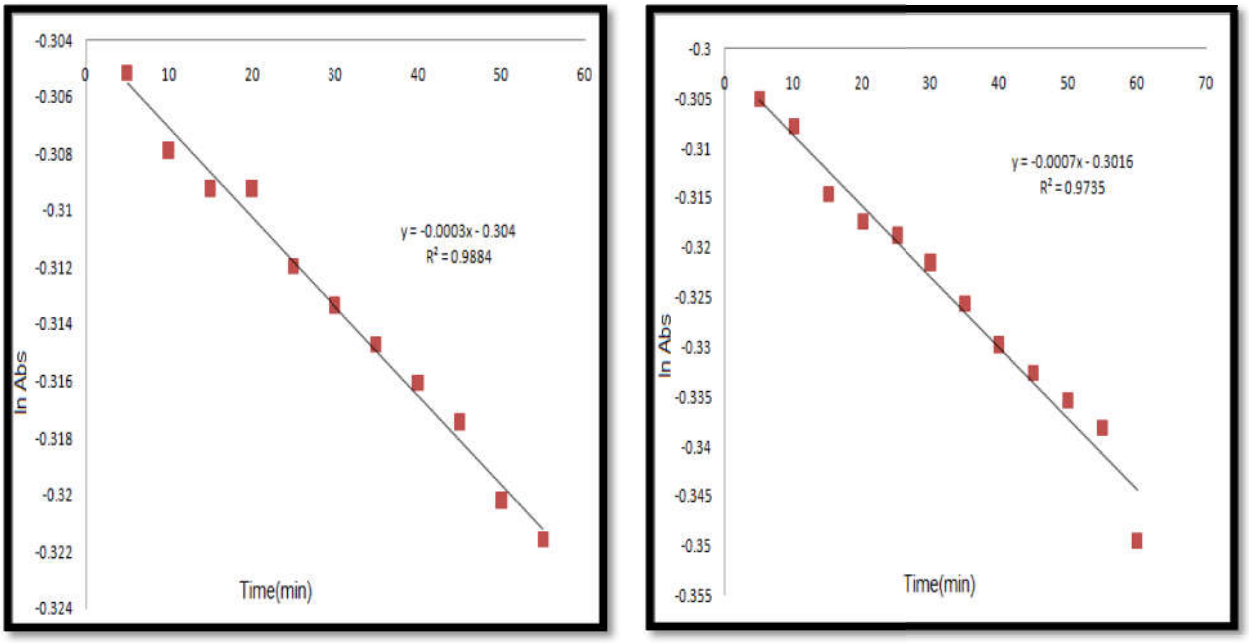


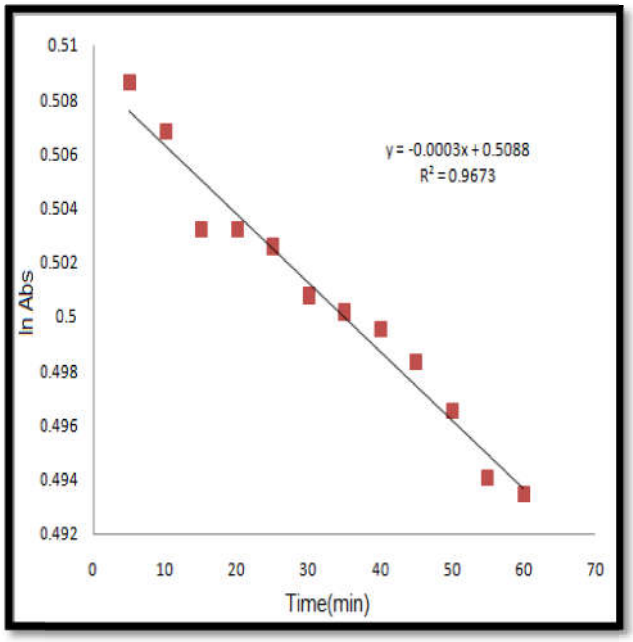
Figure (3.32): The application of the first order reaction equation for complex of Cd (II)-chelator at 293K temperatures: A) Catechin B) Curcumin C) Vitamin C

Table (3.46): Absorbance at time t for Cd(II)-chelator complexes at 298K

Time(min)	Catechin		Curcumin		Vitamin C	
	A	LnA	A	LnA	A	LnA
5	0.737	-0.30517	0.737	-0.30517	1.662	0.508022
10	0.735	-0.30788	0.735	-0.30788	1.661	0.50742
15	0.734	-0.30925	0.73	-0.31471	1.66	0.506818
20	0.734	-0.30925	0.728	-0.31745	1.651	0.501381
25	0.732	-0.31197	0.727	-0.31883	1.65	0.500775
30	0.731	-0.31334	0.725	-0.32158	1.649	0.500169
35	0.730	-0.31471	0.722	-0.32573	1.648	0.499562
40	0.729	-0.31608	0.719	-0.32989	1.646	0.498348
45	0.728	-0.31745	0.717	-0.33268	1.645	0.49774
50	0.726	-0.32021	0.715	-0.33547	1.642	0.495915
55	0.725	-0.32158	0.713	-0.33827	1.639	0.494086
60	0.725	-0.32158	0.705	-0.34956	1.638	0.493476



(A) **(B)**



(C)

Figure (3.33): The application of the first order reaction equation for complex of Cd (II)-chelator at 298K temperatures: A) Catechin B) Curcumin C) Vitamin C

Table (3.47): Absorbance at time t for Cd(II)-chelator complexes at 303K

Time(min)	Catechin		Curcumin		Vitamin C	
	A	LnA	A	LnA	A	LnA
5	0.736	-0.30653	0.736	-0.30653	1.495	0.402126
10	0.735	-0.30788	0.734	-0.30925	1.492	0.400118
15	0.734	-0.30925	0.734	-0.30925	1.49	0.398776
20	0.733	-0.31061	0.732	-0.31197	1.488	0.397433
25	0.731	-0.31334	0.731	-0.31334	1.487	0.396761
30	0.730	-0.31471	0.729	-0.31608	1.485	0.395415
35	0.730	-0.31471	0.728	-0.31745	1.484	0.394741
40	0.729	-0.31608	0.723	-0.32435	1.482	0.393393
45	0.728	-0.31745	0.721	-0.32712	1.478	0.39069
50	0.726	-0.32021	0.717	-0.33268	1.476	0.389336
55	0.722	-0.32573	0.712	-0.33968	1.475	0.388658
60	0.72	-0.3285	0.709	-0.3439	1.472	0.386622

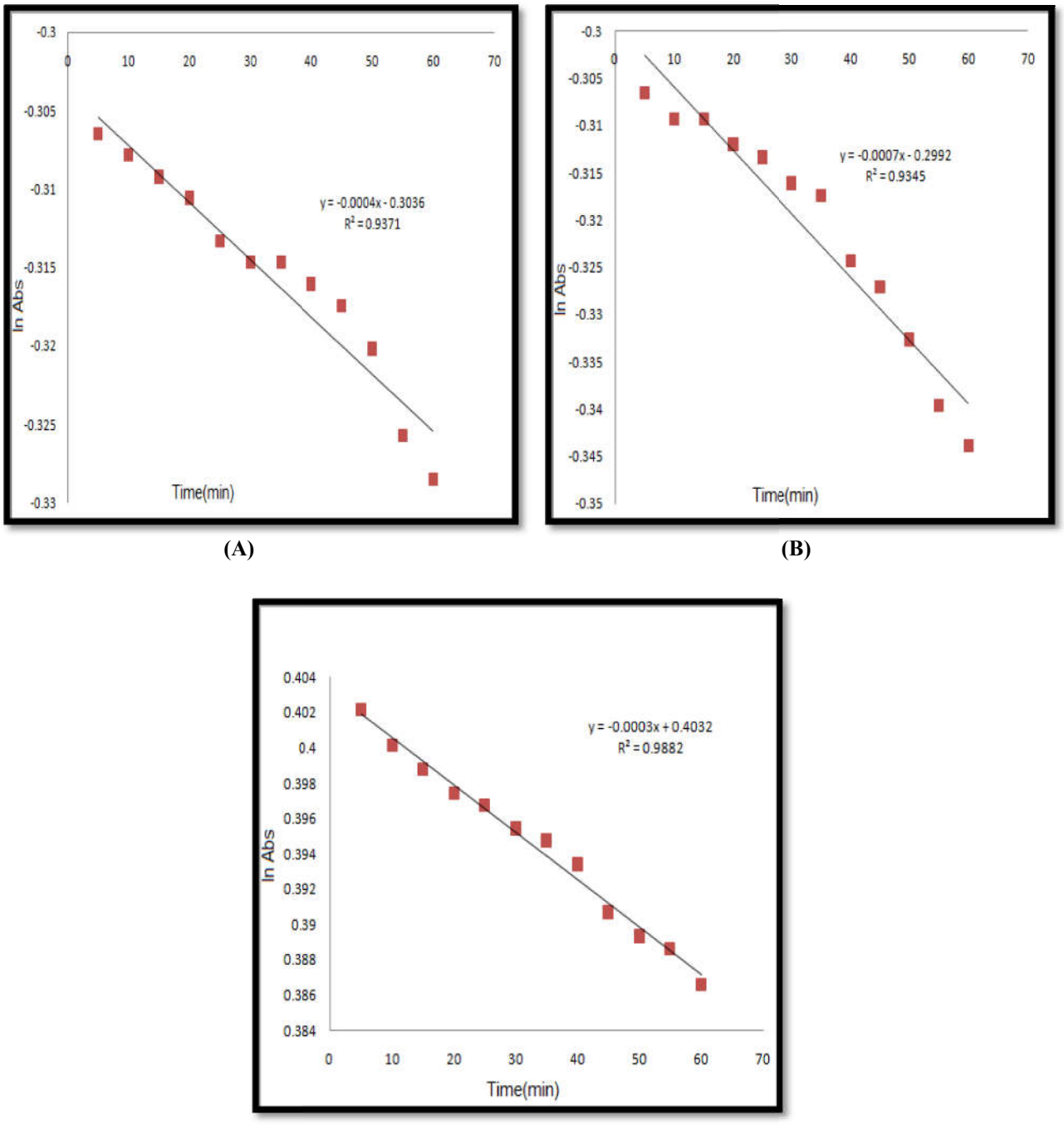


Figure (3.34): The application of the first order reaction equation for complex of Cd (II)-chelator at 303K temperatures: A) Catechin B) Curcumin C) Vitamin C

Table (3.48): Absorbance at time t for Cd(II)-chelator complexes at 308K

Time(min)	Catechin		Curcumin		Vitamin C	
	A	LnA	A	LnA	A	LnA
5	0.733	-0.31061	0.731	-0.31334	1.504	0.408128
10	0.728	-0.31745	0.73	-0.31471	1.502	0.406798
15	0.726	-0.32021	0.729	-0.31608	1.498	0.404131
20	0.725	-0.32158	0.728	-0.31745	1.496	0.402795
25	0.724	-0.32296	0.727	-0.31883	1.491	0.399447
30	0.724	-0.32296	0.725	-0.32158	1.489	0.398105
35	0.723	-0.32435	0.722	-0.32573	1.486	0.396088
40	0.722	-0.32573	0.72	-0.3285	1.485	0.395415
45	0.720	-0.3285	0.718	-0.33129	1.483	0.394067
50	0.718	-0.33129	0.716	-0.33408	1.481	0.392718
55	0.715	-0.33547	0.715	-0.33547	1.479	0.391366
60	0.712	-0.33968	0.712	-0.33968	1.477	0.390013

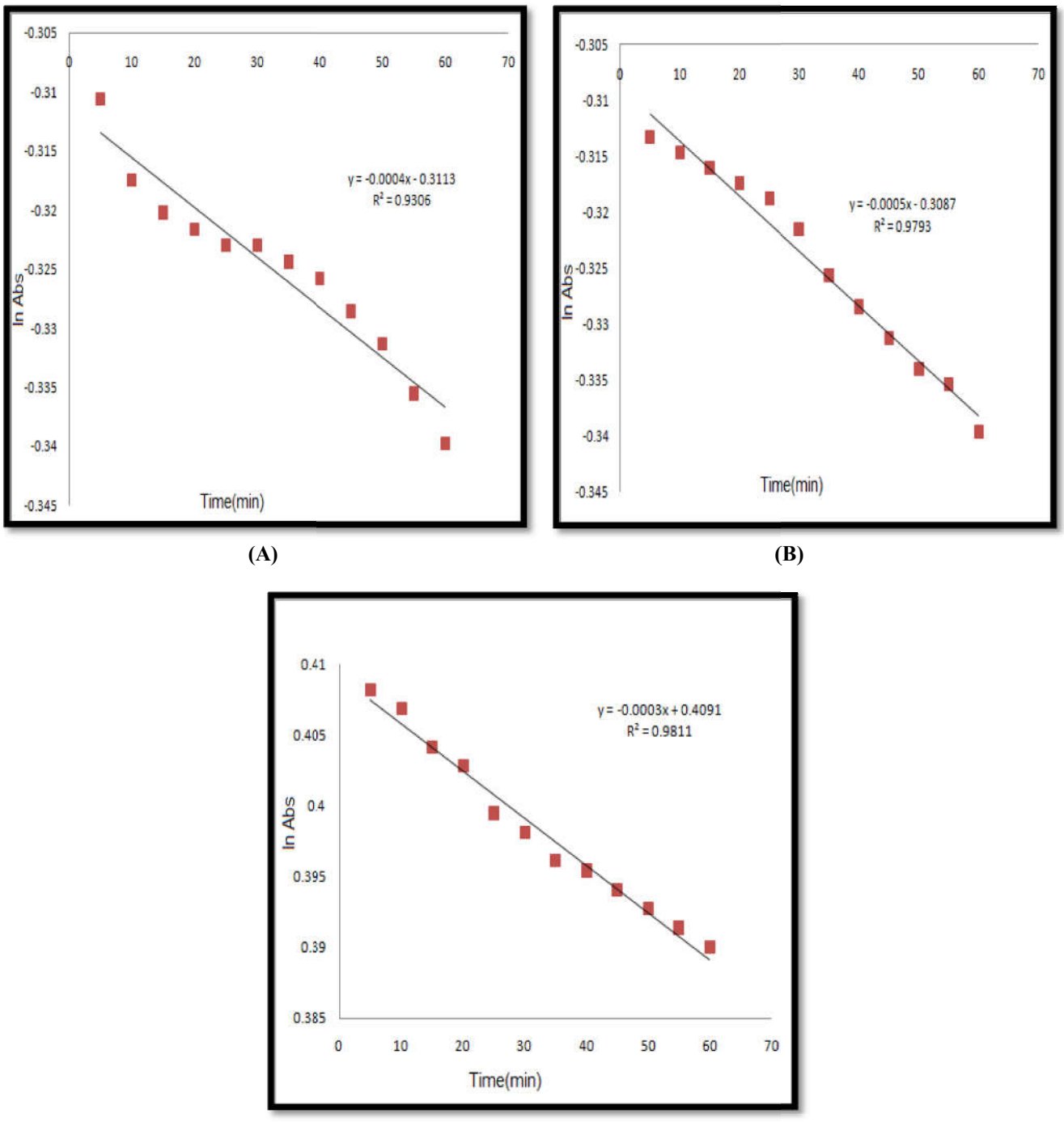


Figure (3.35): The application of the first order reaction equation for complex of Cd (II)-chelator at 308K temperatures: A) Catechin B) Curcumin C) Vitamin C

Table (3.49): Rate constant and R^2 of the first order reaction for complex [Cd (II) – Catechin] at 293,298,303,308K temperature.

Complex	*temp*	*k(min^{-1})*	*R^2*
Cat-Cd	293	$2x10^{-4}$	0.9644
Cat-Cd	298	$3x10^{-4}$	0.9884
Cat-Cd	303	$4x10^{-4}$	0.9371
Cat-Cd	308	$4x10^{-4}$	0.9306

Table (3.50): Rate constant and R^2 of the first order reaction for complex [Cd (II) – Curcumin] at 293,298,303,308K temperature.

complex	*temp*	*k(min^{-1})*	*R^2*
Cur-Cd	293	$11x10^{-4}$	0.9612
Cur-Cd	298	$7x10^{-4}$	0.9735
Cur-Cd	303	$7x10^{-4}$	0.9345
Cur-Cd	308	$5x10^{-4}$	0.9793

Table (3.51): Rate constant and R^2 of the first order reaction for complex [Cd (II) – Vitamin C] at 293,298,303,308K temperature.

complex	*temp*	*k(min^{-1})*	*R^2*
VitC-Cd	293	$3x10^{-4}$	0.9486
VitC-Cd	298	$3x10^{-4}$	0.9673
VitC-Cd	303	$3x10^{-4}$	0.9882
VitC-Cd	308	$3x10^{-4}$	0.9811

3.8.3 First order Pb-antioxidants interaction at four temperature

Table (3.52): Absorbance at time t for Pb(II)-chelator complexes at 293K

Time(min)	Catechin		Curcumin		Vitamin C		Quercetin	
	A	LnA	A	LnA	A	LnA	A	LnA
5	0.745	-0.29437	0.845	-0.16842	1.685	0.521766	0.166	-1.79577
10	0.744	-0.29571	0.841	-0.17316	1.683	0.520578	0.164	-1.80789
15	0.741	-0.29975	0.832	-0.18392	1.679	0.518198	0.163	-1.81401
20	0.740	-0.30111	0.825	-0.19237	1.675	0.515813	0.16	-1.83258
25	0.737	-0.30517	0.818	-0.20089	1.668	0.511625	0.158	-1.84516
30	0.735	-0.30788	0.811	-0.20949	1.655	0.503801	0.155	-1.86433
35	0.734	-0.30925	0.803	-0.2194	1.632	0.489806	0.152	-1.88387
40	0.732	-0.31197	0.793	-0.23193	1.621	0.483043	0.149	-1.90381
45	0.732	-0.31197	0.785	-0.24207	1.615	0.479335	0.146	-1.92415
50	0.731	-0.31334	0.778	-0.25103	1.608	0.474991	0.145	-1.93102
55	0.729	-0.31608	0.754	-0.28236	1.599	0.469378	0.141	-1.959
60	0.728	-0.31745	0.73	-0.31471	1.596	0.4675	0.138	-1.9805

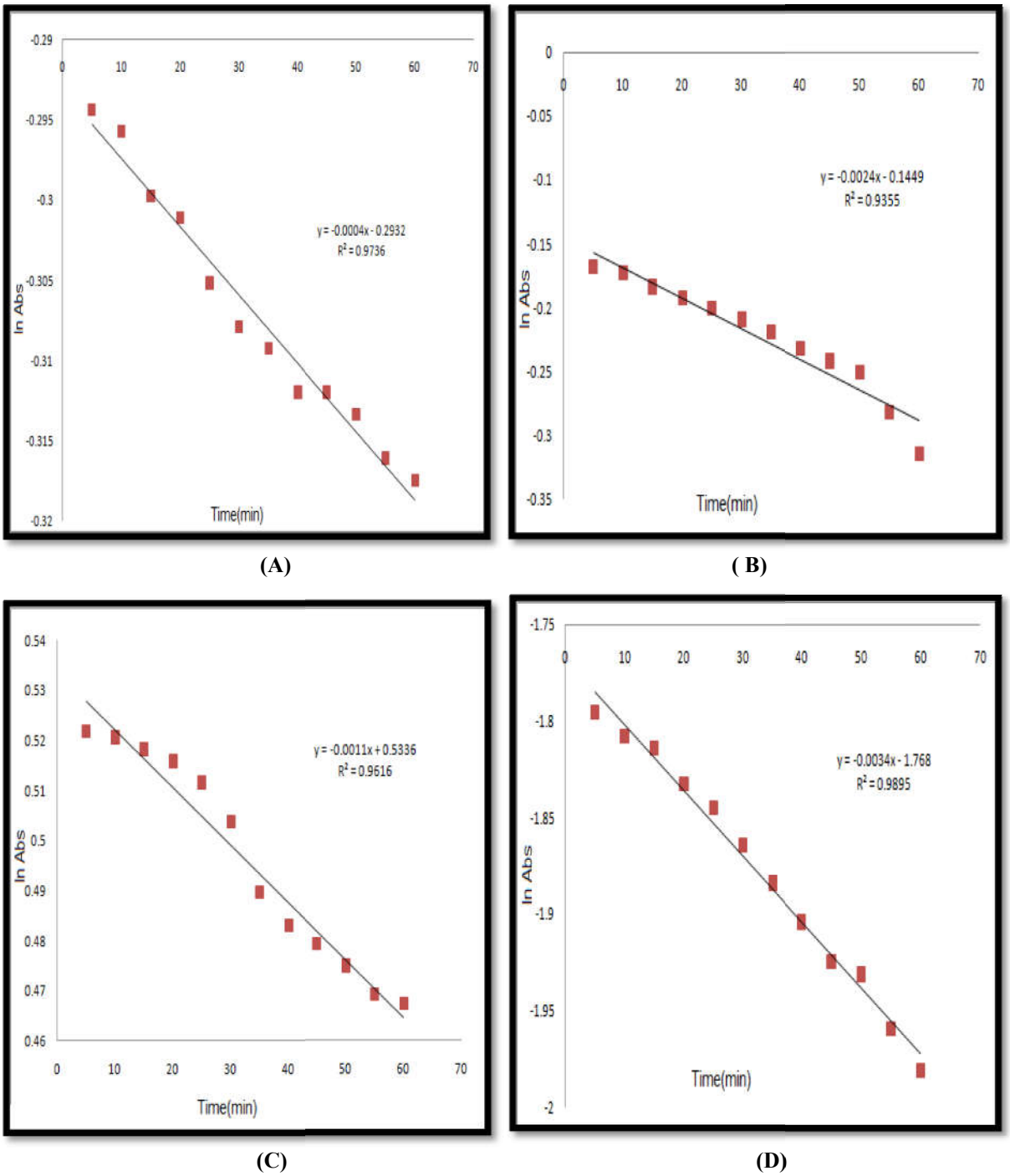


Figure (3.36): The application of the first order reaction equation for complex of Pb (II)-chelator at 293K temperatures: A) **Catechin B) Curcumin C) Vitamin C D) Quercetin**

Table (3.53): Absorbance at time t for Pb(II)-chelator complexes at 298K

Time(min)	Catechin		Curcumin		Vitamin C		Quercetin	
	A	LnA	A	LnA	A	LnA	A	LnA
5	0.755	-0.28104	0.965	-0.03563	1.493	0.400788	0.122	-2.10373
10	0.754	-0.28236	0.944	-0.05763	1.49	0.398776	0.121	-2.11196
15	0.753	-0.28369	0.942	-0.05975	1.488	0.397433	0.12	-2.12026
20	0.753	-0.28369	0.932	-0.07042	1.483	0.394067	0.119	-2.12863
25	0.750	-0.28768	0.929	-0.07365	1.475	0.388658	0.117	-2.14558
30	0.749	-0.28902	0.928	-0.07472	1.472	0.386622	0.116	-2.15417
35	0.747	-0.29169	0.918	-0.08556	1.468	0.383901	0.115	-2.16282
40	0.745	-0.29437	0.913	-0.09102	1.465	0.381855	0.113	-2.18037
45	0.744	-0.29571	0.897	-0.1087	1.462	0.379805	0.112	-2.18926
50	0.742	-0.29841	0.886	-0.12104	1.459	0.377751	0.11	-2.20727
55	0.74	-0.30111	0.881	-0.1267	1.457	0.37638	0.109	-2.21641
60	0.732	-0.31197	0.876	-0.13239	1.453	0.37363	0.107	-2.23493

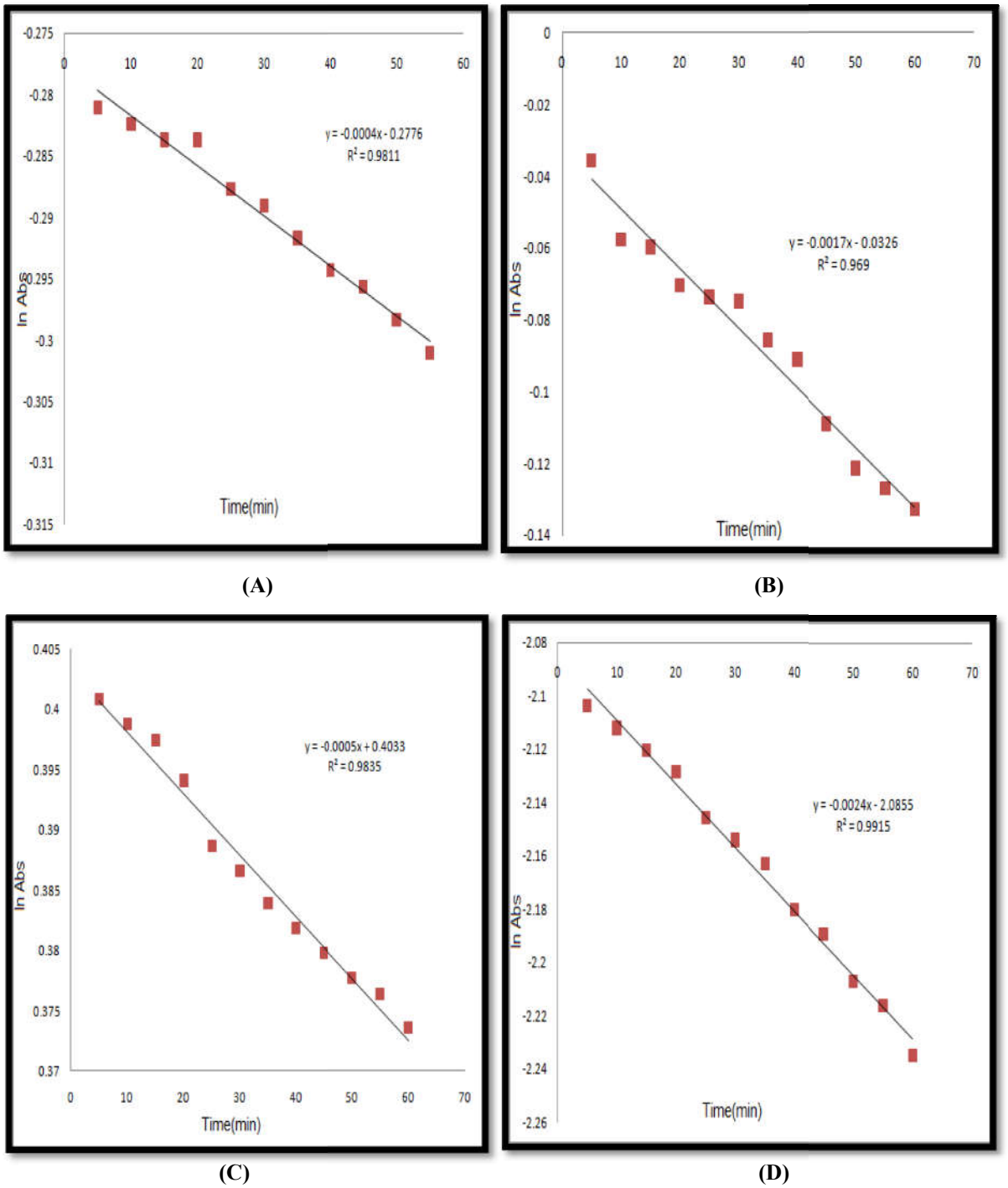


Figure (3.37): The application of the first order reaction equation for complex of Pb (II)-chelator at 298K temperatures: A) **Catechin B) Curcumin C) Vitamin C D) Quercetin**

Table (3.54): Absorbance at time t for Pb(II)-chelator complexes at 303K

Time(min)	Catechin		Curcumin		Vitamin C		Quercetin	
	A	LnA	A	LnA	A	LnA	A	LnA
5	0.721	-0.32712	1.014	0.013903	1.502	0.406798	0.093	-2.37516
10	0.719	-0.32989	1.008	0.007968	1.499	0.404798	0.091	-2.3969
15	0.718	-0.33129	1.000	0	1.494	0.401457	0.089	-2.41912
20	0.716	-0.33408	0.996	-0.00401	1.492	0.400118	0.088	-2.43042
25	0.715	-0.33547	0.975	-0.02532	1.488	0.397433	0.087	-2.44185
30	0.715	-0.33547	0.973	-0.02737	1.487	0.396761	0.087	-2.44185
35	0.712	-0.33968	0.968	-0.03252	1.484	0.394741	0.086	-2.45341
40	0.711	-0.34108	0.96	-0.04082	1.481	0.392718	0.085	-2.4651
45	0.708	-0.34531	0.958	-0.04291	1.473	0.387301	0.086	-2.45341
50	0.707	-0.34672	0.953	-0.04814	1.471	0.385942	0.084	-2.47694
55	0.703	-0.3524	0.944	-0.05763	1.47	0.385262	0.083	-2.48891
60	0.700	-0.35667	0.94	-0.06188	1.469	0.384582	0.083	-2.48891

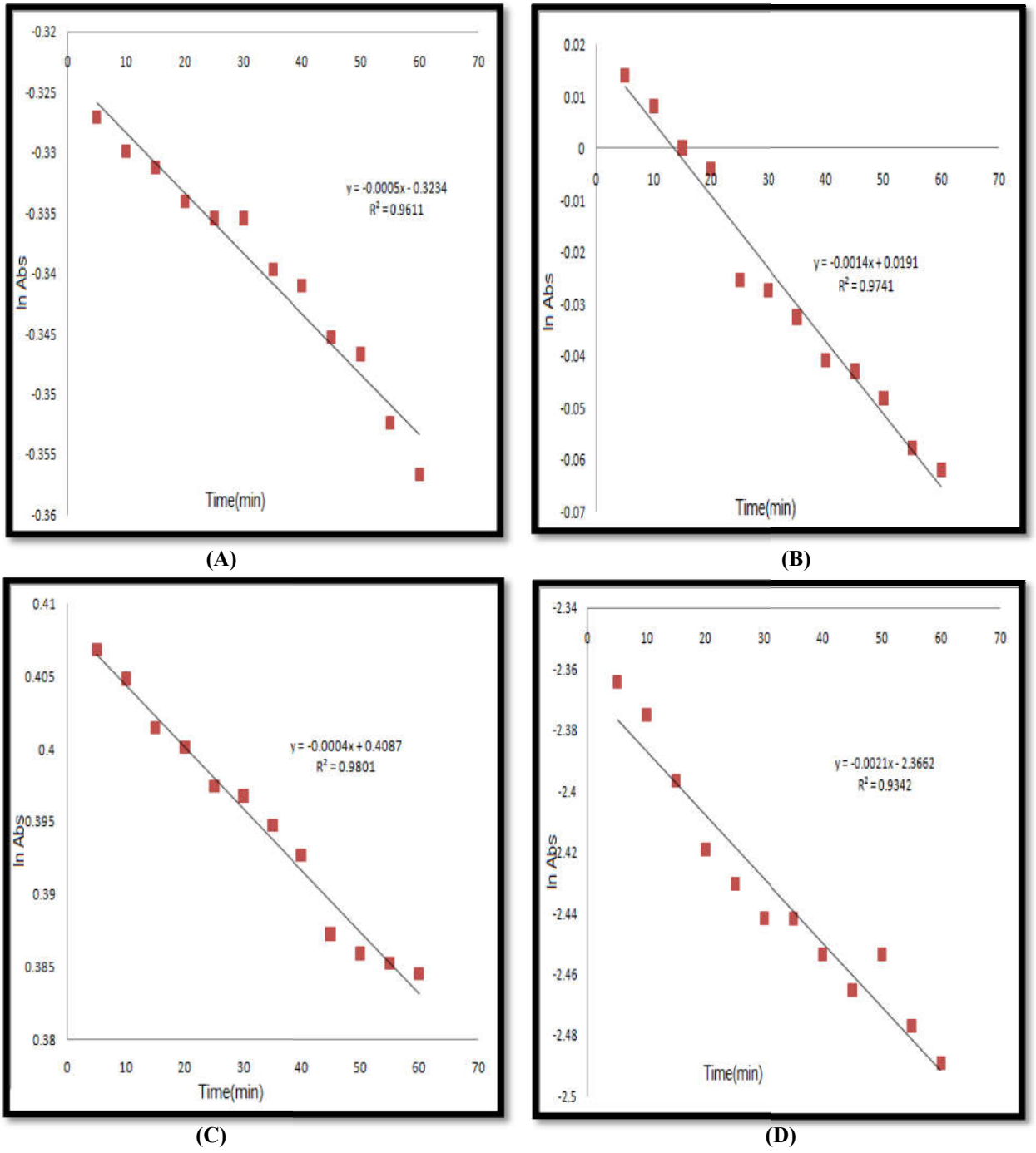


Figure (3.38): The application of the first order reaction equation for complex of pb (II)-chelator at 303K temperatures: A) **Catechin B) Curcumin C) Vitamin C D) Quercetin**

Table (3.55): Absorbance at time t for Pb(II)-chelator complexes at 308K

Time(min)	Catechin		Curcumin		Vitamin C		Quercetin	
	A	LnA	A	LnA	A	LnA	A	LnA
5	0.701	-0.35525	0.961	-0.03978	1.543	0.433729	1.107	0.101654
10	0.701	-0.35667	0.94	-0.06188	1.542	0.43308	1.1	0.09531
15	0.698	-0.35954	0.938	-0.06401	1.538	0.430483	1.099	0.094401
20	0.696	-0.36241	0.937	-0.06507	1.534	0.427879	1.098	0.09349
25	0.696	-0.36241	0.93	-0.07257	1.53	0.425268	1.097	0.092579
30	0.694	-0.36528	0.927	-0.0758	1.529	0.424614	1.096	0.091667
35	0.69	-0.37106	0.925	-0.07796	1.527	0.423305	1.096	0.091667
40	0.689	-0.37251	0.921	-0.0823	1.525	0.421994	1.09	0.086178
45	0.688	-0.37397	0.913	-0.09102	1.521	0.419368	1.086	0.082501
50	0.685	-0.37834	0.911	-0.09321	1.519	0.418052	1.084	0.080658
55	0.682	-0.38273	0.905	-0.09982	1.512	0.413433	1.081	0.077887
60	0.682	-0.38273	0.899	-0.10647	1.505	0.408793	1.081	0.077887

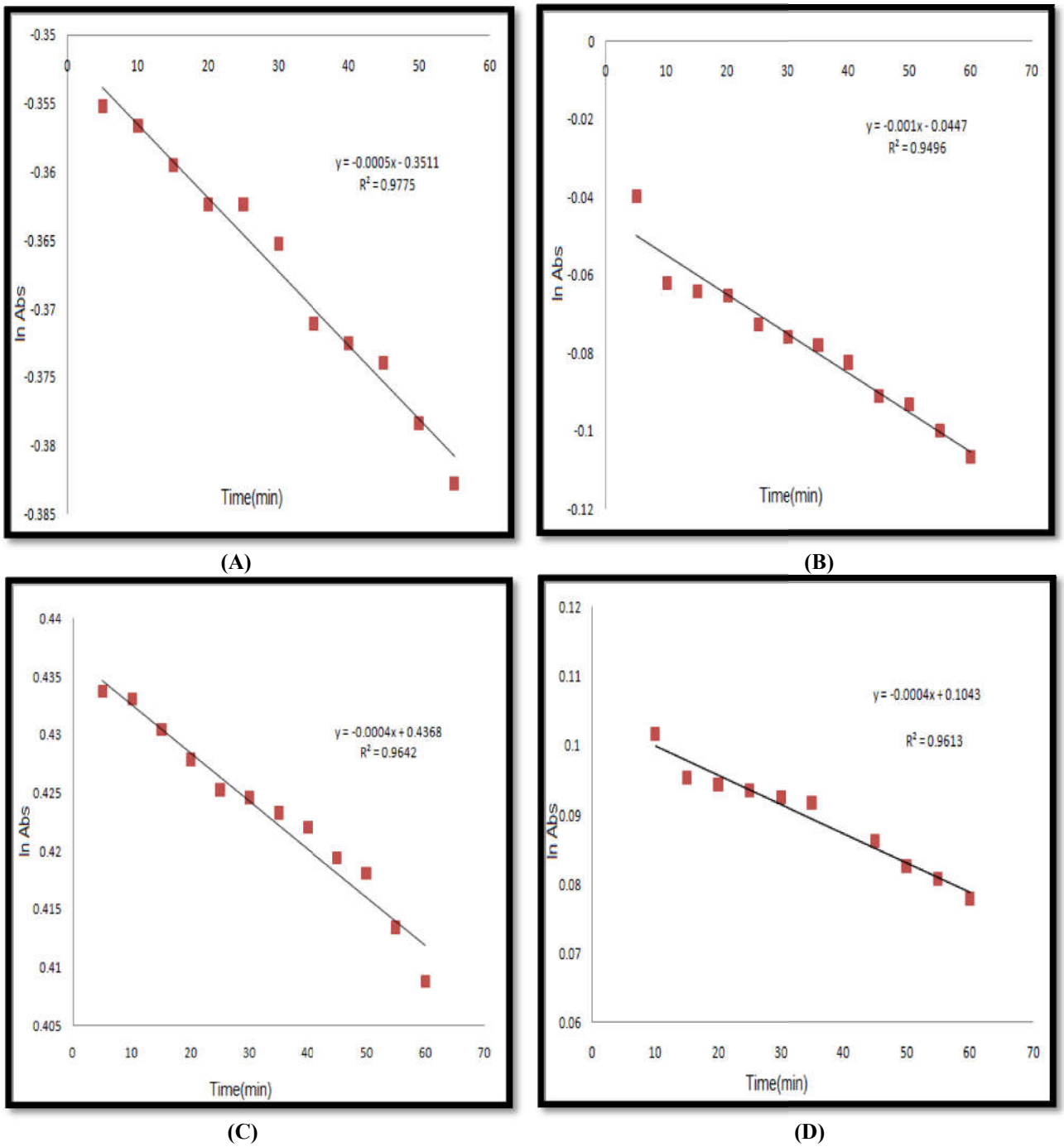


Figure (3.39): The application of the first order reaction equation for complex of Pb (II)-chelator at 308K temperatures: A) **Catechin B) Curcumin C) Vitamin C D) Quercetin**

Table (3.56): Rate constant and R^2 of the first order reaction for complex [pb (II) – Catechin] at 293,298,303,308K temperature

complex	*temp*	*k(min^{-1})*	*R^2*
Cat-Pb	293	$4x10^{-4}$	0.9736
Cat-Pb	298	$4x10^{-4}$	0.9811
Cat-Pb	303	$5x10^{-4}$	0.9611
Cat-Pb	308	$5x10^{-4}$	0.9775

Table (3.57): Rate constant and R^2 of the first order reaction for complex [pb (II) – curcumin] at 293,298,303,308K temperature.

complex	*temp*	*k(min^{-1})*	*R^2*
Cur-Pb	293	$2.4x10^{-3}$	0.9355
Cur-Pb	298	$1.7x10^{-3}$	0.969
Cur-Pb	303	$1.4x10^{-3}$	0.9741
Cur-Pb	308	$1.0x10^{-3}$	0.9496

Table (3.58): Rate constant and R^2 of the first order reaction for complex [pb (II) – Vitamin C] at 293,298,303,308K temperature.

complex	*temp*	*k(min^{-1})*	*R^2*
VitC-Pb	293	$11*10^{-4}$	0.9616
VitC-Pb	298	$5*10^{-4}$	0.9835
VitC-Pb	303	$4*10^{-4}$	0.9801
VitC-Pb	308	$4*10^{-4}$	0.9642

Table (3.59): Rate constant and R^2 of the first order reaction for complex [Cd (II) – Quercetin] at 293,298,303,308K temperature.

complex	*temp*	*k(min^{-1})*	*R^2*
Qur-Pb	293	$3.4*10^{-3}$	0.9895
Qur-Pb	298	$2.4*10^{-3}$	0.9915
Qur-Pb	303	$2.1*10^{-3}$	0.9342
Qur-Pb	308	$0.4*10^{-3}$	0.9613

The data for the application of a first order equation were presented in figures (3.28) to (3.39) and the obtained strained lines were obvious which indicate a first order interaction between these metal ions and the four chelators. The data were presented in table (3.37) to (3.55)

The results of a rate constant were presented in tables (3.41) to (3.44) for Ni-antioxidants , tables(3.49) to (3.51) for Cd-antioxidants and tables(3.56) to (3.59) for Pb-antioxidants.

The second order equation was applied as well as the graph curve did not show us a straight line so it was considered the first order is the order of impact.

Conclusions

The following points summarize the important conclusions that can be drawn from the present work

1. This research was conducted to evaluate the efficiency of some antioxidant as chelating agents for the detoxification of Cadimum , Nickel and lead using spectrophotometric techniques.
2. The four chelators were able to interact with Pb II ,Ni II and Cd II. The resultsshow that curcumin is the most efficiency chelator for the three ions whichwere reflected by a high value of K_{eq}.
3. On a view of the binding energy compounds, enthalpy and entropy during complex formation, it seems that the spontaneity of the process were enthalpy driven as reflected by a high negative values of enthalpy for group I and III and high positive values of enthalpy For group II, with increase in entropy change for all groups.
4. The stoichiometric ratio was varied between (1:1) depends to the kind of metal and ligand.
5. The kinetic show all complexes formed were first order depending on a linearity of the straight line.

Suggestion for Further work :

On the bases of experience gained during this work, one can suggest the following:

1. Using other techniques for this study of complexation and calculated thermodynamicparameters as, conductivity, fluorescence and polarography if presented.
2. Using other antioxidant for as a chelating agents.
3. Adsorption studies for lead and Cademum by a biosorbent material as a water treatment.

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كما تمت دراسة تكافؤية هذه المعقدات باستخدام طريقة التغيرات المستمرة (طريقة جوب) وكانت (1:1) في جميع المعقدات. وتم حساب ثابت الاستقرار في اربعة درجات حرارية في المدى (293 ،298 ،303 ، 308 كلفن) والتي تمتلك القيم بالترتيب التالي عند درجة 293 كلفن:

مع الكادميوم بالترتيب التالي:-

Curcumin-Cd ($16.25x10^4$) >VitaminC-Cd ($1.46x10^4$) >Catechin-Cd ($0.79x10^4$).

مع الرصاص بالترتيب التالي:-

Curcumin-Pb ($4.76x10^4$) > Quercetin-Pb ($4.52x10^4$) > Vitamin C-Pb($1.86x10^4$)> Catechin-Pb($0.69x10^4$).

مع النيكل بالترتيب التالي:-

Quercetin-Ni($9x10^4$) > Curcumin-Ni($2.37x10^4$) > Vitamin C-Pb ($1.69x10^4$) > Catechin-Ni ($1.54x10^4$).

يتبين من قيم ثابت الاستقرار اعلاه بان الـCurcumin هو الاكثر تأثيرا من بين هذه المواد الاربعة مع كل من الكادميوم و الرصاص بينما الـ Quercetin هو الاكثر تأثيرا مع النيكل.

كما تم حساب الدوال الثرموداينميكية ، طاقة كبس°ΔG و الانثاليبي °ΔH والانتروبي °ΔS عند الدرجات الحرارية الاربعة . وان القيم السالبة لطاقة كبس الحرة تشير الى تلقائية عمليه التعقيد هذه وباعثة للحرارة اذأن °ΔH سالبة القيم ماعدا التآثر مع Ni(II)-Curcumin, Ni(II)-Quercetin, Pb-(II)-Catechin, Cd(II)-Catechinفأن التغير في الانثاليبي يمتلك قيم موجبة، اما التغير في الانتروبي°ΔS موجب في جميع المعقدات باستثناء Pb(II)-Quercetin.

واظهرت الدراسة الحركية ان هذا التأثر يخضع الى المرتبة الاولى الكاذبة لهذه المخلبيات مع كل من ايونات الكادميوم والرصاص والنيكل.

الخلاصة

هناك مجموعة واسعة من مركبات البوليفينولات تدعى بالفلافونويدات، وتعد من مضادات الأكسدة الغذائية. و تتواجد في مجموعة واسعة من الخضار والفواكه، والشاي الأخضر وتعرف بالأصباغ.

لدى العديد من الفلافونويد القدرة على تكوين معقدات مع الايونات المعدنية . يمكن استخدامها في إنتاج المكملات الغذائية، والطب، وإزالة المعادن الثقيلة السامة .ان العلاج المخلبي هو استخدام عوامل مخلبية (عوامل معقدة) لإزالة المعادن السامة مثل النيكل والكادميوم، والرصاص عن طريق تحويلها إلى شكل خامل كيميائيا يمكن أن تفرز دون مزيد من التفاعل مع الجسم.

يعد الرصاص واحدا من أكثر الملوثات البيئية التراكمية الخطرة التي تؤثر على جميع النظم البيولوجية من خلال التعرض لمصادر الهواء والماء والغذاء. وهو من المعادن الثقيلة السامة التي من المعروف أن تحفز مجموعة واسعة من الفسيولوجية والكيمياء الحيوية الخلل الوظيفي في البشر .ولا يزال التسمم بالرصاص مشكلة صحية هامة.

لذا تم في هذه الرسالة دراسة التأثر لبعض العوامل المخلبية المعروفة مثل (Curcumin,Quercetin, Vitamin C and Catechin) مع ايونات النيكل و الكادميوم والرصاص وإمكانية تكوين معقدات آمنة معها وحساب ثابت الاستقرار وبعض الدوال الثرموداينميكية ودراسة حركيةهذه المعقدات باستخدام الطرق الطيفية.

تمت القياسات الطيفية (فوق البنفسجية- المرئية) في محلول 40% ايثانول\ماء للتأثر مع الـQuercetin و 60% ايثانول\ماء للتآثر مع الـCurcumin و تمت القياسات مع Vitamin C ,Catechin باستخدام الماء كأفضل وسط لهذا العامل.

الاطياف الالكترونية للمخلبيات الحرة في محلول الايثانول\ماء تميزت بوجود حزمة واحدة لكل من Curcuminλ_{max}=429nm ، Catechinλ_{max}=278nm ، Vitamin C λ_{max}=256nm ، بينما اظهر طيف ال Quercetin حزمتين عند λ_{max1}=373nm، λ_{max2}=256nm .

إن إضافة محلول ايونات النيكل ، الكادميوم ، الرصاص الى محلول هذه المخلبيات يظهر زياده في الامتصاصية للأطياف الالكترونية مع Catechin, Curcumin فضلا عن تأثير قليل جداً على الطول الموجي. في حين اضافتها الى الـ Vitamin C , Quercetin يظهر نقصان في الامتصاصية وإزاحة حمراء للطول الموجي ويعزى هذا التغيير إلى تكوين معقدات معها.

دراسة الخواص الثرموداينميكية والحركية لتداخلات مضادات الأكسدة مع ايونات النيكل و الكادميوم والرصاص

رسالة مقدمه إلى

كلية العلوم – جامعة ديالى

وهي كجزء من متطلبات نيل درجة

الماجستير في علوم الكيمياء / الكيمياء الفيزياوية

مقدمه من قبل الطالب

حيدر نزار حسين

بكالوريوس علوم كيمياء / الجامعة المستنصرية

بأشراف

أ.د احمد نجم عبد

أ.م.د الهام مجيد الرفيعي

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