Ministry of Higher Education and

Scientific Research

University of Diyala

College of Science

Department of Chemistry

Removal of Cadmium and Nickel Ions from Its Binary Systems by Adsorption on Copper Oxide Nanoparticles

A Thesis Submitted to the

Council of the College of Science, University of Diyala

In Partial Fulfillment of the Requirements for the Degree

of Master of Science in Chemistry

by

SALLY KAMIL SAADI

B.Sc. In Chemistry Science 2014

College of Science – University of Diyala

Supervised by

Prof. Dr. Karim Henikish Hassan   **Lect. Dr. Areej Ali Jarullah**

2018 AD   **IRAQ**   **1439 AH**

بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ

وَاصْبِرْ لِحُكْمِ رَبِّكَ فَإِنَّكَ بِأَعْيُنِنَا وَسَبِّحْ بِحَمْدِ رَبِّكَ حِينَ تَقُومُ ﴿٤٨﴾

صدق الله العظيم
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We certify that this thesis *(Removal of Cadmium and Nickel Ions from Its Binary Systems by Adsorption on Copper Oxide Nanoparticles)* was carried out under our supervision in Chemistry Department, College of Science, Diyala University in partial fulfilment of the requirement for the degree of master of science in chemistry by the student **(SALLY KAMIL SAADI)**.

(Supervisor)   **(Supervisor)**

Signature: Signature:

Name: Dr. Karim Henikish Hassan   Name: Dr. Areej Ali Jarullah

Title: Professor   Title: Lecturer

Date: /   / 2018   Date: /   / 2018

Head of the Department of Chemistry

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

Scientific Certification

I certify that the thesis entitled *(Removal of Cadmium and Nickel Ions from Its Binary Systems by Adsorption on Copper Oxide Nanoparticles)* presented by **(SALLY KAMIL SAADI)** has been evaluated scientifically, therefore, it is suitable for debate by examining committee.

Signature:

Name: Dr. Takialdin A. Himdan

Title: Professor

Date: /   / 2018

Linguistic Certification

I certify that the thesis entitled *(Removal of Cadmium and Nickel Ions from Its Binary Systems by Adsorption on Copper Oxide Nanoparticles)* presented by **(SALLY KAMIL SAADI)** has been corrected linguistically, therefore, it is suitable for debate by examining committee.

Signature:

Name: Dr. Ghazwan Adnan Mohammed

Title: Assistant Professor

Date: /   / 2018

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

(Member)
Signature:
Name: Dr. Hussein Ismael Abdullah
Title: Assistant Professor
Date: /   / 2018

(Member)
Signature:
Name: Dr. Ammar Jasim Mohammed
Title: Assistant Professor
Date: /   / 2018

(Member / Supervisor)
Signature:
Name: Dr. Karim Henikish Hassan
Title: Professor
Date: /   / 2018

(Member /Supervisor)
Signature:
Name: Dr. Areej Ali Jarullah
Title: Lecturer
Date: /   / 2018

Approved by The Council of College of the Science, University of Diyala.

(The Dean)
Signature:
Name: Dr. Tahseen Hussein Mubarak
Title: Professor
Date: /   / 2018

DEDICATION

For my first friend, who facilitated all the difficulties and shared every step of progress in science and knowledge with me...

My beloved Father

For my guardian angel, my refuge, the pure affection. The most valuable thing in my life. No words are sufficient to describe my appreciation for you....

My beloved Mother

For the bright candles, my supporters in this life. It is a bliss having you

My sister Raghed and her family
My sister Hind and her family
My brother Nawfal and his family
My brother saad and his family

For all of you, I dedicate my work.

SALLY...

ABSTRACT

In this study, the copper oxide nanoparticles prepared by (sol-gel) method and simple method using *Fig* Leaves Extract .They are characterized by X-ray diffraction, Scanning electron microscope, Transmission electron microscope and Atomic force microscope techniques. XRD spectrum reveals that particle size obtained is about (21.11) nm for (SGP.CuO.NP) and (7.31) nm for (FLEP.CuO.NP), which agreed fairly well with SEM and TEM data. Surface morphology as a main nanoparticles phenomenon is studied in term of SEM, TEM and AFM.

Water pollution with many heavy metals is a major damage for environment, therefore the copper oxide nanoparticles prepared are used to remove cadmium and nickel ions in binary system from dilute aqueous solution. In this field, a number of factors have been studied for effect the percentage removal of metals in binary system onto adsorbents, the time required to remove (Cd^{+2} and Ni^{+2}) ions in binary system to reach equilibrium was studied and showed that contact time were (30) min and (15) min for removal of two metals on (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces respectively. The removal of cadmium (II) and nickel (II) ions was found to be slightly reduce by increasing the concentration of adsorbate and increase by increase the weight of the surface, studying the adsorption of cadmium and nickel ions in binary systems at different values of pH (2, 4, 6 and 8) indicated that the best adsorption of two heavy metals on two surfaces prepare at pH 6 whereas the effect of temperature on each metals removal in binary system showed that the percentage removal is reduced by increasing the temperature, which means that the process is exothermic.

Calculated values of the thermodynamic functions of the adsorption process, such as ΔG, ΔH and ΔS, indicates the process of adsorption is spontaneous, exothermic and less randomness at metals binary ion–metal oxide nanoparticles. It also showed that the ability of (FLEP.CuO.NP) surface adsorption of nickel and cadmium ions was higher than that of (SGP.CuO.NP) surface.

Temkin isotherm was found to be the best one described removal of Cd (II) ions on (SGP.CuO.NP) and Freundlich isotherm be the best described removal of Cd (II) on (FLEP.CuO.NP) in single system. The best type described removal of Ni (II) ions on two adsorbents is Freundlich. All these were noted from the correlation coefficients values.

The removal Cd (II) ions in presence of different initial concentration of Ni (II) ions on (SGP.CuO.NP) in all tested isotherm in binary system and adsorption Ni (II) ions in presence of different initial concentration of Cd (II) on (SGP.CuO.NP) indicates that Laungmiur equation regression fit are best than that for the Freundlich and Temkin, and at adsorption Cd (II) ions in binary system on (FLEP.CuO.NP) in presence Ni (II) with various initial concentrations the Freundlich isotherm is better than other isotherms in this study. In case adsorption of Ni (II) ion in presence Cd (II) ion with various initial concentration on (FLEP.CuO.NP) the Temkin isotherm is the best one described adsorption processes.

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List of Symbols and Abbreviations

Symbol or Abbreviation	Definition
Q_e	Adsorption capacity of the adsorbent at equilibrium time
AAS	Atomic absorption spectrophotometer
AFM	Atomic force microscope
Avg	Average
θ	Bragg's angle
BET	Brunauer, Emmett, and Teller
CEC	Cation Exchange capacity
C_t	Concentration of adsorbate after any time
FLEP.CuO.NP	Copper oxide nanoparticles prepare by *Fig* Leaves Extract
SGP.CuO.NP	Copper oxide nanoparticles prepare by sol-gel method
R^2	Correlation coefficient
D	Crystallite size
DLS	Dynamic light scattering
EDX	Energy dispersive X-ray spectroscopy
ΔH	Enthalpy
ΔS	Entropy
A_T	Equilibrium binding constant
C_e	Equilibrium concentration of adsorbate
FTIR	Fourier transform infrared spectroscopy
K_f	Freundlich constant related with adsorption capacity
n	Freundlich constant related with adsorption intensity
FWHM	Full width at half maximum
R	Gas constant
ΔG	Gibbs free energy
●	Indicate the presence heavy metal in that industry
IR	Infrared spectroscopy
C_0	Initial concentration of adsorbate
JCPDS	Join committee on power diffraction standards
a	Langmuir constant related with adsorption capacity

b	Langmuir constant related with energy of adsorption
min	Minute
R%	Percentage removal of adsorbate
pH	Power of hydrogen
b_T	Related to heat of adsorption
rpm	Revolution per minute
SEM	Scanning electron microscope
SAED	Selected area electron diffraction
B_T	Temkin isotherm constant
T	Temperature
TG-DTA	Thermal gravimetric differential thermal analysis
K	Thermodynamic equilibrium constant
TEM	Transmission electron microscope
UV- visible	Ultraviolet - visible spectroscopy
v	Volume of solution
m	Weight of adsorbent
XRD	X-ray diffraction

Chapter One
(Introduction)

1.1. General introduction

The term 'environment' describes living and nonliving surroundings related to organisms. It includes physical, chemical and biological factors and processes that determine the growth and survival of organisms. Today, human activities affect all of the Earth's ecosystems. Earth's natural systems provide ecosystem services are needed to survival such as: air and water purification, climate regulation, and plant pollination[1].

Water is an important commodity for life on earth and is something which is needed daily activities[2].So, it is very a suitable to say that water is vital, both as universal solvent as well as being an important component of metabolic process within the human body. Fresh and clean water is a major for the existence of life[3].

Pollution is any unpleasant or harmful change in the environment that results from the chemical, physical or biological impacts of social activities or human industrial[4]. Any substance causing nuisance or harmful effects or uneasiness to the organisms then that particular substance may be called as the pollutant[5]. There are several types of environmental pollution such as; (water pollution, air pollution, light pollution, radiation pollution, noise pollution & soil pollution), the agents which cause environmental pollution known as pollutants[6], nowadays, lack of clean water is an important problem around the world because the quick development of different industries, a huge quantity of wastewater has been generated from industrial processes and it has been discharged in water and soils systems[7].

The presence of heavy metals ion (e.g. hexavalent chromium, cadmium lead… etc.) are one of the major concern and that used target pollutants in research studies of the well- documented human health problems associated to these compounds and also their high toxicity[8,9].

Water pollutants include those that are biodegradable, such as sewage effluent, which cause no permanent harm if adequately treated and dispersed, as well as those which are non-biodegradable, such as chlorinated hydrocarbon pesticides, certain industrial dyes, organic compounds, heavy metals in some industrial effluents. ***Table (1.1)*** shows the main pollutant types[10].

Table (1.1): Pollutant types

Category	Examples
Organic chemicals	Phenol, phenol derivatives, polychlorinated biphenyls, oil, pesticides, dyes
Inorganic chemicals	Salts, nitrate, metals and their salts
Organo metallic chemicals	Methyl mercury, tri butyl tin, tetra ethyl lead
Radio active elements	Radon, radium, uranium
Biological	Micro organisms , pollens

Industrialization has big interest to the human species but on the other side it has many dangers mainly because of waste production and also because of it is poor disposal system[11]. Industrial effluents contaminate the air, soil, and water which are considered to be one of the basic reasons of short life expectancy in the developing countries[12].

Heavy metal contamination of waste water is of significant concern worldwide because the release of these metals into aquatic and soil environments potentially impacts human   health and ecosystems.

Heavy metal toxicity could result, for instance, from drinking-water such as; (lead pipes), raised the concentration of the metal in air at source of emission and intake by food chain[13-15]. Many methods have been used to remove heavy metals from water and wastewater, mainly chemical precipitation, ion-exchange, membrane separation, classical adsorption processes, electrolysis, etc… [16].

Adsorption is one of the effective treatment process as compared to other technologies for the remediation of different contaminates from aqueous environment due to the low cost factor moreover it can separate small amount of toxic elements from the large volume solutions. Different kind of adsorbents have been commercialized or developed for the treatment of waste water[17,18].

Green chemistry focuses on the production of desired products without generation of hazardous intermediate by products in chemical reaction processes. Integrating green chemistry principles into nanotechnology has led to the identification of environmentally friendly reagents that are multifunctional, which they can serve as a reducing agent as well as a capping agent[19,20].

Nanoparticles can be synthesized from oxides of various metals such as iron, copper, titanium, manganese, magnesium, zinc, silica and aluminum. Metal elements have a distinct property to form oxides with a large variety of structural and electronic properties[21]. Metal oxide nanoparticles show higher extent of adsorption as compared to natural sized oxide due to metal-ligand precipitation or formation of ternary ligands[22].

1.2. Heavy metals

1.2.1. Defining of heavy metals and human effect

The phrase "heavy metal" refers to any metallic chemical element that has a relatively high density with atomic number above 20, inorganic materials and poisonous at low concentration[23,24]. Source of heavy metals are rocks and are delivered into the environment (water, soil, air) either naturally or by human activities. The metals such as (Pb, Cu, Zn, Ni, Hg and Cd) are found as divalent cations in many soils natural and wastewater, however (As and Cr) are found in multiple oxidation state[25,26]. Heavy metals are often stable and tend to persist and accumulate in the environment and they can not be analyzed or destroyed[27].

The metals may be present in solution as free ions, soluble salts, associated ions with dissolved inorganic or organic ligands, or binding to particulate matter. Unlike organic contaminants, in human organisms causing adverse impact to many vital function. That is why toxic metals like (copper, nickel, zinc, cadmium, mercury, chromium and lead) have to be removal from industrial wastewater because they accumulate in the living organisms causing different diseases and troubles[28,29]. The detrimental effects for heavy metals on the human health are summarized in *Table (1.2)* [30-35].

Table (1.2): The detrimental effects for some heavy metals on the human health.

Heavy metal	Diseases
Arsenic	Skin lesions, visceral cancers ,vascular disease
Cadmium	Kidney damage, hypertension, human carcinogen, stomach problem, diarrhea and sometimes death.
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic.
Copper	Nausea, vomiting, headache, diarrhea, respiratory difficulties, liver and kidney failure.
Nickel	Cancer of lungs, nose and bone, dermatitis, nausea, coughing, chronic asthma, abdominal cramps, diarrhea, vertigo, and lassitude.
Zinc	Depression, lethargy, neurological signs and increased thirst
Lead	Damage the fetal brain, damage the kidney and liver, circulatory system and nervous system.
Mercury	Impairment of speech, hearing, vision and movement rheumatoid arthritis, diseases of the kidneys, circulatory system and nervous system.

Heavy metal pollution of water is dangerous environmental disturbances which impact the fineness of water[36,37]. The toxicity of heavy metals is related to the formation of complexes with proteins, in which carboxylic acid (-COOH), amine ($-NH_2$), and thiol (-SH) groups are involved. When metals bind to these complexes, important enzyme and protein structures are affected[30].

1.2.2. Heavy metals in industrial wastewater

The definition of industrial wastewater is ''any wastewater generated from any manufacturing, processing, institutional, commercial, or agricultural operation, or any operation that discharges other than domestic or sanitary wastewater''[38]. Chemical pollutants in wastewater are either organic or inorganic. Organic consists mainly of protein, fats and carbohydrates. Inorganic pollutants of wastewater are free ammonia, organic nitrogen, nitrites, nitrates and trace element such as heavy metals[39]. Increased use of metals and chemicals in process industries has resulted in generation of large quantities of effluent that contains high level of toxic heavy metals and their presence poses environmental–disposal problems due to their non-degradable and persistence nature. In addition mining, mineral processing and extractive-metallurgical operations also generate toxic liquid wastes[40]. With rapid development of industries such as metals wastewaters are directly or indirectly discharged into the environment increasingly[41]. Many processes such as smelting activities, battery industrial, plating and mining discharge of municipal sewage and industrial wastewater include heavy metals such as, chromium, copper, cadmium, lead, nickel, mercury, and zinc[42]. *Table (1.3)* explains the heavy metals produced from the varied industries[38].

Table (1.3): Heavy metals generated from different industries

Industry	Heavy metals							
	As	Cd	Cr	Cu	Hg	Pb	Ni	Zn
Paper mills		●	●	●	●	●	●	●
Organic industry	●	●	●		●	●		●
Fertilizer	●	●	●	●	●	●	●	●
Petroleum refining	●	●	●	●	●	●	●	●
Steel works	●	●	●	●	●	●	●	●
Aircraft plating, finishing		●	●	●	●		●	
Flat glass, cement			●					
Textile mills			●					
Tanning			●					
Power plant			●					

The symbol (●) refers the presence heavy metal in that industry

Cadmium is widely utilized in many industrial processes, as shown in *Figure (1.1)* [43]:
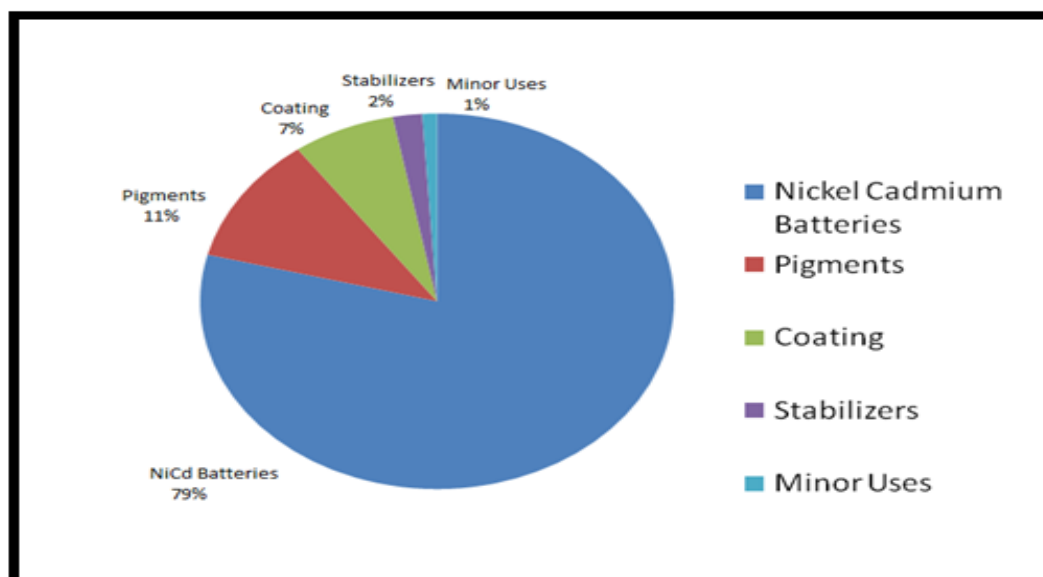
Figure (1.1): Cadmium uses in industries

1.2.3. Treatment of heavy metals

Since the household waste water and sewage generated by cities is a major source of water pollution, so it became necessary to subject them to treatment to reduce the heavy metals biodegradable before it is put into water sources. To mitigate the heavy metals pollution, many processes like; chemical precipitation, chemical oxidation, electrochemical treatment, reverse osmosis, ion exchange, membrane technologies, filtration, coagulation[44-46], But these procedures are expensive, ineffective[46], high energy consumption and production of a secondary waste product, poisonous sludge that would require further special handling[45,47], requiring large quantities of chemical reagent[47], and complicated operation and maintenance[48]. Some of those current methods have some drawbacks, including inefficient metal removal, especially in treatment of wastewater contaminated with trace concentrations of (heavy metals) in a bout of (1-100) mg/L[44,45]. Among these techniques adsorption is one of the best methods for removal of heavy metals from water because it is simple to operate, highly efficient and low-cost[49]. Adsorption is mainly based on the utilization of solid adsorbents from organic, inorganic, biological and low cost materials[50]. The common adsorbents primarily include, activated carbons, zeolites, clays, alumina, biomass and polymeric materials[51]. However, many adsorbents suffer from low adsorption capacities and separation inconveniences. Therefore, there is still a requirement for the development of new adsorbents and systems[50].

An excellent adsorbent should have a higher surface area and short equilibrium time, so that it can be used to adsorption high amount of pollutants a short time. In addition, it should not generate very high amount of sludge.

Nano adsorbents could be employed most effectively not only in a very low concentration range (≈1) ppm of pollutants, as well as in a high concentration range (≈1000) ppm[52].

1.3. Adsorption processes

The phenomenon of concentration of molecules of a gas or liquid at a solid surface is called **(Adsorption)**, and may be defined as the processes of accumulation of any substance giving higher concentration of molecular species on the surface of another substance as compared to that in the bulk. When a solid surface exposed to a gas or a liquid, molecules from the gas or the solution phase accumulate or concentration at the surface. Adsorption is a well-established and powerful technique for treating domestic and industrial effluents. The substance that concentrates at the surface is called **(adsorbate),** and the material upon whose surface the adsorption takes place is called **(adsorbent)**[53,54].

The adsorbent material must have some important properties, such as; high internal volume accessible to the different target components, a high surface area, particularly the internal surface area, pore size distribution and the nature of the pores that markedly influence the type of adsorption processes[55]. For example adsorbents; silica gel, porous clays, resins, bioadsorbents, fly ash, agriculture waste, nanotubes, and metal oxide nanoparticles[56-58].The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable **(desorption process)**[41].

The phenomenon of adsorption is a spontaneous process and hence, is attained by a decrease in free energy (ΔG) of the system. It is also accompanied with a decrease in the entropy (ΔS) that follows directly from the fact that the molecules at the surface are in more ordered state than in the solution[53].The mechanism adsorption using adsorbent shown in *Figure (1.2)*[59].
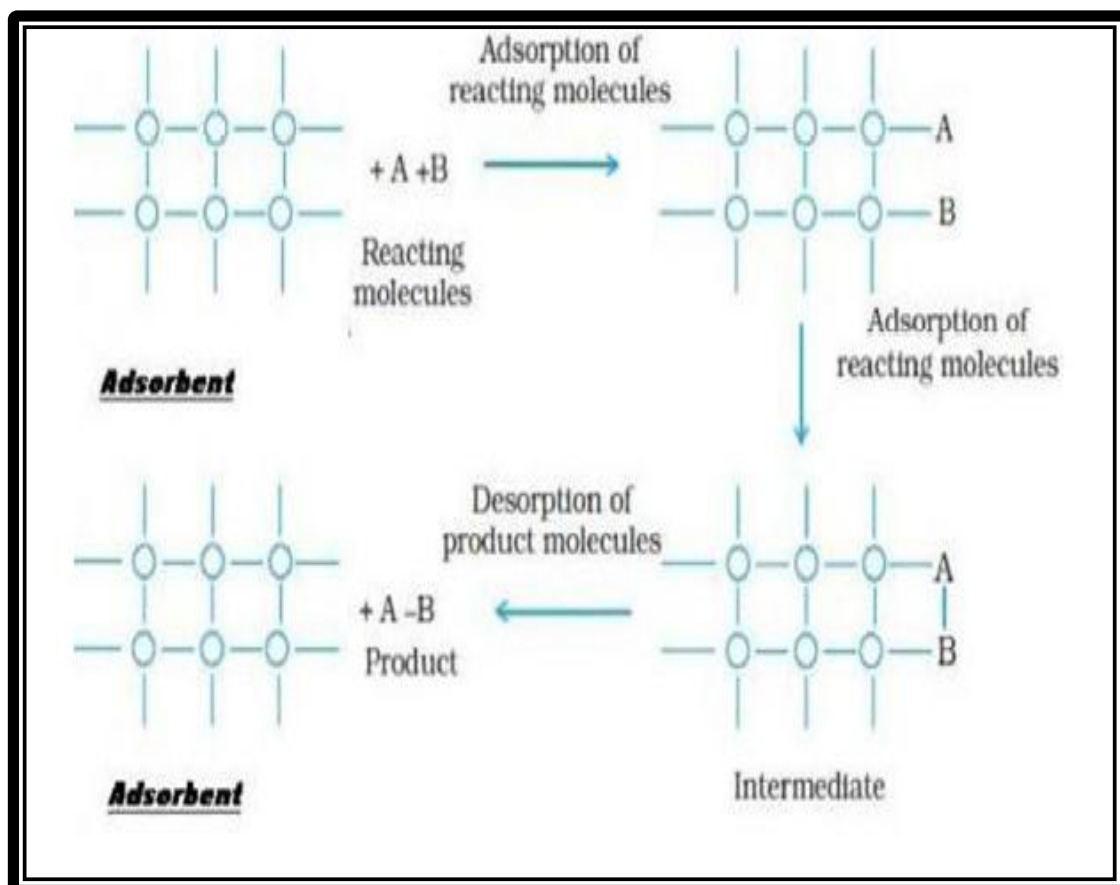
Figure (1.2): Mechanism of adsorption

1.3.1. Application of the adsorption processes

Adsorption has many applications including the following[60-62].

1. **Pollution:** Various adsorbents were utilized for refining of wastewater to separate the pollutants and toxic gases on suitable substances.

2. **Soil science:** Interaction and adsorption of clays and soils with pesticides is of major importance in soil science, because processes such as effective pesticides work, the biodegradation, and the toxicity of pesticide depend to a great range upon the nature of adsorption of the organic chemical by the silicate.

3. **Catalysis:** The adsorption of reactants on the catalytic surface as a first step in the reaction is a requirement to catalyzed reaction.

4. **Chromatographic analysis:** The chromatographic analysis is based on a certain fact is (solid) may adsorb to varying range the different constituents of a mixture present in a solution, adsorbent such as gel, alumina and clays which act as stationary phase.

5. **Medicine and pharmacology:** The importance of active surface materials is based on their adsorption properties, which have many applications, like isolation and purification of widely differing biochemical and pharmaceutical products, vitamins, enzymes, antibiotics chromatography and extraction of drugs from urine or serum in order to be detected by different methods in clinical laboratories.

6. **Industry:** Applications of adsorption important such as; decolorization, deodorization and taste improvement of drinking, the clarification of sugar liguor by charcoal, color materials removal from vegetable oils by adsorption activated charcoal and clays.

1.3.2. Forces of the adsorption

The forces of the adsorption process in solution are usually considered as follows[10,62]:

1. Ion-exchange: replacement of counter ions of the double layer by similarly charged solute ions.

2. Ion pairing: electrostatic interactions between counter ions.

3. Acid-base interaction: hydrogen-bond formation between adsorbent and solute.

4. Adsorption by polarization of π-electrons: interaction between aromatic molecule groups and positive charges at the adsorbent surface.

5. Adsorption by dispersive forces.

6. Hydrophobic bonding: attractive interaction between hydrophobic groups of solute molecules and hydrophobic groups of adsorbent.

1.3.3. Types of adsorption

Forces of attraction exist between adsorbate and adsorbent. These forces of attraction can be due to Vander Waals forces of attraction which are weak forces or due to chemical bond which are strong forces of attraction. On the basis of type of forces of attraction existing between adsorbate and adsorbent, adsorption can be classified into two types: physical adsorption or chemical adsorption[60].

I. Physical adsorption

When the force of attraction existing between adsorbate and adsorbent are weak VanderWaal forces of attraction, the process is called (physical adsorption) or (physisorption) as in *Figure (1.3)*[63]:

II. Chemical adsorption:

When the force of attraction existing between adsorbate and adsorbent are chemical forces of attraction or chemical bond, the process is called (chemical adsorption) or (chemisorption) as in *Figure (1.3)* [63]:

Physical adsorption   *Chemical adsorption*
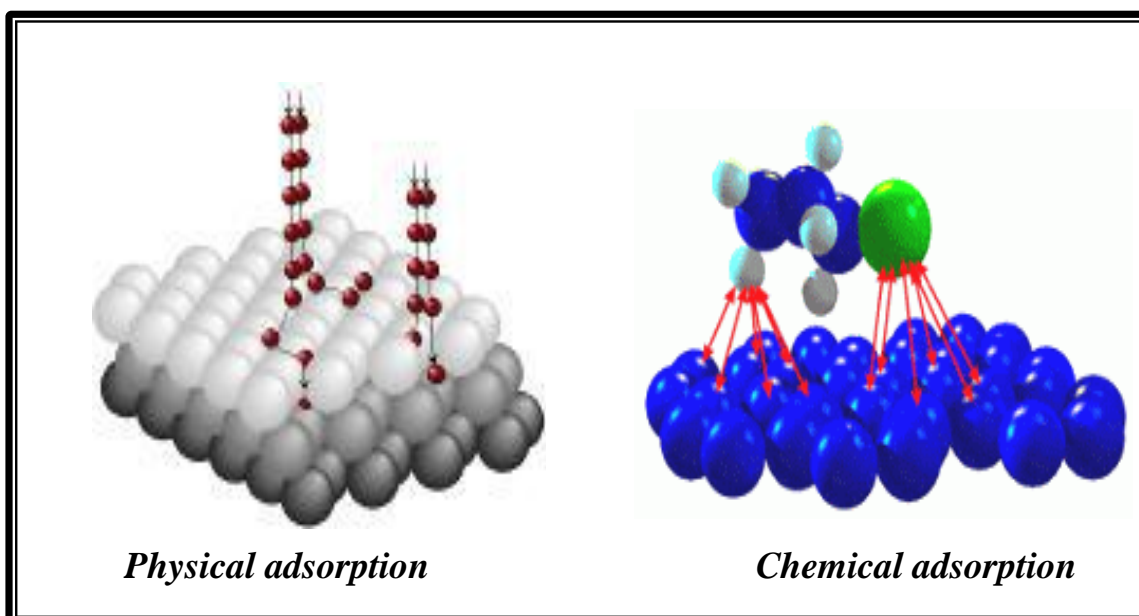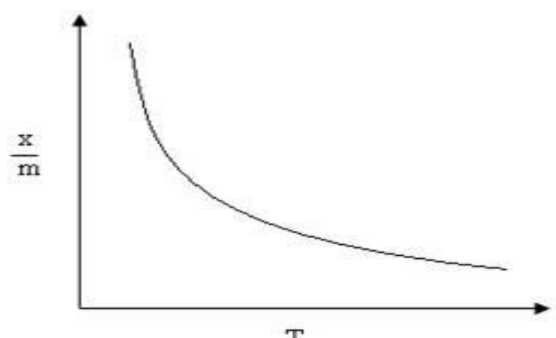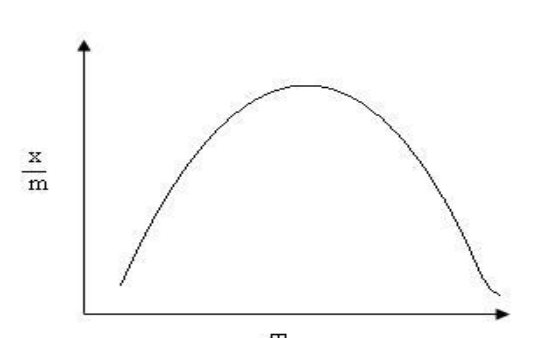
Figure (1.3): Physical and chemical adsorption

There are many differences between physical adsorption and chemical adsorption which can be explained as in, *Table (1.4)* [64-66].

Table (1.4): Difference between physical and chemical adsorption.

Physical adsorption	Chemical adsorption
It occurs when adsorbate molecules accumulated onto adsorbent surface by Vander Waals forces.	It occurs when adsorbate molecules accumulated onto adsorbent surface by chemical bond (ionic or covalent bond).
Heat of adsorption is low (20-40) KJ/mole, where the adsorption processes decreases with increases in the temperature.	Heat of adsorption is high (40-400) KJ/mole, where the adsorption processes increases with increases in the temperature.
The adsorption processes is reversible with increasing temperature or decreasing of pressure cause desorption.	The adsorption processes is irreversible.
It is non-specific	It is highly specific
The adsorption of multilayer	The adsorption of monolayer
No reactions on the surface.	Reactions on the surface may take place; dissociation, catalyst, reconstruction.
No electron transfer although polarization of adsorbent may occur.	Electron transfer leading to bond formation between adsorbate and surface.
It does not require activation energy.	It is required activation energy.
 x = amount of absorbate m = amount of absorbent	 x = amount of absorbate m = amount of absorbent

1.3.4. Adsorption mechanism from solution

The adsorption processes of solute onto surface solid is even more difficult to be treated theoretically than the corresponding of gas on solid processes cause the role of a solvent becomes more explicit[64]. The processes also depended on the nature of interactions between of solute and solvent in the solution phase and in the interfacial region, as well as on their interactions with the sorbent[67]. This process is relatively a complex phenomenon. It varies from adsorption of individual (gases, vapors, and pure liquids) in that solution contains at least two components forming a closely packed layer on the surface.

Adsorption from solution by porous surface may take place basically in the following steps[68]:

(I)   Transport of solute molecules from the bulk of solution to the exterior surface of the adsorbent material.

(II)   Movement of solute molecules across the interface and adsorption onto external surface sites occurs.

(III) Migration of solute molecules within pores of the adsorbent.

(IV)   Interaction of solute molecules with available sites on the interior surfaces, bounding the pore of the adsorbent and capillary spaces of the adsorbent.

One or more of the previous steps may control the rate by the amount of solute adsorbed onto the solid particle.

1.3.5. Factors influencing adsorption processes

The main factors that affect the percentage of adsorption are:

(1) Contact time

Contact time impacts the adsorption processes, where the time required for the adsorption processes to reach equilibrium varies and based on the surface nature and the available adsorption sites[1]. It can be defined as the longest time when the adsorption process is complete and the balance or change is slight[38,69].

(2) Nature of adsorbent

The nature of the adsorption process depended on the physical and chemical characteristics of the adsorbent, such as the charge distribution of the adsorbent, dimension of the pores and the effect of the adsorbent porosity depended on the relationship between the dimension of the adsorbent pores and of the adsorbed molecules[38,64,69,70].

The weight of the sorbent has a great effect on the adsorption processes and the extent of the adsorption increase with increase of surface area of the adsorbent. Hence, finely powder metals and porous substance having large surface area perform well as adsorbent[71]. The surface area for a given weight of the adsorbent is inversely proportional to the particles size of solid. It follows from this that the more finely divided or the more porous the solid, the greater is the surface area and hence the greater is the adsorption capacity. Subsequently, the increase in active sites of the surface will lead to an increase in adsorptive capacity[69].

(3) Nature of adsorbate

The adsorption percentage depends on the adsorbate nature and the chemical and physical properties, such as polarity, size of adsorbed molecule, stereochemistry and the presence of different substituent groups in the molecule would rule the ability of the molecule to be adsorbed on a specific surface[10]. It is decrease with increasing solubility of the solute in a solvents[60,67]. The initial concentration of heavy metals has an effect on the adsorption percentage cause it acts as driving force to overcome the resistance of the metal transfer from the solution phase to the solid phase[72].

(4) Effect of the mixed solute

The presence of many metal ions in the wastewater, there may be impacts of the separation sites. Hence the importance of describe the manner of ions in mixtures of solution and also the importance of studying the effect of single metal concentration on the uptake of other ions[73].

The uses of adsorption for purification of effluents, the metal (pollutants) to be adsorbed will be mixture of several metals rather than a single one. The materials may mutually promote adsorption, may work relatively a single one. The compounds may mutually enhance adsorption, may act comparatively autonomous or may overlap with one another. In solutes which contain mixed of pollutants, each solute completes in some way with the adsorption of the other. The degree of mutual inhibition of competing should be related to the relative size of the molecules being adsorbed, to the relative adsorptive affinities and the relative concentrations of the solutes.

The presence of the other solutes in the mixture adversely affects adsorptions of the first, leading to much more rapid breakthrough of this material[74].

(5) Effect of the solvent

The solvent molecules compete with solute molecules in adsorption process to occupy the distributed adsorption sites on the adsorbent. This competition depends on the interaction between solute and the adsorbent surface, solvent and adsorbent material and the interaction between solute and solvent. Therefore, the resultant of these interactions is greater as the interacting groups are similar in polarity[75].

(6) Effect of the temperature

The impact of temperature onto percentage from adsorption depends on the type of adsorption and nature of both adsorbate and adsorbent. It is known that adsorption decreases with increasing temperature means, depending on the "Le-Chatelier's" principle, that this sorption is an exothermic process and occurs as a physisorption. On the other hand, increasing adsorption with a rise in temperature means "adsorption processes endothermic". In chemisorption, the quantity adsorbed may (decreases or increases) with rising temperature depending on the type of interaction and the bonding between the surface and the adsorbed molecules[10,70,76].

(7) Effect of the pH

The effect of pH on adsorption processes is due to the distribution of the surface charge of the adsorbent which can be changed. Also, the pH of the solution change has a great effect on the extent of the adsorption through its influence on the adsorbate, the chemical state of the adsorbent, and the solvent. This effect can be observed through the competition on (H^+) and (OH) ions and their overlapping with the adsorbent surface or the adsorbate or the solvent.

The degree of ionization of a species is affected by pH (e.g., a weak acid or a weak basis). This in turn affects adsorption. As a result of this interaction, the varying extent of adsorption either increases, decreases, or remains unchanged according to the adsorbate functional groups[76].

1.4. Adsorption isotherms

The adsorption processes is commonly studied through graphs famous as adsorption isotherm. It is the graph between the amount of solute adsorbed on the surface of adsorbent (Q_e) ion of the solute in the solution and the equilibrium concentration (C_e) at constant temperature[77]. Several different types of isotherms have been presented in the literature; the isotherm shape depends on the type of (adsorbent and adsorbate), and intermolecular interactions between the adsorbate and adsorbent. Adsorption isotherms are typically nonlinear because of the energetic heterogeneity and the limited active sites of the solid partition[78].

Various isotherms were observed and classified by Giles and Coworkers, to describe the adsorption on solid active surface as in *Figure (1.4)*[79], which are;

1. **S-curves:** Indicative of vertical or flat orientation of adsorbed, there is strong inter-molecular attraction within the adsorbed layer, and the adsorbate is nonfunctional. In the initial part of an S-curve, the more solute is already adsorbed, the easier it is for additional amounts to become fixed.

2. **L-curves:** Where the sites are few and widely separated and a monolayer adsorption is formed, so as this type refers to as normal Langmuir isotherms indicative of molecules adsorbed flat on the surface like carbon series or cyclic hydrocarbons. The solute is adsorbed; the harder it is for additional amounts to become fixed.

3. **H-curves:** It is that attained when there is high adsorption affinity as in the case of high molecular weight compounds like: proteins and polymer, this isotherm can be observed even if the solution is very dilute.

4. **C-curves:** It is a constant-partition linear curves which are given by substances, that penetrate into the adsorbent more readily than the solvent does[79 – 81].
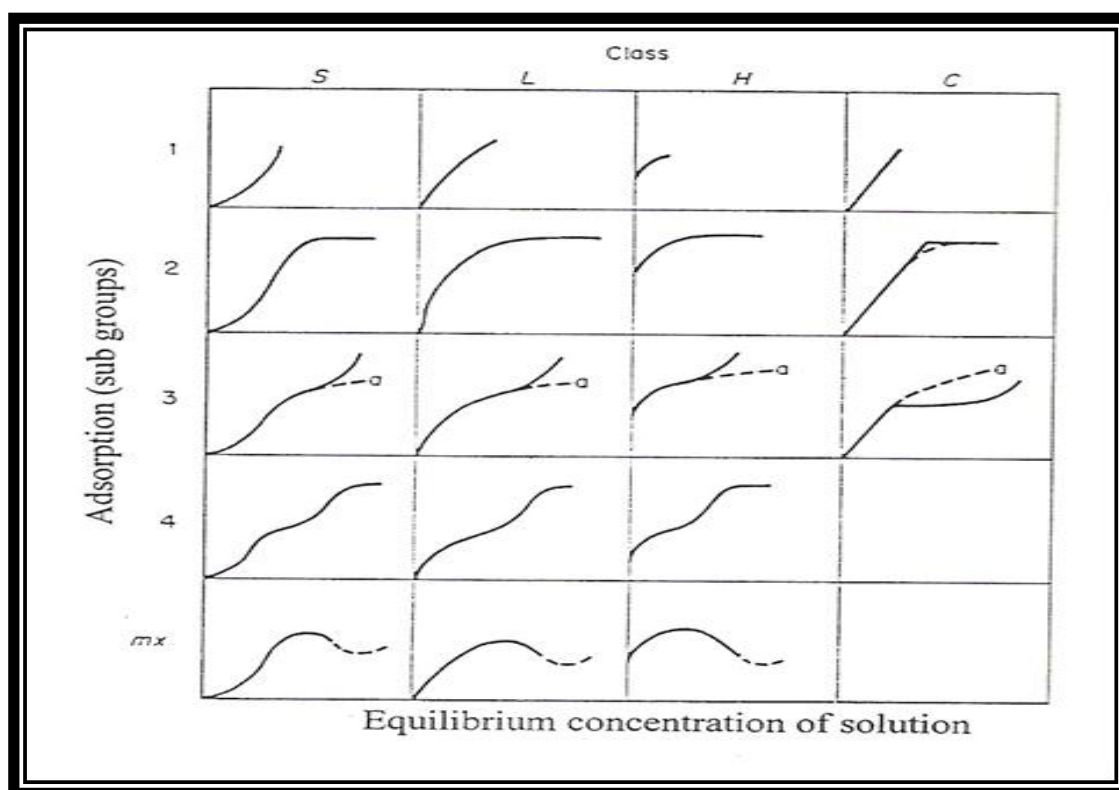
Figure (1.4): Adsorption isotherms as in Giles classification

1.5. Theories of adsorption

There are many types of adsorption isotherms and the most important ones are the following;

1.5.1. Langmuir isotherm

The American chemist Iraving Langmuir who was a awarded the Nobel Prize for chemistry in 1932 for "his discovies and researches in the realm of surface chemistry", are developed the relationship between the amount of gas adsorbed on surface and the pressure of that gas in 1916[82].

A model is set up that depends upon there being a fixed number of adsorption sites on adsorbent surface, each site capable of holding one molecule of adsorbate. All sites are equivalent in their affinity for adsorption of molecules, and the surface is uniform so that there is no interaction between the adsorbed molecules.

Langmuir adsorption is monomolecular, it does not consider the case that further adsorption may take place on the adsorbate that is already present on the surface. The Langmuir isotherm can be expressed as follow[83-85]:

$$\frac{C_e}{Q_e} = \frac{1}{ab} + \frac{C_e}{a} \;\ldots\ldots\; (1.1)$$

Where**:**

Q_e: The adsorption capacity at equilibrium per unit weight of adsorbent, **(mg/g)**.

C_e: The equilibrium concentration of adsorbate after adsorption, **(mg /L)**.

a: The Langmuir constant which is a measure of adsorption maximum capacity, **(mg/g)**.

b: The Langmuir constant which is a measure of energy of adsorption ,**(L/mg)**
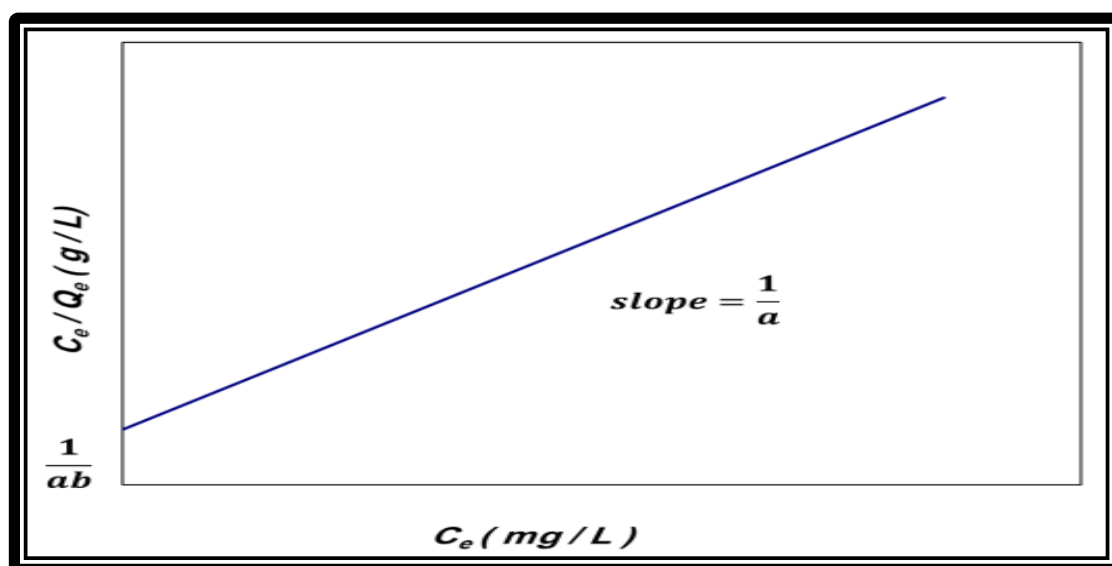
Figure (1.5): The linear form of Langmuir isotherm

This form can be used as a linearization of experimental data by plotting (C_e/Q_e) aganist (C_e) as shown in *Figure (1.5)*. The Langmuir's constants **(a)** and **(b)** can be evaluated from the slope **(1/a)** and intercept **(1/ab)** of the linear equation[83].

1.5.2. Freundlich isotherm

Herbert Max Finley Freundlich, a German physical Chemist, in 1926 presented an empirical adsorption isotherm for non-ideal system. In the derivation of Langmuir isotherm, it has been assumed that there is independence and similarity in binding energy at each adsorption site. This linear relationship is obeyed by many but not all adsorbates at low concentration[82].

His proposal was based on the experimental measurements. Freundlich adsorption isotherm equation may be derived assuming a heterogeneous surface with adsorption on each class of sites obeying the Langmuir equation.

The heterogeneous adsorption sites have different potential energies and different geometrical shapes on the surface, so the affinity from site to site toward the same molecule is different. The equation of Freundlich is as follows[85-87]:

$$Q_e = K_f \, C_e^{\,1/n} \ldots\ldots\ldots (1.2)$$

Where:

Q_e: quantity of adsorbate adsorbed per unit weight of adsorbent at equilibrium, **(mg/g)**.

C_e: equilibrium concentration of adsorbate in solution after adsorption, **(mg/L)**.

n: adsorption process extent.

K_f: Freundlich constant, **(mg/g)**.

The Freundlich constants can be obtained from the slope and intercept of the plot between the **(log Q_e)** versus **(log C_e)** after taking logarithms both side of equation **(1.2)** we get:

$$\log Q_e = \log K_f + 1/n \log C_e \ldots\ldots\ldots (1.3)$$

If **(log Q_e)** is plotted against **(log C_e)** a straight line should be obtained as shown in *Figure (1.6)*. The slope of the line will give the value of **(1/n)** and the intercept on the Y-axis gives the value of **(log K_f)**[83].
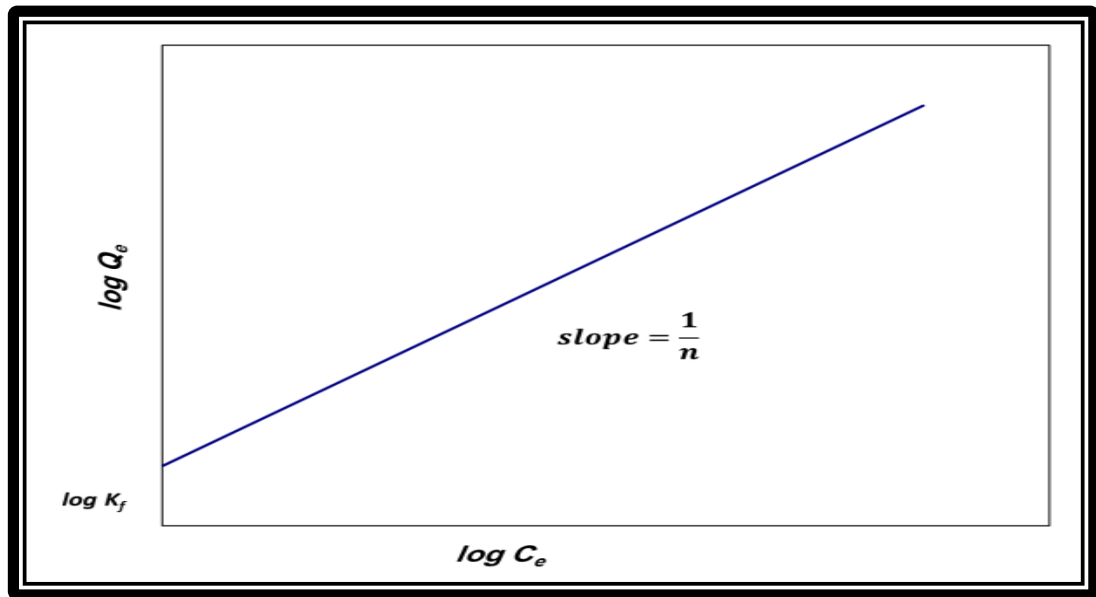
Figure (1.6): The Linear relationship Freundlich isotherm

1.5.3. Temkin isotherm

Temkin isotherm contains a factor that explicitly takes into account (adsorbing species- adsorbent interaction). This isotherm assumes that:

1. The heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent –adsorbate interactions.

2. The adsorption is characterized by a uniform distribution, and that energy, up to some maximum binding energy.

The Temkin isotherm is given by the following equation[82,88]:

Qe = B$_T$ ln (A$_T$. C$_e$)……… (1.4)

Where:

A$_T$: is the equilibrium binding constant, **(L/g)**.

B$_T$: the Temkin isotherm constant which can be obtained as follow:

$$B_T = RT / b_T .... (1.5)$$

Where:

b_T: is related to heat of adsorption, **(J/mol)**.

R: is the universal gas constant, **(8.315 J/mol.K)**.

T: is the absolute temperature, **(K)**.

A linear form of Temkin isotherm was obtained by rearranging equation **(1.4)**:

$$Qe = B_T \ln A_T + B_T \ln Ce \ldots\ldots\ldots \ (1.6)$$

The Temkin constants **(A_T)** and **(B_T)** were obtained from the slope and intercept of the plot between the Q_e and $\ln C_e$.

1.6. Nanomaterials

Nano material is defined as a physical substance with one dimension at the lowest between (1-100) nm, $(1nm = 10^{-9}m)$ have received considerable interest because of the unique properties different from their bulk counterparts[89,90]. There are various applications for nanotechnology such as fuel cells, hydrogen storage, antibacterial activity, homogeneous and heterogeneous catalysis, electronics, optics, magnetism, material sciences, medical and biological sciences[91]. Modern advances in field nanotechnology have drove to the development of adsorbent nanoparticles for chromatographic uses. The morphology feature, high surface and small size made these materials to be utilized in removal technology.

The large surface area of the nanoparticles supplies more sites on the sorbent that increases the sorption capacity. Nanomaterial exhibit configuration of distinctive novel properties which can be used for separation of heavy metals from wastewater or water in the advance development of water treatment technologies.

Many nano-sized materials, such as metal oxide, zeolites, carbon-based nanoparticle, nano-clays, nano composites, have been used as adsorbent to remove heavy metal ions from water or wastewater[92]. Metals oxides nanoparticles are a highly valued material with various applications in optical, electrical and mechanical devices, catalysts, gas sensors, sunscreens and cosmetics[93].

Many physical and chemical methods have been utilized for preparation of nanoparticles. However, a number of methods present disadvantages including use of high-energy consumption, hazardous products, toxic solvents…. etc., therefore there is an essential need to develop environment friendly methods for synthesis of metal nanoparticles.

The development of eco-friendly technologies in material synthesis is of considerable importance to expand their biological applications. Nowadays, varieties of green nanoparticles with well-defined chemical composition, size, and morphology have been synthesized by different methods and their applications in many innovative technological areas have been explored[94]. The renewable nature of plant extracts, eco-friendly aqueous medium and mild reaction conditions make the method advantageous over other hazardous methods. In the last years, different kind plants extract and their products have received attention due to its low cost, energy-efficient and nontoxic behavior in approach for synthesis of metal nanoparticles[95].

1.7. Copper oxide nanoparticles (CuO)

Copper oxide is a composition from two elements copper in the block d and oxygen in the block p of the table periodic. It is reduced to metallic copper when it meets with hydrogen or carbon monoxide under high temperature[96]. Copper (II) oxide belongs to the monoclinic crystal system. The lattice parameters for CuO are (a = 4.6837, b = 3.4226, c = 5.1288, α = 90°, β = 99.54°, γ = 90°). In the crystal copper ions is coordinate by 4 oxygen ions in an approximately square planar configuration, as shown in *Figure (1.7)* [97]:
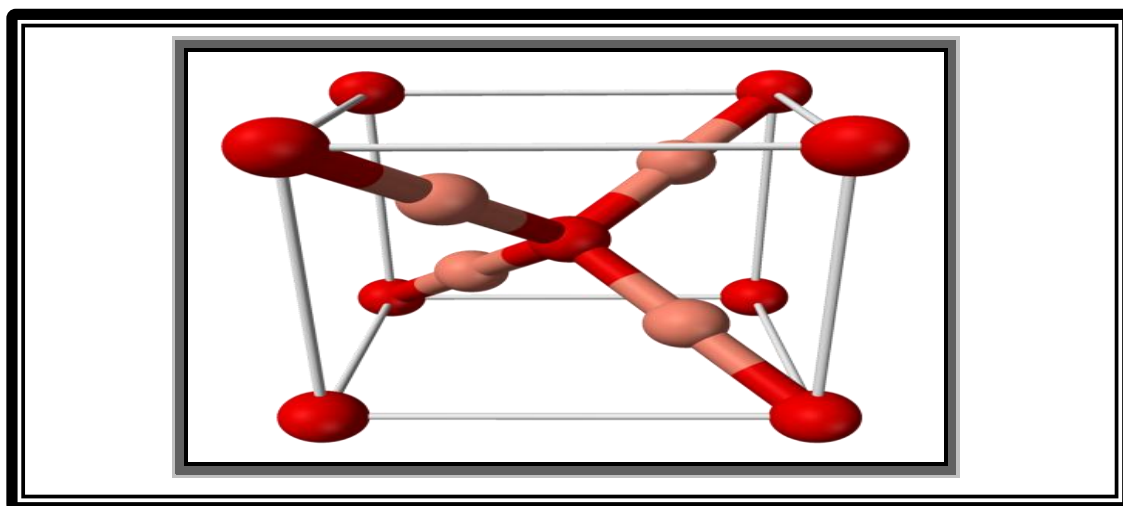
Figure (1.7): The crystal structure of CuO nanoparticles

Metal oxide (CuO) nanoparticle is a powder insoluble in (H_2O), soluble in $(NH_4)_2CO_3$, dilute acid, NH_4Cl, potassium cyanide solution and it dissolves slowly in ammonia solution and alcohols[96].

Copper oxide nanoparticle is a semiconductor. Semiconductor materials have been more particularly interesting cause of their great practical importance in electronic and optoelectronic devices, such as electro chemical cell[98]. The utilized of CuO nanoparticle to remove heavy metals from polluted water has greater interest by research cause copper oxide nanoparticle has important properties is high efficiency and low cost. nanoparticle appear good and sorption efficiency and greater active sites[99].

There are many methods for the synthesis of copper oxide nanoparticle such as: sonochemical, vapor deposition, electrochemical method, combustion, colloid thermal synthesis process, microwave irradiation, thermal oxidation, pulsed wire explosion methods, precipitation, and sol-gel[100- 102]. The sol-gel technique is considered as one of the most important and famous technique to synthesis nanoparticle. Chemical synthesis methods lead to presence of some toxic chemicals absorbed on the surface that may cause adverse effects in medical applications[103].

Green synthesis of nanoparticles using plant extracts is an emerging area of research and is potentially advantageous over chemical or microbial synthesis as it eliminates the elaborate process and can also meet large-scale production with the properties synthesis green low cost and quite novel[104].

Recently, green synthesis of different nanoparticles by plants such as neem alfalfa , lemon grass , tamarind , bark extract , leaf extract ,fruit , tea and coffee powder , peel extract and flower extract….ect.[105]

1.8. Literature Survey

Nanoparticle preparation and study of nanoparticles are important in the recent research. Nano-metals find applications in diverse fields, such as adsorbent, catalysis, optics, magnetism, material science and even in medical and biological sciences.

(Aparna, et. al, 2012), studied the preparation of copper oxide nanoparticles and was characterized its morphology and size by using (XRD, TEM, TG-DTA and SEM). The X- ray pattern revealed cupric oxide nanoparticle to have monoclinic structure and TEM photo graph shows that all particles size have good agreement with the size of XRD calculations[106].

(Arora, 2013), synthesized CuO by simple precipitation method. It was characterized by utilizing (XRD, TEM and Magnetic measurements techniques). The result of X-ray diffraction studies describe that copper oxide was formed as CuO and it has monoclinic structure and it consists of one unpaired electron and is paramagnetic. The result of TEM technique show that the particle size ranges between (12-35) nm[107].

(Phiwdang, et. al, 2013), prepared copper oxide nanoparticles used precipitation method utilizing various precursors such as; copper chloride and copper nitrate. The products were characterization by XRD, SEM and FT-IR spectroscopic and results explain that the formation of CuO nanoparticles with varies (morphology, size and shape) can be carried out utilizing varied precursors[108].

(Devi and Singh, 2014), in their research showed the preparation of copper oxide nanoparticles using *Centella asiatica* (L.) leaves extracts at room temperature. Copper oxide nanoparticles size and morphology are determined by characterization techniques such as; UV-visible spectroscopy, SEM, EDX and IR spectroscopy. (CuO) nanoparticles prepared by this method can be used for the photo catalytic degradation of methyl orange as it can reduce methyl orange in aqueous medium in the absent of reducing agents[99].

(Mayekar, et. al, 2014), studied the preparation of copper oxide nanoparticles by wet chemical precipitation method and characterized by using (X-ray diffraction, Scanning electron microscopy and Energy dispersive X-ray spectroscopy). The results of X-ray diffraction showed that copper oxide nanoparticles was formed and it has monoclinic structure with a particle size range (20-30) nm width and (100-200) nm length[109].

(Sutradhar, et. al, 2014), prepared copper oxide nanoparticles by using tea leaf and coffee powder extracts under control microwave irradiations and was suggested to use irradiate copper salt and extracts of tea and coffee in (1:3) ratio in a microwave at (540) W. The synthesized nanoparticles were characterized by some technique such as (Scanning electron microscope, X-ray diffraction, UV-visible spectroscopy and Fourier transform infrared spectroscopy. The copper oxide nanoparticles exhibited antibacterial activity against two human pathogenic bacteria[110].

(Kumar, et. al, 2015), discussed the preparation and characterization of cupric (II) oxide, it is synthesis by using *Alo Vera* leaf extracts, and characterized the product powder using some techniques such as (XRD and TEM). Copper oxide are seem to have monoclinic phase with average particle size of (20) nm, it is exhibits antibacterial activity against the fish pathogens[111].

(Naika, et. al, 2015), discussed the synthesis of copper oxide nanoparticles by using *Gloriosa Superba* L. plant extract as fuel by solution combustion synthesis. Copper oxide nanoparticles as prepared are in nano scale and there morphology and size are characterized using; Scanning electron microscopy and UV-Visible spectroscopy. The particle size ranges (5-10) nm. Copper oxide nanoparticles prepared exhibited antibacterial activity against the pathogenic bacteria[112].

(Hariprasad, et. al, 2016), studied the preparation of CuO nanoparticles from *Arevalanata* leaf by simple method of green chemical reduction at room temperature, and their antimicrobial activity was investigated. The formed copper oxide nanoparticles was characterized using Uv-Vis, FTIR, SEM and TEM. Results proved the antimicrobial activity of it[113].

(Nagajyothi, et. al, 2017), studied the synthesis of CuO nanoparticles and anticancer activity against human cervical carcinoma cell. It was synthesis by green route using the aqueous black bean extract. The CuO powder was characterized by (Raman spectroscopy, DLS, TEM, SEM, EDX, SAED and FT-IR). The XRD explain that the average size of the nanoparticles was (26.6) nm. The CuO nanoparticles anticancer activity was also studied[114].

The adsorption of heavy metal ions on different adsorbents such as (metal oxide, zeolites, clays, activated carbon …etc) have been studied extensively in order to find a specific adsorbent for each ion to be used in the treatment of wastewater in the environment.

(Srivastava, et. al, 2006), discuss the adsorption of Cd (II) and Ni (II) ion onto the bagasse fly ash from single, and binary systems. The best condition for adsorption ions at different initial concentrations (10-100) mg/L, pH = (6), contact time (5) hour, temperature (30) $^{\circ}$C, quantity of the bagasse fly ash (10) mg/L. The single ion equilibrium adsorption data fitted to Redlich – Peters and Freundlich models were better than the Laungmuir model, while the binary adsorption data fitted to extended Freundlich model gave data satisfactorily and adequately. The adsorption capacity of Ni (II) ions is better than that for Cd (II) ions for the binary metal solutions and are in agreement with the single – ions adsorption data[115].

(Elouear, et. al, 2009), studied the removal of Ni^{+2} and Cd^{+2} ions from dilute solutions used sewage sludge ash in single and binary system. The impacts of contact time, pH, initial metal ion concentration and temperature on the removal of these metal ions were studied. The results indicated that the affinity of the sewage sludge ash for Ni^{+2} removal was greater than that Cd^{+2} from single and binary solution under the same condition[116].

(Boujelben, et. al, 2009), studied the uptake two metals of copper ions and nickel ions in (single and binary) systems by iron oxide-coated sand and factor inflecting on the adsorption are; (equilibrium time, temperature, pH and initial concentration). Adsorption processes have been applied to Freundlich and Laungmuir models. An adsorption from binary metals were endothermic.

The removal of copper was better than nickel. Sorption of Ni^{+2} and Cu^{+2} ions on single system is more effectives than on binary one[117].

(El-Said, et. al, 2010), studied the competitive removal of cadmium and mercury ions by rice husk ash from single and binary systems. The optimum condition of the adsorption were contact time (6) hour, temperature (25) $^{\circ}$C, rice husk dosage of (10) g/L at pH (6). The adsorption capacity of Cd (II) is more than that for Hg (II) in the binary solutions and is in agreement with the single – component adsorption data. Isotherms for the binary adsorption of Cd (II) and Hg (II) ions by the rice Husk have been analyzed by utilized Langmuir, and Freundlich models[118].

(Boparai, et. al, 2011), investigated the adsorption of cadmium ions at concentration range of (25- 450) mg/L onto nano zerovalent iron surface. From temperature effect on kinetics, an endothermic adsorption processes. Kinetics well fitted using a pseudo second- order model, and the calculated activation energy for adsorption was (54) KJ/mol indicating the adsorption process to be chemisorption. The adsorption isotherms obtained were fitted well into the Laungmuir and Temkin isotherms showing that the adsorption processes was endothermic and spontaneous in nature[119].

(Debnath and Ghosh, 2011), studied the adsorption reactions of Cd (II) and Cu (II) ions with nanoparticles agglomerates of titanium (IV) oxide from single and binary component systems at pH (5). The kinetics of the cadmium ion adsorption on the titanium (IV) oxide was found to follow a pseudo-second order rate equation. The adsorption data fit well with the Laungmuir and Redlich- Peterson models. Thermodynamic adsorption at equilibrium investigated that the removal reaction were spontaneous and endothermic[120].

(Chigondo, et. al, 2013), consider the adsorption of Pb (II) and Cu (II) ions from aqueous solutions by using baobab (Adsononsia digitata) fruit shells. The adsorption of lead (II) was found maximum at (pH=5.5) using adsorbent of (0.7) g, while the adsorption of copper (II) was found to be optimum at (pH=6) using adsorbent (0.9) g. Results indicate that the Temkin model gave a better fit to the experimental data with (R^2 values for lead (II) = 0.9977 and copper (II) = 0.9967) than Langmuir, and Freundlich models[121].

(Izidoro, et. al, 2013), synthesis pure zeolite (X, A) and was characterized with the use of devices (XRD, SEM, BET and CEC). Results indicated from XRD and SEM that pure zeolites X and A were obtained from fly ash samples, possessing high CEC at (3.1-3.9) meq/g. Zeolite X and A were utilized in removal of Zn^{+2} and Cd^{+2} ions in single and binary systems. It was showed that Zn (II) ion is more preferentially uptake onto zeolite than Cd (II) ion in both single, and binary systems under similar experimental condition. The adsorption of both ions by zeolite A was less impacted by presence of a competitive ion, in opposite than zeolite X[122].

(Roy and Bhattacharya, 2013), studied separated Cd (II), Co (II) and Ni (II) ions in binary, ternary and single systems by γ- Fe_2O_3 nanotubes. The adsorption capacity of Cd (II) is (94.33) mg/g, Ni (II) is (86.206) mg/g, and Co (II) is (60.60) mg/g. The adsorption kinetics results indicated to be pseudo–second order. The adsorption process followed Langmuir isotherm compared to Freundlich model[52].

(Sdiri, et. al, 2014), discuss the use of natural clay (Calcareous and Smectitic clay) for the adsorption of Cu (II) and Zn (II) from aqueous solutions in single and binary systems. The best conditions for adsorption of copper (II) and zinc (II) ions were found to be pH = 6, mixing (1) g/L of each original and treated time (60) min, initial concentration of Cu (II) and

Zn (II) (300) µM and Cu (II) (600) µM, agitation speed of (200) rpm, temperature at (25) °C for single and binary systems. The adsorption of each metal ions in single and binary systems obey to the Langmuir isotherm. In binary system, the adsorption capacity decreased for Cu (II) and Zn (II) due to competitive influence. The adsorption processes are endothermic using calcareous clay, but exothermic process using smectitic sample[123].

(Contreras, et. al, 2015), studied the removal of cadmium (II), lead (II), and chromium (VI) in single and mixture aqueous solutions by cerium oxide nanoparticles. The adsorption processes were carried out at (pH = 5, and 7), the metal ions concentration from (1 – 10) mg/L, the dose cerium oxide from (0.064 - 0.640) g/L. Pb (II) adsorption capacity (128.1) mg/g, Cd (II) (93.4) mg/g, and Cr (VI) (34.4) mg/g were obtained. The type of system (single and multi-component) did not affect sorption capacity. The pH impacted the adsorption of cadmium (II) and chromium (VI) ions, but not lead (II) ions[124].

(Saikrishna and Babu, 2015), studied the preparation of nickel oxide nanostructure using solution combustion technique employing glycine as a fuel and characterized the surface area by BET analyzer and studied the ability for removal of Cu (II) and Pb (II) ions from aqueous solution using nickel oxide nanostructure. The processes reached equilibrium in (30) min, the pH of solution for removal copper (II) and lead (II) ions in aqueous solution were found to be (9) for lead ion, and (7) for copper ion. The adsorption isotherms obtained fitted well into the Freundlich and Langmuir model at concentration of metal ions ranging from (0.1 - 1.0) mg/L[125].

(Taman, et. al, 2015), studied the removal of Fe (III) and Cd (II) binary system by copper oxide nanoparticles, and considering their adsorption properties; (pore size distribution, surface area, the chemical structure and morphology). Results showed that pH (6) was the most stable one, contact time (20) min at different solution concentration (250, 100, 50, and 25) mg/L. The adsorption processes were determined using both Langmuir and Freundlich isotherms, Cd (II) ion adsorption data fitted well to Langmuir equation but Fe (III) ion one fitted to Freundlich equation[126].

(Alswat, et. al, 2016), in their research studied the applicability of the prepared (zeolite/copper oxide) and (zeolite/iron oxide) nanocomposites to sorption of lead and arsenic from aqueous solution, The best condition for adsorption of lead and arsenic were found to be contact time (40) min, dose of adsorbent (0.15) g. The percentage removal of Pb and As, 97.2 % and 96.8 %, respectively, concentration of each metal ion (100) mg/L, the pH aqueous solution between (4) and (6), kinetic data were best described by pseudo-second order model. Freundlich and Laungmuir isotherm models were applied to the equilibrium data[127].

(Hassan and Mahdi, 2016), prepared CuO and Fe_3O_4 nanomaterials, structural characterization using X-ray diffraction indicated that the particle size of CuO and Fe_3O_4 were (7.43) nm and (12.04) nm respectively, this is being confirmed by scanning electron and atomic force microscopy techniques, and these oxide utilized to remove lead ions from its aqueous solution by adsorption. The test data refer to removal efficiency of 84.162 % using copper oxide, and 88.028 % using iron oxide[128].

1.9. Aims of the study

1. Preparation of copper (II) oxide nanoparticles using (sol-gel) and *Fig* Leaves Extract methods and characterization them by using (X-ray diffraction, Scanning electron microscope, Transmission electron microscope and Atomic force microscope).

2. Utilize of copper (II) oxide nanoparticles prepared by two methods different as a nanoadsorbents materials for the removal of cadmium (II) and nickel (II) ions from their binary systems.

3. Determining the ideal condition for the adsorption of Cd^{+2} and Ni^{+2} ions in binary system such as (contact time, quantity adsorbent, pH, temperature, initial concentration).

4. Determination of the appropriate adsorption isotherm of nickel (II) and cadmium (II) ions in each of the binary and single systems using the two prepared adsorbents.

5. Thermodynamic studies of adsorption processes of metals ion in binary system.

Chapter Two

(Experimental)

2.1. Instruments

2.1.1. Instruments and tools used in preparation

The instruments and tools that are used in this study were listed below with their details, origin, and place of measurement.

Table (2.1): The instrumentation used in this study.

NO.	Instruments names	Details & Origin	Place of measurement
1	**Electric Balance**	KERN $_{ACJ/ACS}$, ACS 120-40, WB 12 AE 0308, max 120 g, d= 0.1 mg, **(Germany)**	The Laboratories of Chemistry Department, College of Science, University of Diyala, Iraq
2	**Oven**	BINDER , Hotline International (20-360°C), **(Germany)**	
3	**pH Meter**	PH/Ion Benchtop WTW inoLab PH Meters 7110 Benchtop Meters, **(Germany)**	
4	**Hot Plate Magnetic Stirrer**	MS-H280-pro ISO LAB Laboratory GmbH, **(Germany)**	
5	**Water Bath with Shaker**	BS – 11, 230 VAC – 50 H$_z$, **(Korea)**	
6	**Centrifuge**	HERMIE LABORTI CHINK Type Z200A, 6000 rpm, **(Germany)**	
7	**Distillation device**	LUZ DE AVISO AGUA INSUFICICENTE, **(Germany)**	
8	**Electrical Furnace**	Type - KR 170 E, Max Temperature 1150°C , 220 V, 13.8 A, 50/60 H$_z$, **(Japan)**	The Laboratories of Physics Department, Collage of Science, University of Diyala, Iraq

2.1.2. Apparatus used in characterization

The apparatus used are shown in ***Table (2.2)*** with their details, origin, and place of measurement.

Table (2.2): Apparatus used in Characterization.

NO.	Apparatus names	Details & Origin	Place of measurement
1	**X-ray Diffraction Spectroscopy (XRD)**	XRD-6000 Cukα (λ=1.5406 A°), 220/50, HZ, SHIMADZU, **(Japan)**	Lab. of X-Ray Diffraction in Central Service laboratory, College of Education Ibn- AL-Haitham, University of Baghdad, Iraq
2	**Atomic Absorption Spectroscopy Photometer (AAS)**	Shimadzu AA-7000, **(Japan)**	Lab. of Atomic Absorption Flame in Central Service laboratory, College of Education Ibn- AL-Haitham, University of Baghdad, Iraq
3	**Atomic Force Microscope (AFM)**	Scanning Probe Microscope, AA 3000 SPM 220 V-Angstrom Advanced Inc, AFM contact mode, **(USA)**	The Special Laboratory of Dr. Abdulkareem M.A. AL-Sammarraie, Iraq
4	**Scanning Electron Microscope (SEM)**	TESCAN , Vega III, Czech **(Republic)**	Lab. of Nano, Ministry of Science and Technology, Iraq
5	**Transmission Electron Microscope (TEM)**	JEOL 2100Plus instrument operated at 200kV, **(UK)**	Electron Microscopy Laboratory, Chemical Analysis Facility, University of Reading, UK

2.2. Materials

2.2.1. The chemical materials

The properties of chemicals used in this work are shown in the following *Table (2.3):*

Table (2.3): The chemicals used.

NO.	Chemicals	Formula	Purity	Molecular mass	Source
1	Copper (II) chloride dihydrate	$CuCl_2.2H_2O$	99 %	170.48	Merck
2	Citric acid	$C_6H_8O_7.H_2O$	99.9%	210.14	Panreac Espana
3	Sodium hydroxide	NaOH	99 %	40	Alpha chemical
4	Hydrochloric acid	HCl	37 %	36.46	J.T. Baker
5	Nickel (II) chloride hexhydrate	$NiCl_2.6H_2O$	99 %	237.599	Panreac Espana
6	Cadmium(II) chloride monohydrate	$CdCl_2.H_2O$	99 %	201.317	India
7	Ethanol absolute	C_2H_5OH	99.9 %	46.069	GCC

2.2.2. Adsorbates used in this study

The heavy metals used as adsorbates in this work were **Ni (II)** and **Cd (II)** ions. Based on it is being strong pollutants need to be removed from wastewater.

2.2.3. Adsorbents used in this study

1- Copper oxide nanoparticles prepared by (sol-gel) method denoted as: **(SGP.CuO.NP)**.

2- Copper oxide nanoparticles prepared by *Fig* Leaves Extract denoted as: **(FLEP.CuO.NP)**.

2.3. Preparation of adsorbents

2.3.1. Preparation of copper (II) oxide nanoparticles using chemical method (sol-gel), (SGP.CuO.NP)

Dissolve (2.5) g of copper (II) chloride dihydrate $(CuCl_2.2H_2O)$ in (30) ml of distilled water with constant stirring, and dissolve (2.94) g of citric acid $(C_6H_8O_7.H_2O)$ in (30) ml of distilled water with constant stirring, the mole ratio of copper (II) chloride dihydrate to citric acid is (1:1).

These two solutions were mixed together in a beaker using a magnetic stirrer at (20) ℃ for (10) min until solution becomes smooth a slimy blue colored, as shown *Figure (2.1-A)* .Sodium hydroxide (NaOH) (8) M was slowly added in the form of drops into the mixed solution to control it pH until reach the value of (7) with continuous stirring till the solution become dark blue color, as shown *Figure (2.1-B)*. It was subsequently raise the temperature of the solution to (60) ℃ for period of (1) hour and then increase the temperature to (80) ℃ for (2) hours, as shown *Figure (2.1-C)*. After that the size of the solution in the glass beaker is reduced and viscosity increased with the beginning of gel formation on the solution surface, particularly in the middle and then all the solution turn to gel, at this moment, the solution is still on the magnetic stirrer at a temperature of (80)℃, as shown in the *Figure (2.1-D)*. After the completion of the solution turned to gel, reduce the temperature of the gel to room temperature.

Where the weight of the gel putting in glass beaker by a sensitive balance and then put it inside the oven a temperature (120) ℃ for (3) hours to become dry gel and decreasing in weight and so the gel blue color, as shown in **Figure (2.1-E)** the evaporation of some of the material by raising the temperature of the dried to (200) ℃ , after (30) min the dry gel began to change shape and the   produce, as shown **Figure (2.1-F, G)** and clacined at (450) ℃ for (2) hours with bring result copper oxide nanoparticle, as shown **Figure (2.1-H)**. **Figure (2.2)** is flow diagram showing the steps for preparing copper (II) oxide nanoparticles using (sol-gel) method.

(A)   **(B)**   **(C)**   **(D)**

(E)   **(F)**   **(G)**   **(H)**
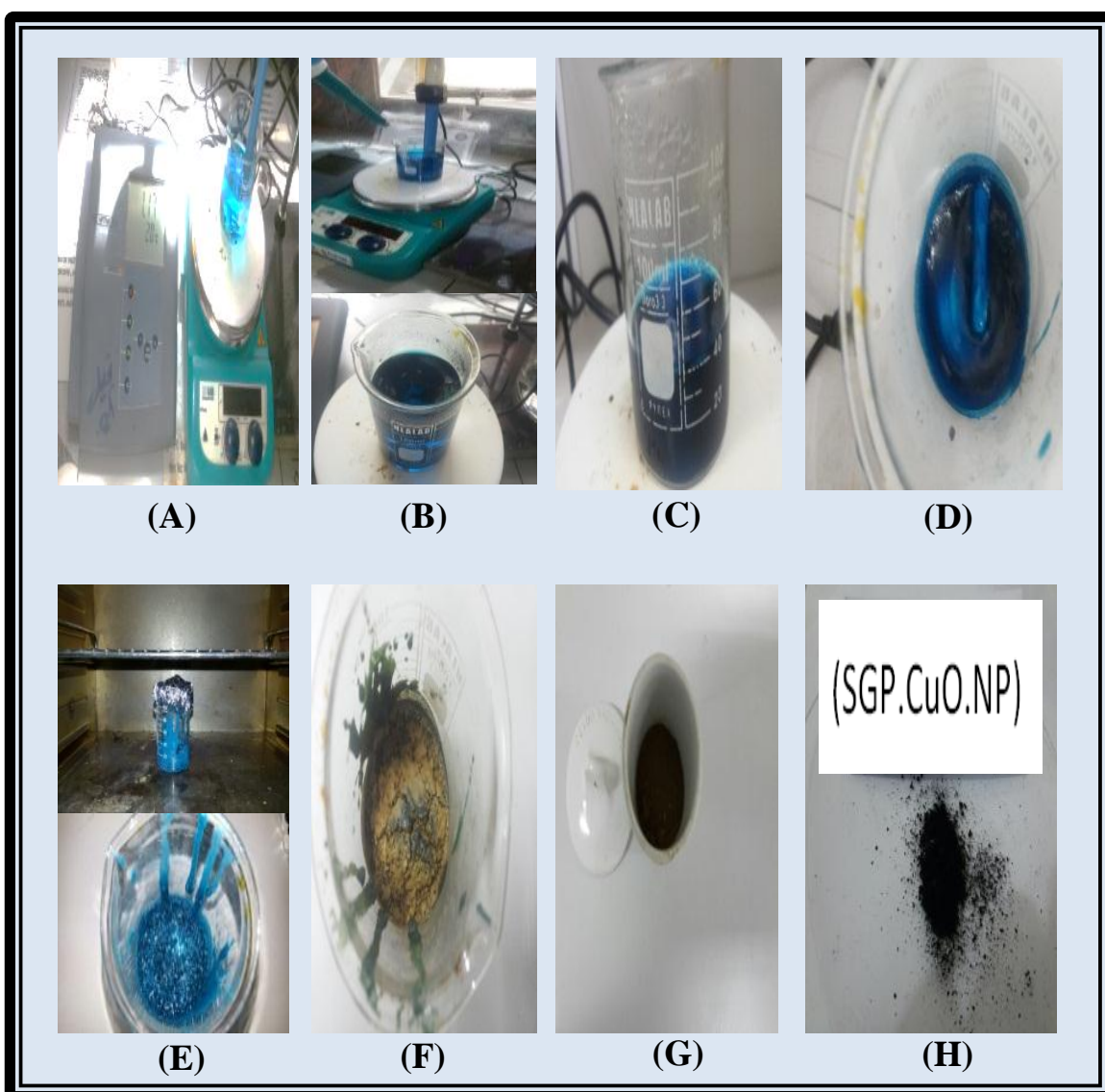
Figure (2.1): Steps of the preparation of copper (II) oxide nanoparticles using (Sol-Gel) method.
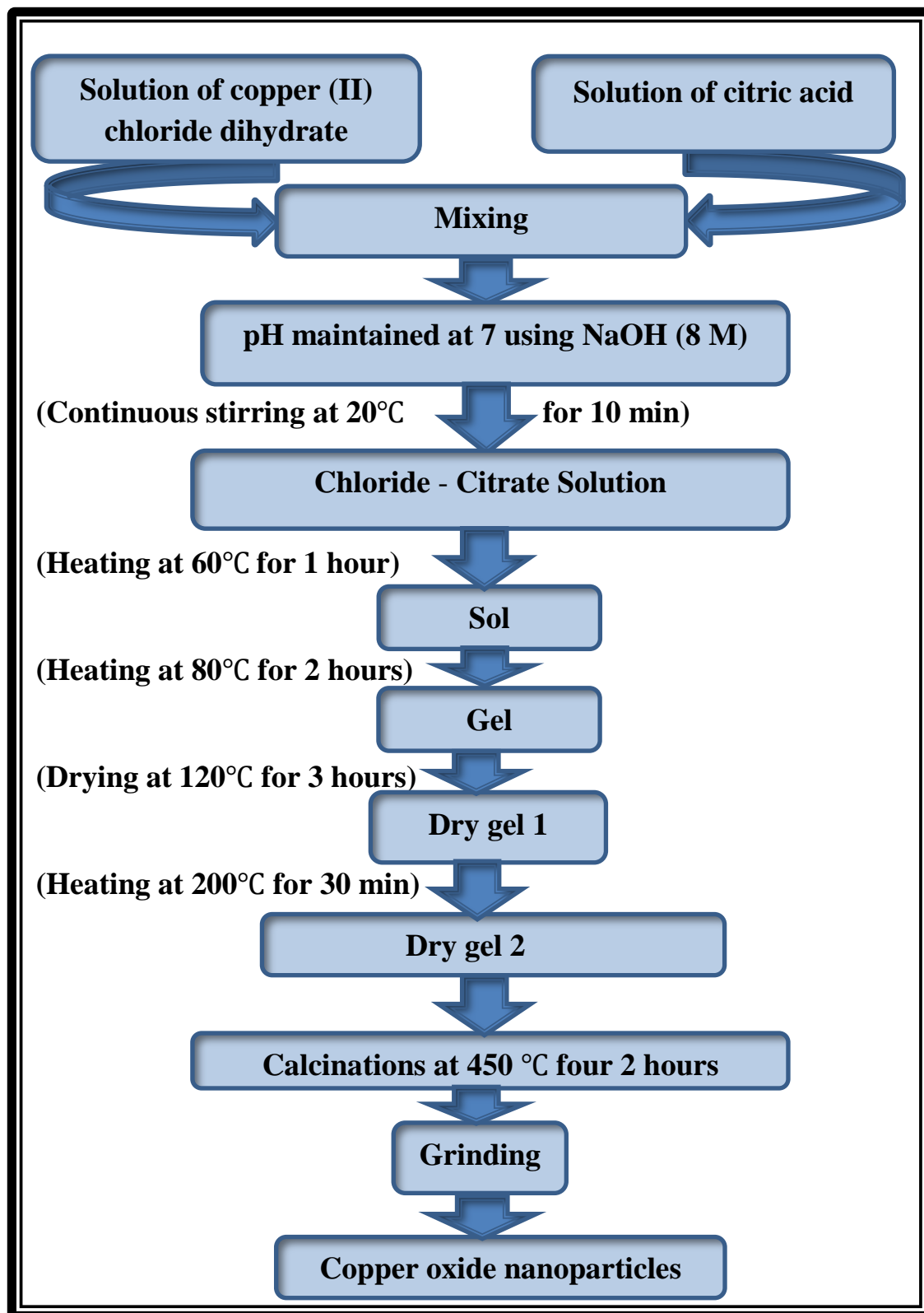
Figure (2.2): Flow diagram showing the steps used in preparing copper (II) oxide nanoparticles using (Sol-Gel) method.

2.3.2. Preparation of copper (II) oxide nanoparticles using *Fig* Leaves Extract, (FLEP.CuO.NP)

The *Fig* Leaves were collected from the tree in a house garden, then cleaned from the suspended dirt by ordinary water then washed with distilled water and dried in shade .They were grinded with electric grinder then sifting them and stored away from wet, as shown in ***Figure (2.3-A, B),*** (5) g of powder *Fig* Leaves was added to (400) ml of deionized water and boiled for (30) min until the solution color change to brown–yellow and then cool the mixture to room temperature and filter it, centrifuge the filtrate at (1200) rpm for (2) min to remove biomaterials and store the extract at room temperature for use in the preparation of the copper oxide nanoparticles, as shown in ***Figure (2.3-C, D, and E)***, dissolve (0.27) g of copper (II) chloride dihydrate ($CuCl_2.2H_2O$) in (400) ml of deionized water with continuous stirring and then (10) ml of the plant extract is added gradually with continuous stirring at room temperature where the color change from light blue to light green, in the next step, raise temperature of solution to (80)℃ and then adjusts pH of the mixture by adding sodium hydroxide (1) M approximately (10) ml where precipitate form a color brown- dark, It is then filtered and washed with deionized water several times and then with ethanol absolute to remove impurities and dry in an oven at (60) ℃ for (2) hours . The steps are shown in ***Figure (2.3-F, G, and H)***. ***Figure (2.4)*** is flow diagram showing the steps for preparing copper (II) oxide nanoparticles using *Fig* Leaves extract.
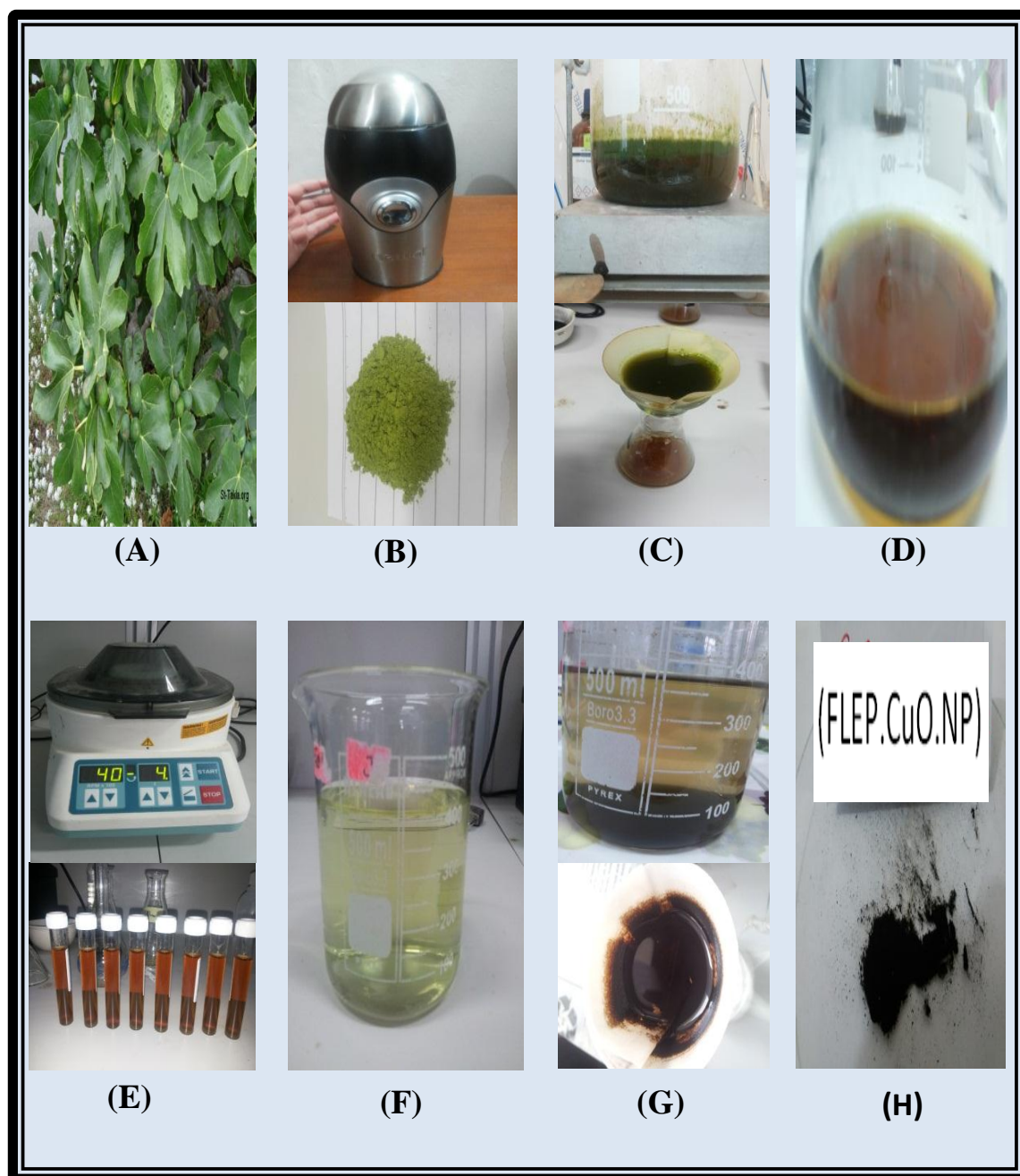
Figure (2.3): Steps of the preparation of copper (II) oxide nanoparticles using Fig Leaves Extract.
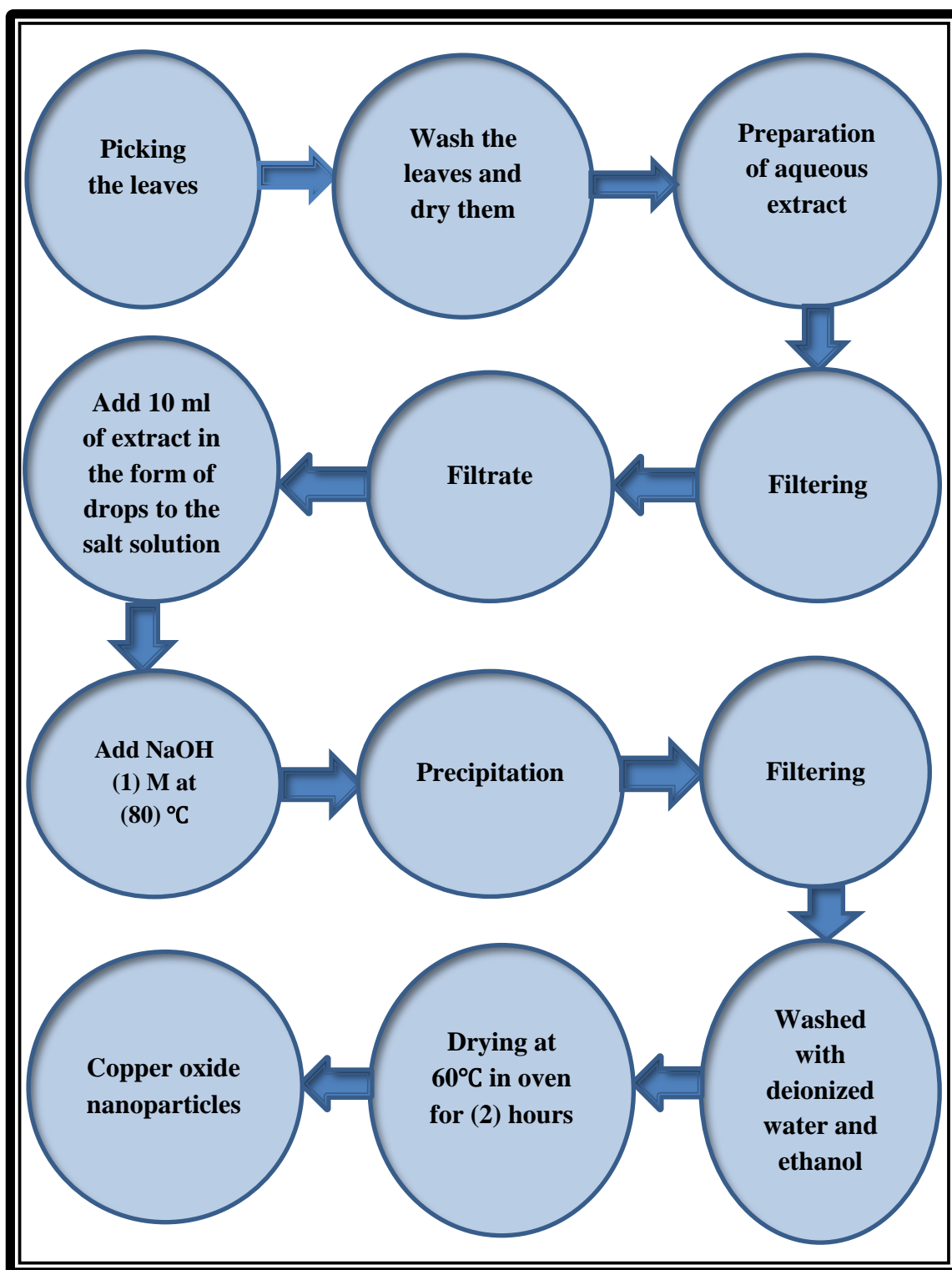
Figure (2.4): Flow diagram showing the steps used in preparing copper (II) oxide nanoparticles using Fig Leaves Extract.

2.4. Preparation of solutions used in adsorption processes

2.4.1. Hydrochloric acid

(0.1) M Solution of HCl was prepared by transferring (0.833) ml of concentration acid (12) M into (100) ml volumetric flask and dilute it to the mark with deionized water.

2.4.2. Sodium hydroxide

(0.4) g of sodium hydroxide was weighed and transferred into (100) ml volumetric flask and the volume was completed to (100) ml with deionized water to produce the (0.1) M of NaOH solution.

2.4.3. Standard stock solution of Ni (II) ions

(1000) mg/L stock solutions of Ni (II) was prepared by weighing (4.04) g of ($NiCl_2.6H_2O$) and dissolve it in deionized water and then dilute it to the mark in (1000) ml volumetric flask. A series of solutions with (20, 40, 60, 80 and 100) mg/L were prepared by adequate volumes dilution from the stock solution and deionized water.

2.4.4. Standard stock solution of Cd (II) ions

Prepared of stock solution (1000) mg/L from cadmium ions by weighing (1.791) g of ($CdCl_2.H_2O$) and dissolve it in deionized water and then dilute it to the mark in (1000) ml volumetric flask. A series of solutions with (20, 40, 60, 80 and 100) mg/L were prepared by adequate volumes dilution from the stock solution and deionized water.

2.5. Optimization of batch adsorption method

The resulting solutions of Ni (II) and Cd (II) single and binary systems were analyzed by Atomic Absorption Spectroscopy Photometer technique. Absorbance of these solutions were measured at a wavelength (λ max) (232.0) nm for nickel and (228.8) nm for cadmium.

2.5.1. Effect of contact time

Eight volumetric flasks with a volume of (100) ml containing (50) ml (25) ml of Ni (II) ion solution and (25) ml of Cd (II) ion solution with initial concentration of (100) mg/L of each one in binary system , pH of 6 and adsorbent with an amount of (0.1) g of (SGP.CuO.NP) or (0.1) g of (FLEP.CuO.NP) was added into each flask, covered with glass of stopper and placed in a water bath shaker at constant temperature (298) K with speed (150) rpm at various time intervals (15, 30, 45, 60, 75, 90, 105 and 120) min and then filtered before analysis to prevent nanoparticles interference with the analysis. The concentrations of binary metal in solution were determined using atomic absorption spectrophotometer.

2.5.2. Effect of adsorbent quantity

The effect of adsorbent quantity was studied using (0.01, 0.05, 0.1, 0.15 and 0.2) g on the removal of Ni^{+2} and Cd^{+2} ions in binary system using a fixed (25) ml of (100) mg/L Ni (II) solution and (25) ml of (100) mg/L of Cd (II) solution, pH of (6), temperature of (298) K and stirring speed of (150) rpm. The contact time for Ni (II) and Cd (II) ions adsorption used was (30) min on (SGP.CuO.NP) and (15) min on (FLEP.CuO.NP).

2.5.3. Effect of pH

Effect of pH was investigated at pH (2, 4, 6 and 8) by the dropwise addition of (0.1) M NaOH or (0.1) M HCl at following conditions; (0.1) g of adsorbent, (25) ml of Ni (II) and (25) ml of Cd (II) solution in binary system, initial concentration (100) mg/L, temperature of (298) K and stirring speed (150) rpm. The contact time was (30 and 15) min for cadmium and nickel ions on two adsorbents (SGP.CuO.NP and FLEP.CuO.NP) respectively.

2.5.4. Effect of temperature

The effect of temperature was studied at (298, 308, 318 and 333) K with the following conditions; (0.1) g of adsorbent, (25) mL of (100) mg/L Ni (II) solution and (25) mL of (100) mg/L Cd (II) solution in binary system, pH of (6) and stirring speed of (150) rpm. The contact time for binary heavy metal ions removal used was (30) min on (SGP.CuO.NP) adsorbent and (15) min on (FLEP.CuO.NP) adsorbent, and calculated value of thermodynamic.

2.5.5. Effect of initial concentration

Different initial concentrations of (20, 40, 60, 80 and 100) mg/L of cadmium (II) and nickel (II) ions in binary system were studied after optimizing all required conditions of batch adsorption method.

2.5.6. Calculation of percentage removal (R %)

The percentage removal **(R %)** was calculated using equation[129, 130].

$$R \% = \frac{(C_o - C_e)}{C_o} \times 100 \qquad \ldots\ldots\ldots\ldots\ldots (2.1)$$

Where:

R%: The percentage metal removal.

C_o: The initial concentration of metal ion, **(mg/L)**.

C_e: The concentration of metal ion after adsorption, **(mg/L)**.

2.6. Study of the adsorption isotherm

The adsorption isotherm for nickel (II) and cadmium (II) ions solution in single and binary systems on the copper oxide nanoparticles prepared by (sol-gel) and *Fig* Leaves Extract at temperature (298) K, pH of 6, (0.1)g adsorbents and stirring speed (150) rpm. The contact time was (30) min for cadmium (II) and nickel (II) ions in single and binary systems on (SGP.CuO.NP) surface and (15) min for nickel (II) and cadmium (II) ions on (FLEP.CuO.NP) surface were used.

In single system, (50) ml of Cd (II) or Ni (II) ions solution of a known concentration from (20-100) mg/L. In binary systems (50) ml, (25) ml of cadmium (II) and (25) ml of nickel (II) ions with initial concentration of Cd (II) solution, varied (20-100) mg/L with presence increasing concentration of nickel ions , in all binary metals isotherm experimental, and the nickel (II) concentration was varied in the range (20-100) mg/L with presence increasing concentration of cadmium ions, in all experimental the equilibrium metal concentration measured using atomic absorption spectrophotometer .The adsorption capacity of adsorbent was calculated using the equation below[129, 130] :

$$Q_e = \frac{(C_o - C_e) \times v}{m} \quad \text{……………..} \quad (2.2)$$

Where

Q_e **:** Adsorption capacity of the adsorbent at equilibrium, **(mg/g)**.

C_o**:** Initial concentration of adsorbate, **(mg/L)**.

C_e**:** Equilibrium concentration of adsorbate after adsorption has occurred, **(mg/L)**.

V: Volume of solution, **(L)**.

m: Weight of adsorbent, **(g)**.

Chapter Three

(Results &Discussion)

3.1. Characterization of the adsorbents

3.1.1. X-ray diffraction

The XRD technique was used to determine and confirm the crystal structure of the nanoparticles. X-ray diffraction pattern of as prepared copper (II) oxide nanoparticles by using two methods are (SGP.CuO.NP) and (FLEP.CuO.NP) are shown in *Figures (3.1)* and *(3.2)*, respectively, with the data of strongest three peaks are shown in *Tables (3.1)* and *(3.2)*. The peaks position of the samples exhibited the monoclinic structure and single phase and are agreements with those reported in JCPDS file **(NO.48-1548)**, no other impurity peak was observed in the (XRD) patterns. The broading of the diffraction peaks indicates that the crystal size is small. Therefore, (FLEP.CuO.NP) has a smaller nanoparticles size than (SGP.CuO.NP), as observed in FWHM in *Figures (3.1)* and *(3.2),* and *Tables (3.1)* and *(3.2)*.

The particle sizes were calculated from Deby-Sherrer formula in given below[131]:

$$D = \frac{0.9\,\lambda}{\beta\cos\theta} \qquad \text{.................. (3.1)}$$

Where:

D: is the crystallite size.

λ: is the wave length of radiation.

θ: is the Bragg's angle.

β: is the full width at half maximum (FWHM).

The estimated particle size of the (SGP.CuO.NP) is (21.11) nm and for (FLEP.CuO.NP) it is (7.31) nm. The presence of sharp peaks in XRD samples and particle size of less than (100) nm refers to the Nano-crystalline nature of the two surfaces.

Table (3.1): The strongest three peaks in XRD of (SGP.CuO.NP).

No.	2θ (deg)	d (Å)	FWHM (deg)	Intensity (counts)
1	35.5758	2.52149	0.35150	955
2	38.8073	2.31864	0.44450	864
3	48.8334	1.86346	0.42270	231
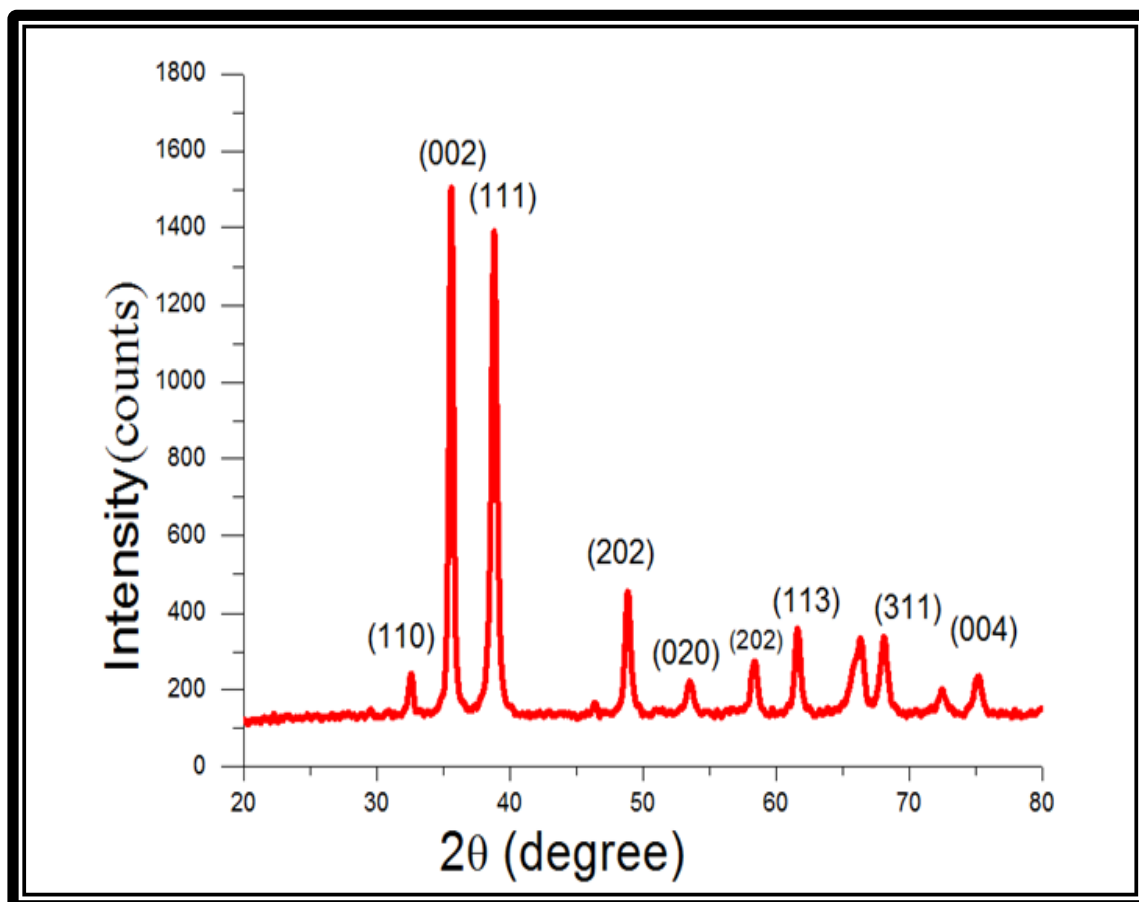
Figure (3.1): XRD of copper (II) oxide nanoparticles prepare using (Sol - Gel) method, (SGP.CuO.NP).

Table (3.2): The strongest three peaks in XRD of (FLEP.CuO.NP).

No.	2θ (deg)	d (Å)	FWHM (deg)	Intensity (counts)
1	38.6473	2.32787	1.24500	214
2	35.5665	2.52213	1.12830	186
3	48.7888	1.86506	1.12000	47
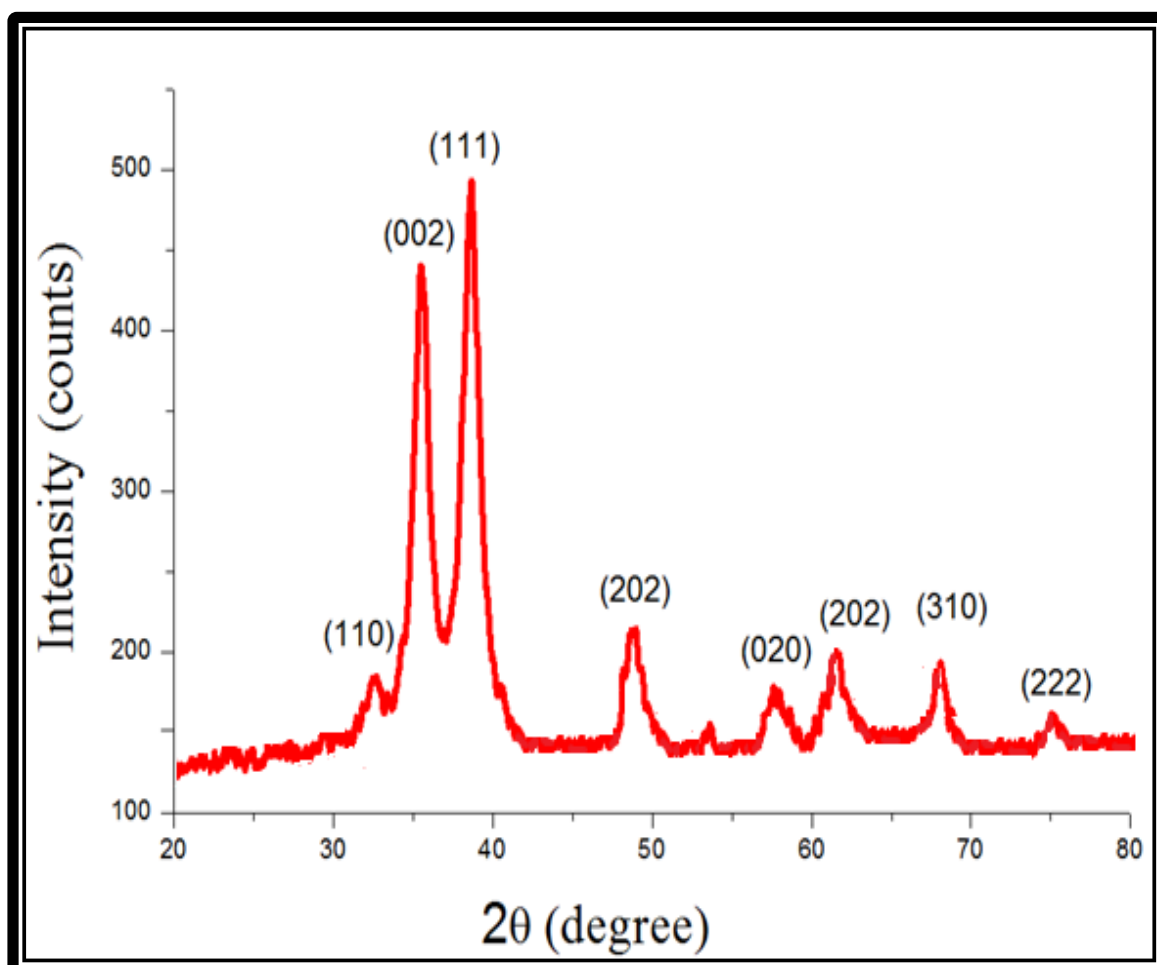
Figure (3.2): XRD of copper (II) oxide nanoparticles prepare using Fig Leaves Extract method, (FLEP.CuO.NP).

3.1.2. Scanning electron microscope

Scanning electron microscope (SEM) was utilized to check morphology of the nanoparticles samples[132,133]. ***Figures (3.3)*** and ***(3.4)*** show the SEM images of (SGP.CuO.NP) and (FLEP.CuO.NP) in which copper oxide nanoparticle appear clearly with the formation irregular particles and spherical with average particles size of (49.69) nm and (34.57) nm respectively as was calculated by using program (Image-J).
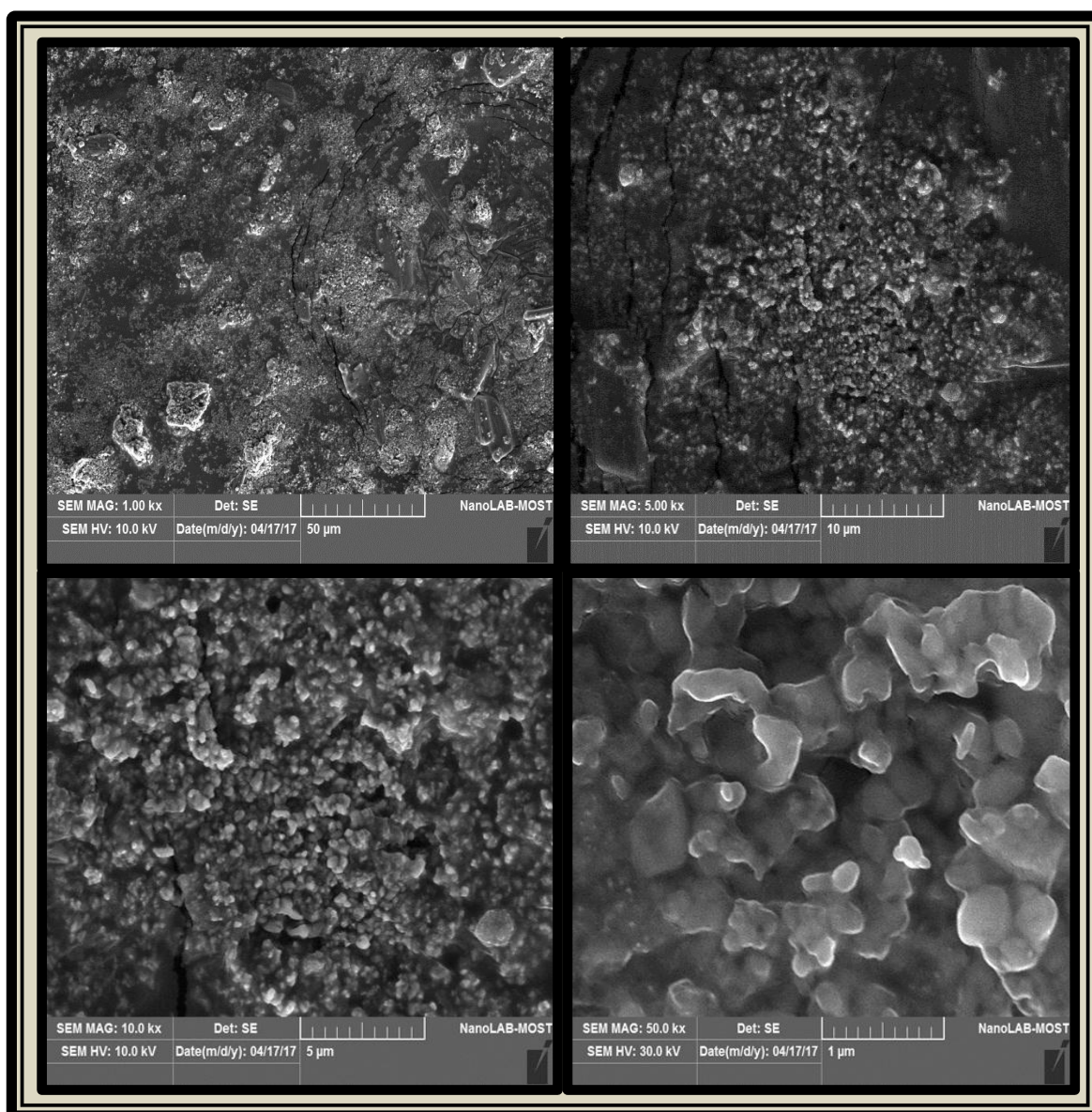
Figure (3.3): SEM images of copper (II) oxide nanoparticles prepare using (Sol-Gel) method, (SGP.CuO.NP).
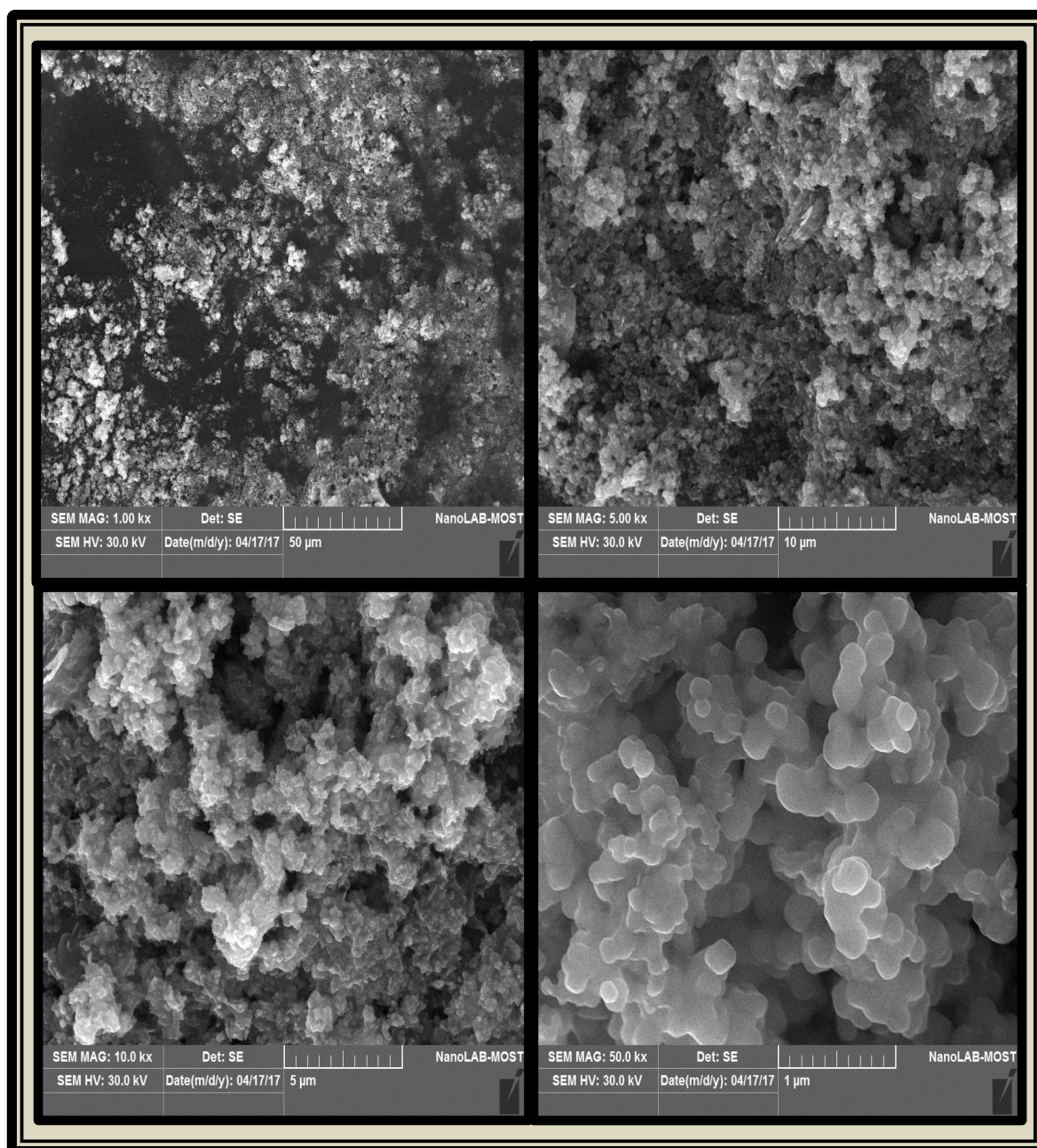
Figure (3.4): SEM images of copper (II) oxide nanoparticles prepare using Fig Leaves Extract, (FLEP.CuO.NP).

3.1.3. Transmission electron microscope

The TEM was used to characterize adsorbent morphology too[112,134]. The TEM images of copper (II) oxide nanoparticles which are prepared by using sol-gel and *Fig* Leaves extract methods are shown in ***Figures (3.5)*** and *(3.6)*, respectively**.** These images clearly indicate that spherical morphology. The (SGP.CuO.NP) particle size is found to be in the range (10 – 40) nm, whereas (FLEP.CuO.NP) in the range (7.5 – 35) nm.
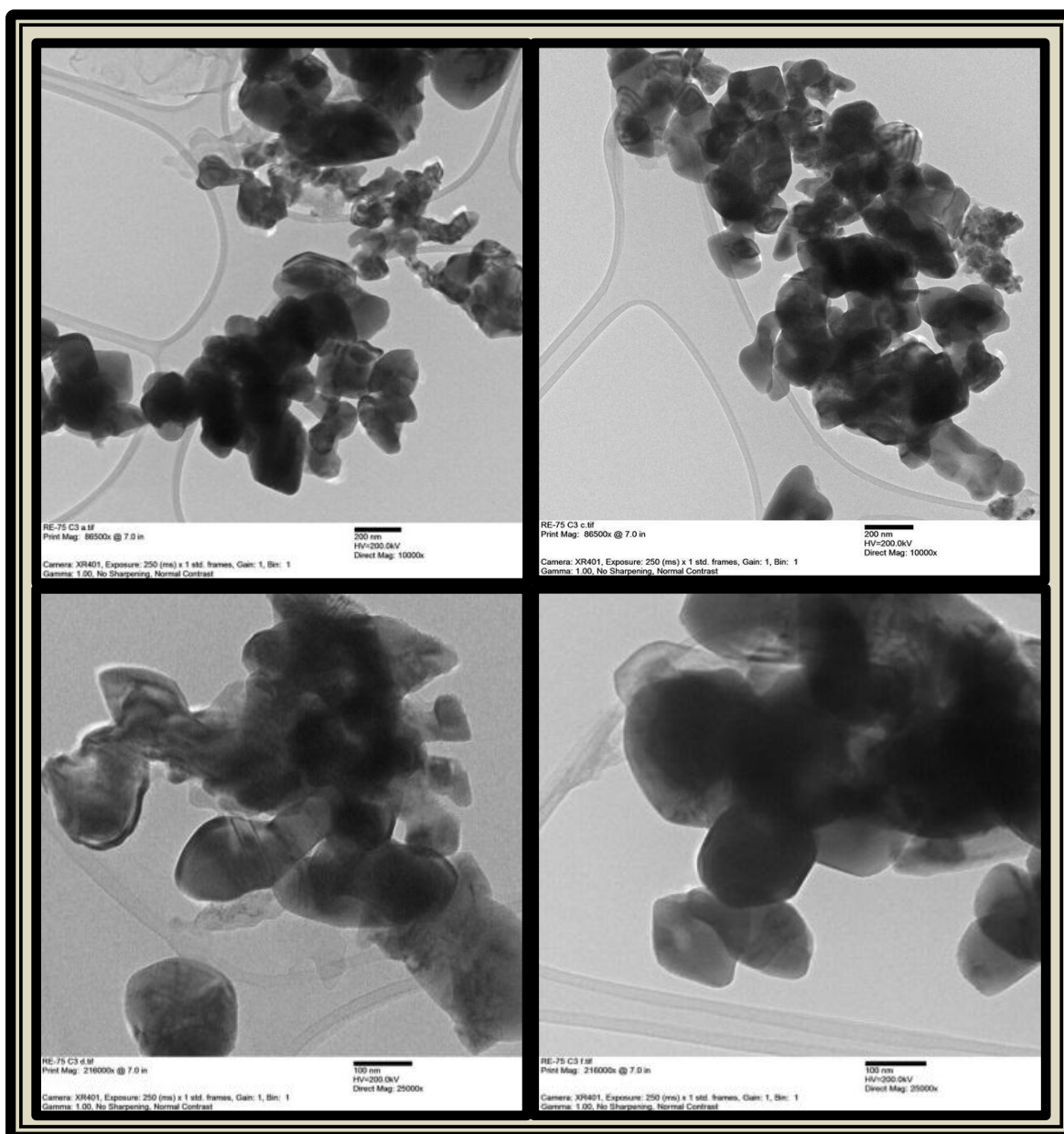
Figure (3.5): TEM images of copper (II) oxide nanoparticles prepare using (Sol-Gel) method, (SGP.CuO.NP).
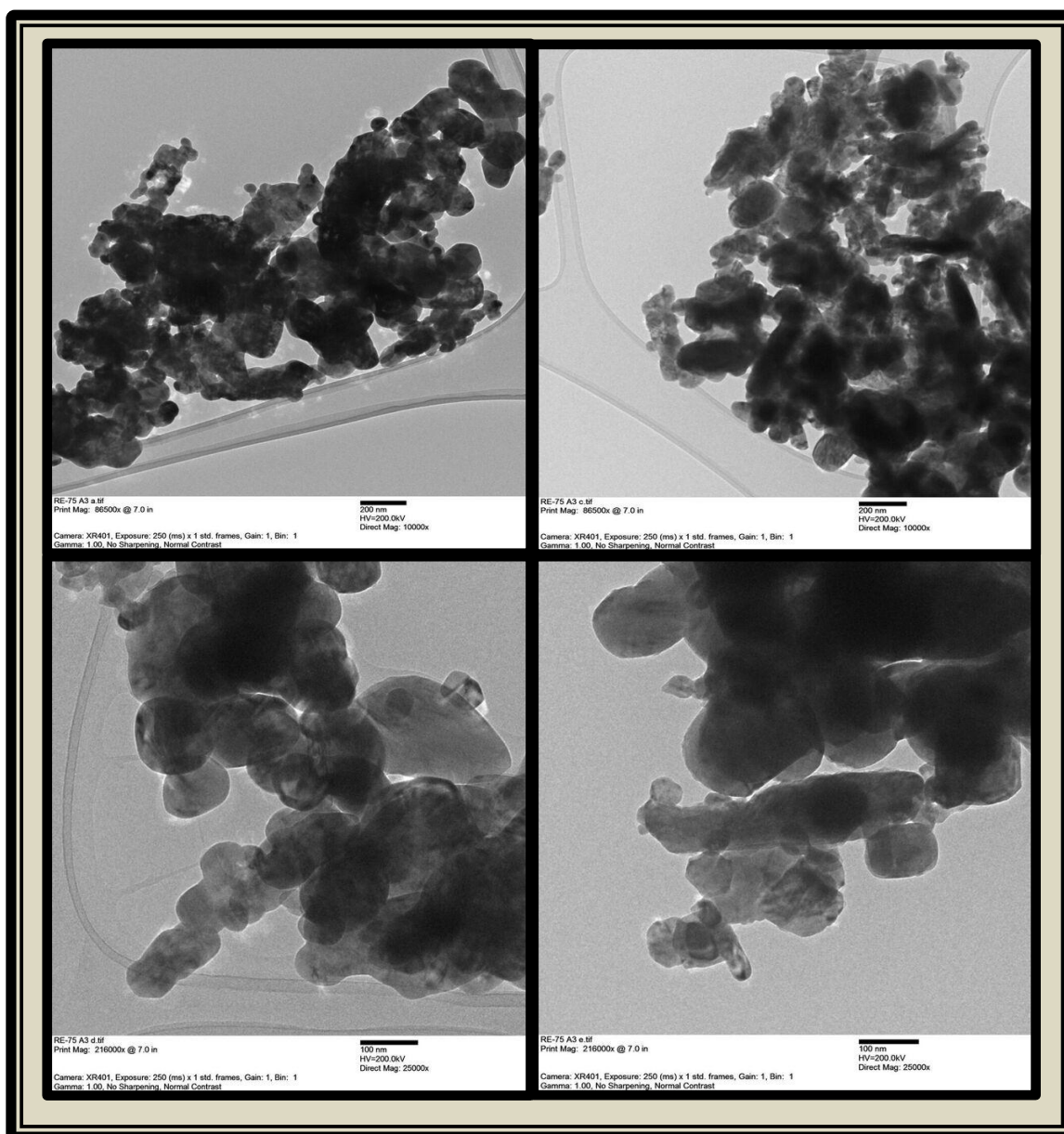
Figure (3.6): TEM images of copper (II) oxide nanoparticles prepare using Fig Leaves Extract, (FLEP.CuO.NP).

3.1.4. Atomic force microscope

The average grain size of surfaces nanoparticles was measured utilizing atomic microscope[135]. The *Figures (3.7)* and *(3.8)* show typical AFM images of the (SGP.CuO.NP) and (FLEP.CuO.NP) respectively. *Figures (3.7)* and *(3.8)* explains images of AFM for (SGP.CuO.NP) and (FLEP.CuO.NP) with (size = 2016 X 2031 nm and size = 2032 X 2027 nm), and ability analytical (pixel = 408,411 and 392, 391), respectively.

The *Figures (3.7-A)* and *(3.8-A)* are AFM images in three dimensions (3D), it explain structure shape for grain, and *Figures (3.7-B)* and *(3.8-B)* is AFM images in two dimensions (2D), it is found that average roughness are (0.769) nm and (0.311) nm, respectively. The Root mean square (RMS) are (0.897) nm and (0.3581) nm, and average diameter of the (SGP.CuO.NP) and (FLEP.CuO.NP) are (89.16) nm and (71.28) nm.

Tables (3.3) and *(3.4),* and *Figures (3.9)* and *(3.10),* show the granularity cumulating distribution and average diameter data of (SGP.CuO.NP) and (FLEP.CuO.NP) respectively.
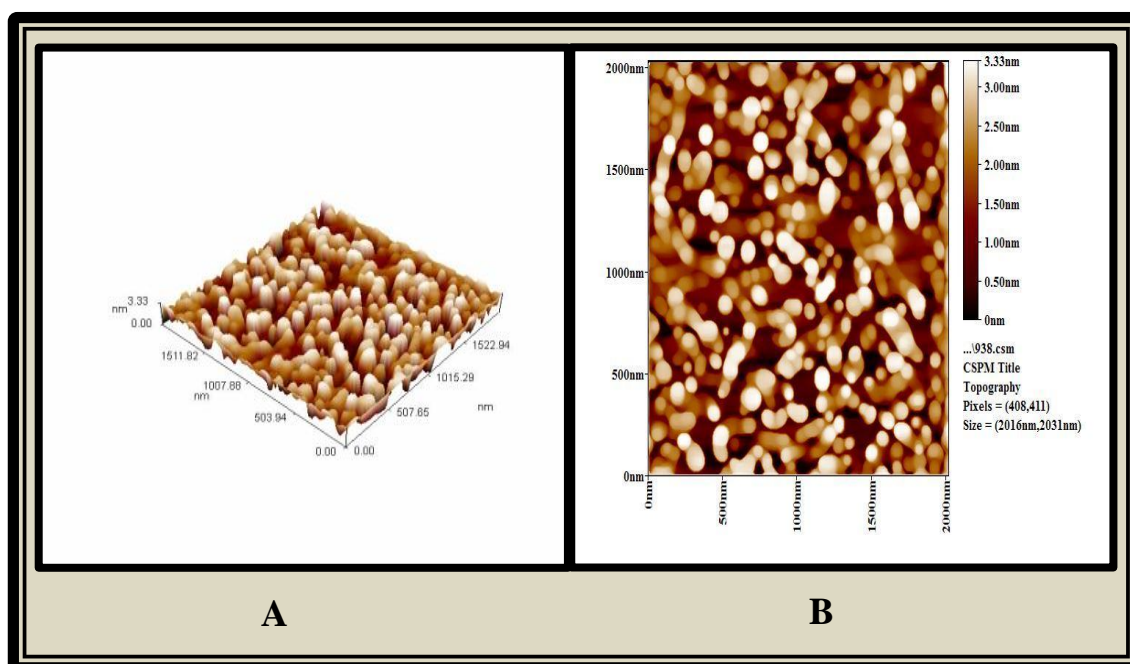
Figure (3.7): AFM images for copper (II) oxide nanoparticles prepare using (Sol-Gel) method, (SGP.CuO.NP).
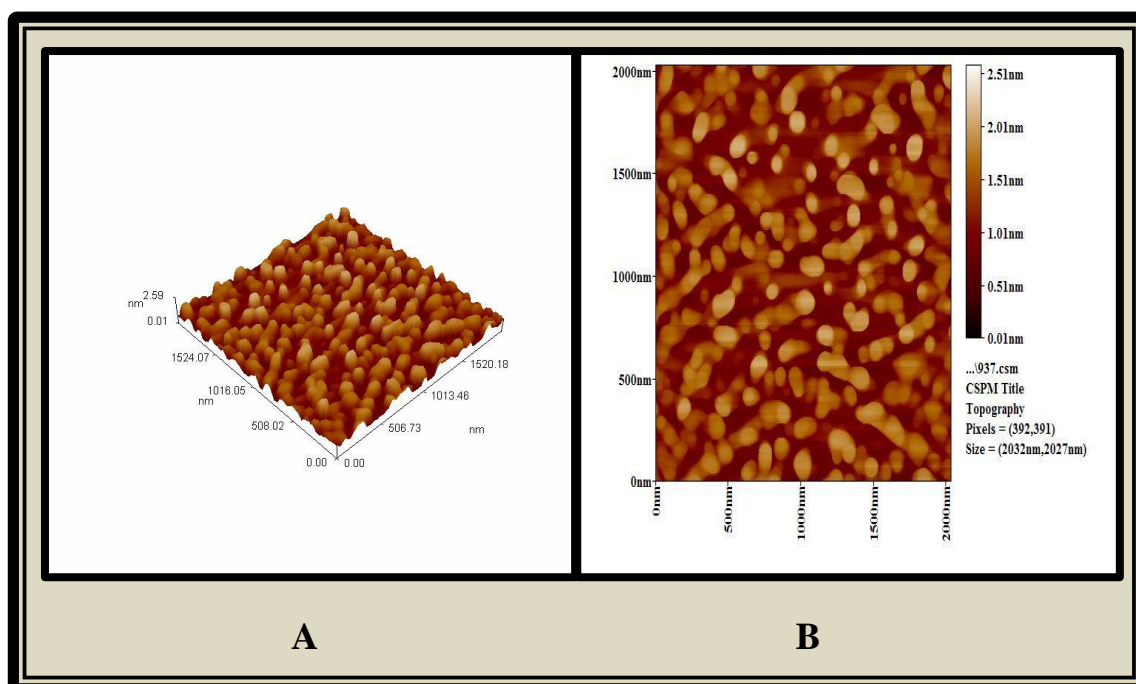
Figure (3.8): AFM images for copper (II) oxide nanoparticles prepare using Fig Leaves Extract, (FLEP.CuO.NP).

Table (3.3): Granularity cumulating distribution and average diameter of copper (II) oxide nanoparticles, (SGP.CuO.NP).

Avg. Diameter :89.16 nm								
Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)
35.00	0.69	0.69	80.00	6.92	40.48	125.00	2.08	88.24
40.00	1.38	2.08	85.00	7.61	48.10	130.00	3.11	91.35
45.00	2.08	4.15	90.00	6.57	54.67	135.00	2.42	93.77
50.00	2.42	6.57	95.00	5.88	60.55	140.00	0.69	94.46
55.00	2.42	9.00	100.00	7.61	68.17	145.00	1.04	95.50
60.00	2.77	11.76	105.00	4.15	72.32	150.00	2.42	97.92
65.00	8.30	20.07	110.00	5.19	77.51	155.00	1.38	99.31
70.00	7.61	27.68	115.00	4.15	81.66	165.00	0.35	99.65
75.00	5.88	33.56	120.00	4.50	86.16	170.00	0.35	100.00
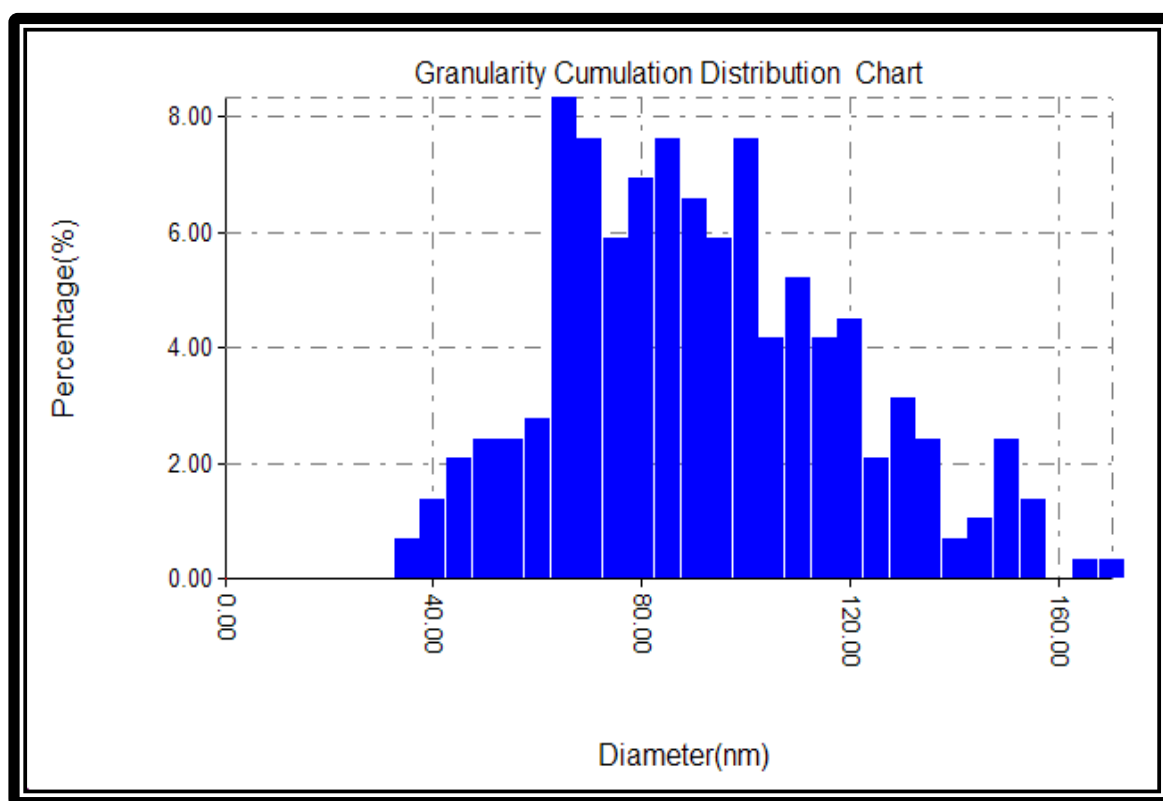
Figure (3.9): Granularity cumulating distribution of (SGP.CuO.NP).

Table (3.4): Granularity cumulating distribution and average diameter of copper (II) oxide nanoparticles, (FLEP.CuO.NP).

Avg.Diameter :71.28 nm								
Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)
15.00	0.47	0.47	65.00	8.39	47.55	115.00	1.40	89.98
20.00	0.93	1.40	70.00	6.53	54.08	120.00	1.86	91.84
25.00	1.63	3.03	75.00	6.76	60.84	125.00	2.56	94.41
30.00	4.43	7.46	80.00	5.83	66.67	130.00	1.17	95.57
35.00	2.80	10.26	85.00	4.20	70.86	135.00	1.63	97.20
40.00	3.26	13.52	90.00	4.43	75.29	140.00	0.23	97.44
45.00	5.13	18.65	95.00	4.20	79.49	145.00	0.70	98.14
50.00	5.13	23.78	100.00	3.26	82.75	150.00	0.93	99.07
55.00	8.62	32.40	105.00	2.80	85.55	155.00	0.70	99.77
60.00	6.76	39.16	110.00	3.03	88.58	160.00	0.23	100.00
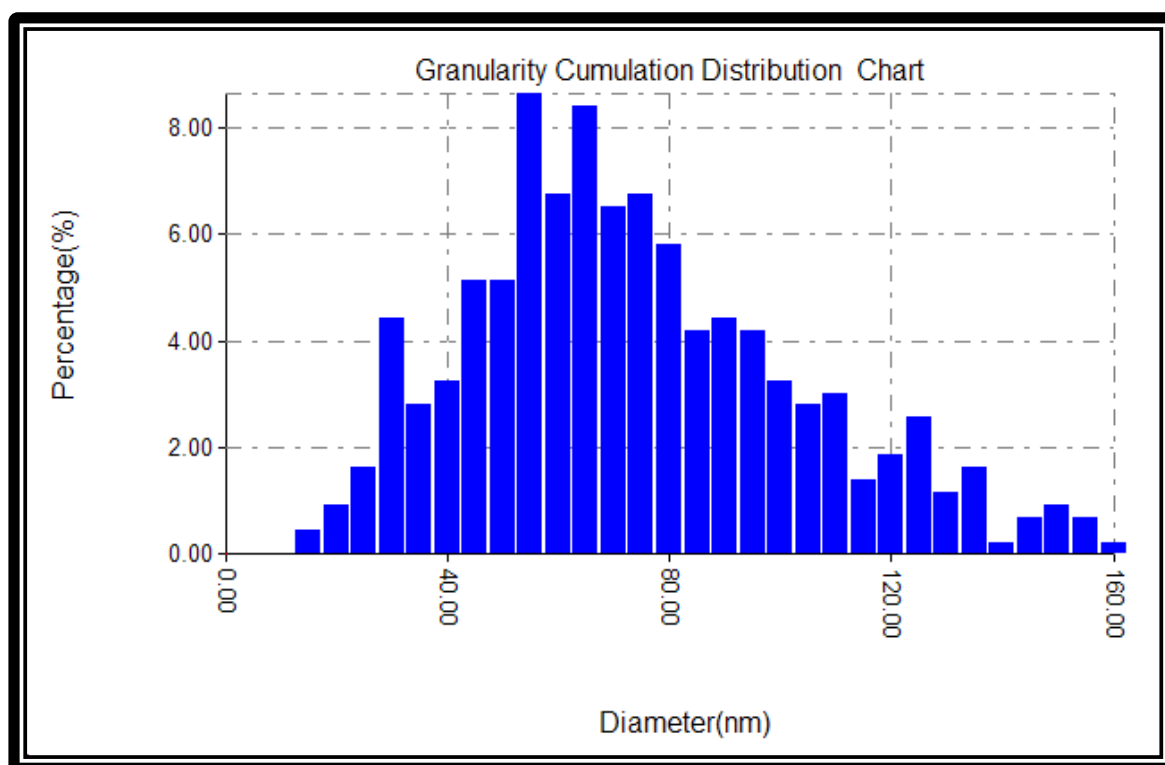
Figure (3.10): Granularity cumulating distribution of (FLEP.CuO.NP).

3.2. Adsorption of cadmium (II) and nickel (II) ions in binary system on the (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces

3.2.1. Effect of contact time on adsorption

The effect of the contact time on the adsorption of Cd (II) and Ni (II) ions in binary system on the (SGP.CuO.NP) and (FLEP.CuO.NP) was studied at (15, 30, 45, 60, 75, 90,105 and 120) min at (298) K, concentration (100) mg/L of each metal ions and pH = 6.

Tables (3.5) and *(3.6)* explain the change of the percentage removal with contact time. As seen from them that equilibrium time required for the adsorption of both ions on the (SGP.CuO.NP) and (FLEP.CuO.NP) are almost (30 and 15) min respectively.

The effect of contact time on the adsorption of Ni (II) and Cd (II) ions in binary system on (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces are also explain in *Figure (3.11)* where increasing in the percent removal at the beginning of contact time of (SGP.CuO.NP) and (FLEP.CuO.NP) with both cadmium (II) and nickel (II) ions, then there was a gradual decline in the percentage removal of Cd^{+2} and Ni^{+2} ions for both surfaces because the rapid initial rate increase followed by a slow rate at later period could be due to availability of excess adsorption sites on the adsorbent[136]. The initial high adsorption rate might possibly be due to ion exchange followed by a slow chemical reaction of the metal ions active groups on the sample[137], and the remaining vacant surface sites are difficult to be occupied due to repulsive force. The metal ions have to traverse further and deeper into the pores encountering much larger resistance[115].

When compared the adsorption of two metals in binary system on the (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces, the (FLEP.CuO.NP) found to show adsorption being better than (SGP.CuO.NP) this is due to the small particles size and the more vacant site and surface area.

Table (3.5): Effect of contact time on the adsorption of Cd (II) and Ni (II) ions in binary system by (SGP.CuO.NP) surface at 298 K.

Time (min)	Cd (II) ions		Ni (II) ions	
	C_t (mg/L)	R%	C_t (mg/L)	R%
15	0.911	99.089	0.931	99.069
30	0.257	99.743	0.680	99.320
45	1.312	98.688	1.312	98.688
60	1.491	98.509	1.580	98.420
75	1.453	98.547	1.693	98.307
90	1.588	98.412	1.990	98.010
105	1.883	98.117	2.043	97.957
120	1.978	98.022	2.470	97.530

Table (3.6): Effect of contact time on the adsorption of Cd (II) and Ni (II) ions in binary system by (FLEP.CuO.NP) surface at 298 K.

Time (min)	Cd (II) ions		Ni (II) ions	
	C_t (mg/L)	R%	C_t (mg/L)	R%
15	0.330	99.670	0.986	99.013
30	0.393	99.602	1.098	98.901
45	0.375	99.625	1.093	98.906
60	0.368	99.636	1.113	98.886
75	0.487	99.513	1.237	98.762
90	0.447	99.553	1.257	98.743
105	0.430	99.570	1.343	98.656
120	0.710	99.290	1.366	98.633
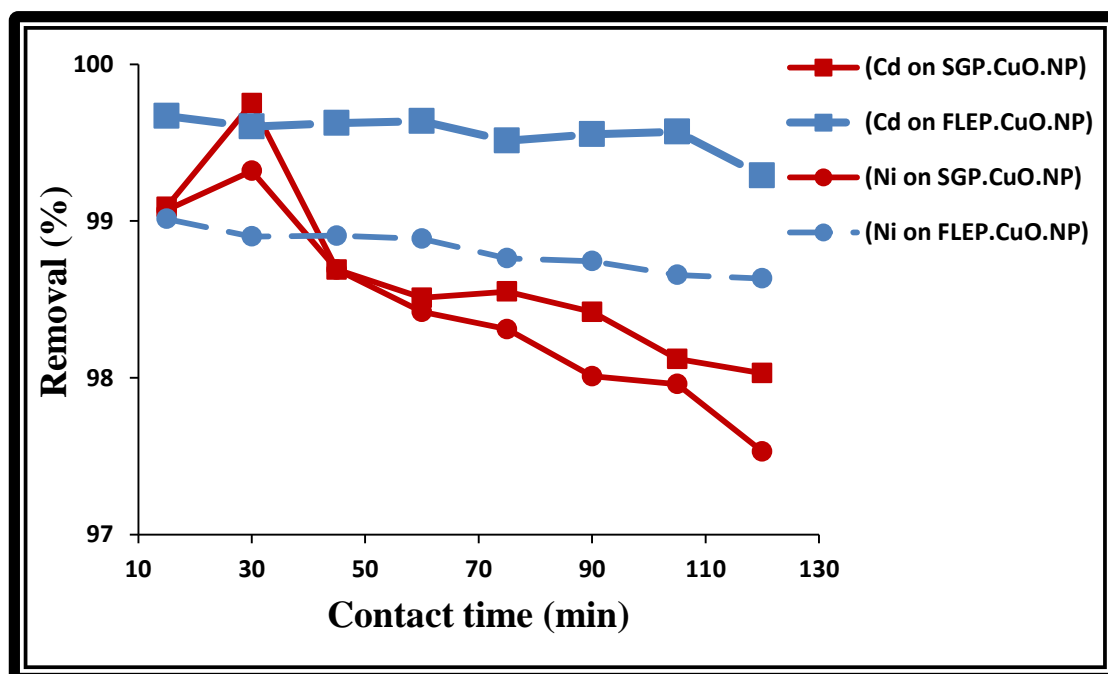
Figure (3.11): Effect of contact time on adsorption of Cd (II) and Ni (II) ions in binary system on the (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces at 298 K.

3.2.2. Effect of adsorbent quantity on adsorption

The effect of the adsorbent quantity of the Cd (II) and Ni (II) ions adsorption in binary system on the (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces, was studied using different quantity of the adsorbent (0.01, 0.05, 0.1, 0.15 and 0.2) g at (298) K, fixed concentration of Ni (II) and Cd (II) ions (100) mg/L in binary system, pH of 6 with contact time for (SGP.CuO.NP) and (FLEP.CuO.NP) are being (30) min and (15) min, respectively.

The influence of adsorbent quantity on the uptake of the binary metals Cd (II) and Ni (II) ions onto (SGP.CuO.NP) and (FLEP.CuO.NP) shown in *Tables (3.7)* and *(3.8),* and in *Figure (3.12)* with increasing the quantity of copper oxide prepared by sol-gel and *Fig* Leaves Extract method, the metals removal will increases too, this means that the increase the amount of oxide nanoparticles increases the percentage removal for binary metals. The increase in the percentage removal can be explained by the increasing surface area where the adsorption take place as it is shown in *Figure (3.12)* optimum adsorbent quantity that can be used in cadmium (II) and nickel (II) removal are (0.1) g, after (0.1) g the percentage removal will be increased slightly[117,118,138].

Table (3.7): Effect of adsorbent quantity on the adsorption of Cd (II) and Ni (II) ions in binary system by (SGP. CuO.NP) surface at 298 K.

Adsorbent quantity (g)	Cd (II) ions		Ni (II) ions	
	C_e (mg/L)	R%	C_e (mg/L)	R%
0.01	3.691	96.308	3.422	96.578
0.05	2.499	97.500	2.018	97.982
0.10	1.486	98.513	1.647	98.352
0.15	1.484	98.515	1.293	98.706
0.20	1.393	98.606	1.095	98.900

Table (3.8): Effect of adsorbent quantity on the adsorption of Cd (II) and Ni (II) ions in binary system by (FLEP.CuO.NP) surface at 298 K.

Adsorbent quantity (g)	Cd (II) ions		Ni (II) ions	
	C_e (mg/L)	R%	C_e (mg/L)	R%
0.01	3.232	96.067	0.534	99.466
0.05	2.396	97.603	0.412	99.587
0.10	0.286	99.713	0.229	99.770
0.15	0.233	99.766	0.200	99.799
0.20	0.089	99.910	0.146	99.853
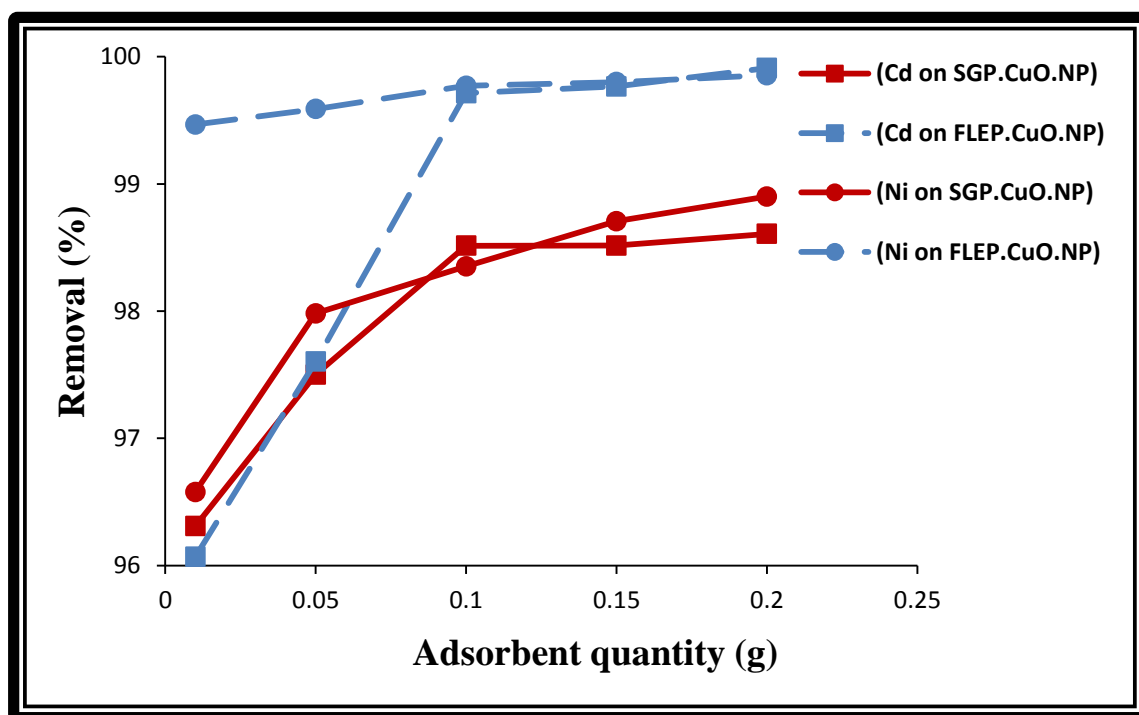
Figure (3.12): Effect of adsorbent quantity on adsorption of Cd (II) and Ni (II) ions in binary system on the (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces at 298 K.

3.2.3. Effect of pH on adsorption

The effect of pH on the percentage removal of the binary heavy metals (cadmium and nickel ions) on the copper oxide prepared by sol-gel and *Fig* Leaves Extract surfaces, was tested at pH (2, 4, 6 and 8) at temperature (298) K, the constant concentration of Ni (II) and Cd (II) (100) mg/L, the contact time of (30 and 15) min for the (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces, and the adsorbent dose (0.1) g. The acidic and alkaline pH of the media was maintained by adding the required amounts of dilute hydrochloric acid and sodium hydroxide solutions. *Tables (3.9)* and *(3.10)* show results obtained for the effect of pH on Cd (II) and Ni (II) adsorption.

It can be observed that the removal of Cd (II) and Ni (II) ions was maximum at pH of 6 on the (SGP.CuO.NP) and (FLEP.CuO.NP).

The pH of metals solution plays an important role in the whole adsorption process and particularly on the percentage adsorption, from *Figure (3.13)* it is shown that percentage removal of binary metals ions by (FLEP.CuO.NP) is better than (SGP.CuO.NP). The removal of metal ions is found to increase with an increase in the pH from 2 to 6 and the metal ion removal was settled at pH more 6. The adsorption of Cd^{+2} and Ni^{+2} ions at low pH 6 is lesser than that at higher pH 6; this is due to the fact that the pH is not suitable for the adsorption of cadmium (II) and nickel (II). For the low pH a significant electrostatic repulsion exists between the positively charged surface of the copper oxide nanoparticles and the cationic metals. Besides, the higher concentration of H^+ in the solution competes with Cd (II) and Ni (II) for the adsorption sites, resulting for the reduced adsorptive of nickel (II) and cadmium (II) ions.

At pH 6 of the binary system, the number of positively charged site decrease and the number of negatively charged sites increase on the surfaces. The metal oxide of the negatively charged surface site on the surfaces the adsorption of Ni (II) and Cd (II) due to electrostatic attraction, at pH values higher than 6, cadmium (II) and nickel (II) ions precipitated out because of the high concentration of (OH^-) ions in the aqueous solution[126,139].

Table (3.9): Effect of pH on the adsorption of Cd (II) and Ni (II) ions in binary system by (SGP. CuO.NP) surface at 298 K.

pH Amount	Cd (II) ions		Ni (II) ions	
	C_e (mg/L)	R%	C_e (mg/L)	R%
2	7.846	92.153	5.970	94.029
4	2.565	97.434	1.945	98.055
6	1.246	98.753	0.913	99.086
8	2.498	97.501	1.478	98.521

Table (3.10): Effect of pH on the adsorption of Cd (II) and Ni (II) ions in binary system by (FLEP.CuO.NP) surface at 298 K.

pH Amount	Cd (II) ions		Ni (II) ions	
	C_e (mg/L)	R%	C_e (mg/L)	R%
2	1.940	98.060	3.304	96.696
4	1.281	98.719	1.747	98.253
6	0.330	99.670	0.674	99.326
8	0.843	99.157	1.376	98.624

.
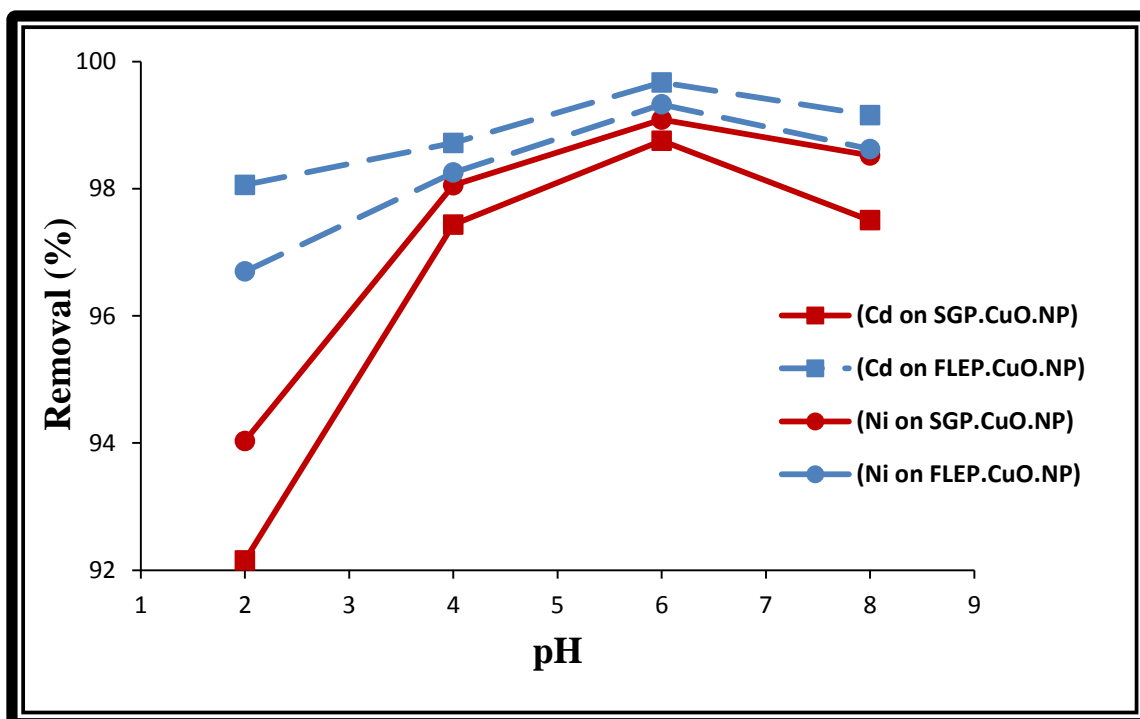
Figure (3.13): Effect of pH on adsorption of Cd (II) and Ni (II) ions in binary system on the (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces at 298 K.

3.2.4. Effect of temperature on adsorption

The effect of temperature on the extent adsorption of the cadmium (II) and nickel (II) ions in binary system on the (SGP.CuO.NP) and (FLEP.CuO.NP) has been studied at four different temperatures (298, 308, 318 and 333) K at pH (6), initial concentration (100) mg/L of each metal ions, quantity of adsorbent (0.1) g, the contact time was of constant at (30) min for (SGP.CuO.NP) and (15) min for (FLEP.CuO.NP).

The experimental data and the general shapes of the cadmium (II) and nickel (II) adsorption on the (SGP.CuO.NP) and (FLEP.CuO.NP) are given in *Tables (3.11)* and *(3.12),* and *Figure (3.14).*

The data show that the percentage removal decrease with increase in temperature. These observe that adsorption of binary metals (Cd and Ni ions) on the (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces are exothermic in all cases, the reduction in the rate of adsorption with increase in the temperature, may be backing weakening of interaction force between the active sites of the adsorption surface and the binary metals ions[140].

Table (3.11): Effect of temperature on the adsorption of Cd (II) and Ni (II) ions in binary system by (SGP.CuO.NP) surface.

Temperature (K)	Cd (II) ions		Ni (II) ions	
	C_e (mg/L)	R%	C_e (mg/L)	R%
298	4.367	95.632	2.909	97.090
308	6.113	93.886	2.954	97.046
318	7.110	92.889	4.117	95.892
333	7.553	92.446	5.277	94.723

Table (3.12): Effect of temperature on the adsorption of Cd (II) and Ni (II) ions in binary system by (FLEP.CuO.NP) surface.

| Temperature (K)	Cd (II) ions		Ni (II) ions	
	C_e (mg/L)	R%	C_e (mg/L)	R%
298	0.261	99.739	1.547	98.452
308	0.758	99.342	1.569	98.430
318	0.764	99.236	3.961	96.039
333	0.980	99.023	4.531	95.469
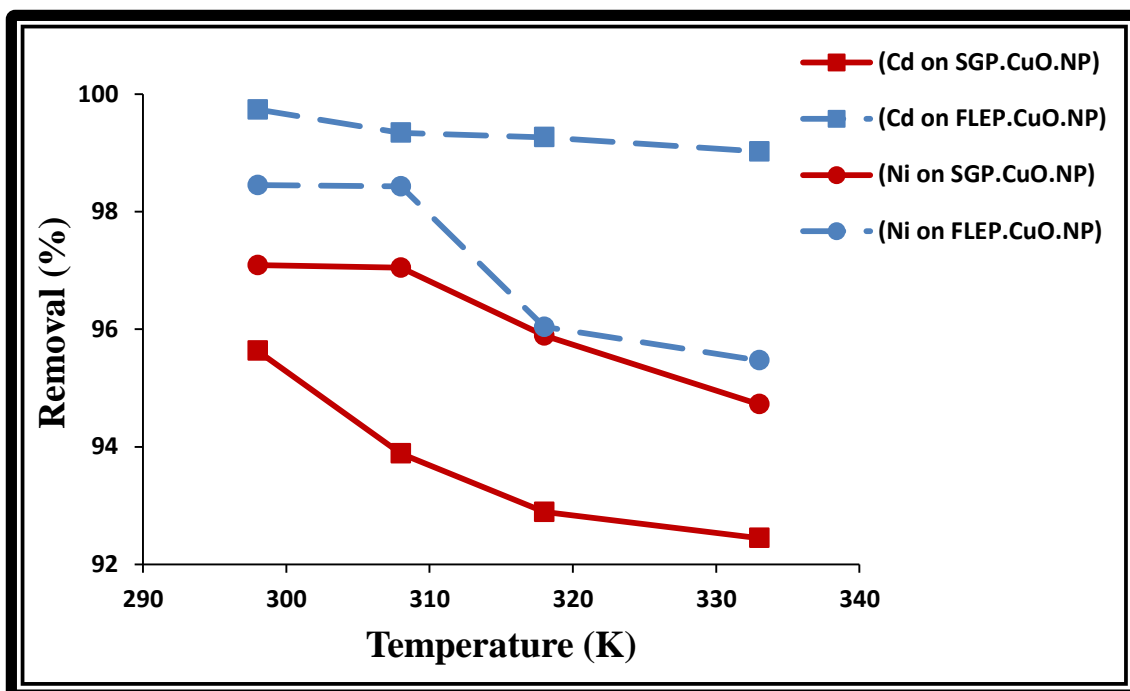
Figure (3.14): Effect of temperature on adsorption of Cd (II) and Ni (II) ions in binary system on the (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces.

3.2.5. Effect of initial concentration

Adsorption of the binary metals (Cd (II) and Ni (II) ions) from an aqueous solution on the (SGP.CuO.NP) and (FLEP.CuO.NP) was studied first at optimum conditions, using different initial concentration of aqueous solution of (20, 40, 60, 80 and 100) mg/L for each metal ions.

The results shown in **Tables (3.13)** and **(3.14)** and **Figure (3.15)** the impact of the initial concentration indicate little decrease in the removal when increasing initial concentration of Cd (II) and Ni (II) ions on both surfaces (SGP.CuO.NP) and (FLEP.CuO.NP). The small decreasing in the percentage of the removal at higher concentration could be attributed to the limited number of active sites of the copper oxide nanoparticles adsorbents, which become more saturated with an increase in the concentration metal ions (Cd^{+2} and Ni^{+2}), and the removal of cadmium (II) and nickel (II) on

the (FLEP.CuO.NP) is better than (SGP.CuO.NP) because of the small nanoparticles size and high surface area that contains a lot of active adsorption sites, will be available[141].

Table (3.13): Effect of initial concentration on the adsorption of Cd (II) and Ni (II) ions in binary system by (SGP. CuO.NP) surface at 298 K.

Initial concentration (mg/L)	Cd (II) ions		Ni (II) ions	
	C_e (mg/L)	R%	C_e (mg/L)	R%
20	0.169	99.153	0.155	99.223
40	0.538	98.653	0.219	98.905
60	1.212	97.653	0.846	98.588
80	3.868	95.165	1.986	97.516
100	5.929	94.070	2.929	97.071

Table (3.14): Effect of initial concentration on the adsorption of Cd (II) and Ni (II) ions in binary system by (FLEP. CuO.NP) surface at 298 K.

| Initial concentration (mg/L)	Cd (II) ions		Ni (II) ions	
	C_e (mg/L)	R%	C_e (mg/L)	R%
20	0.550	99.775	0.028	99.860
40	0.141	99.647	0.133	99.667
60	0.301	99.493	0.256	99.573
80	0.467	99.405	0.386	99.517
100	0.620	99.380	0.965	99.035
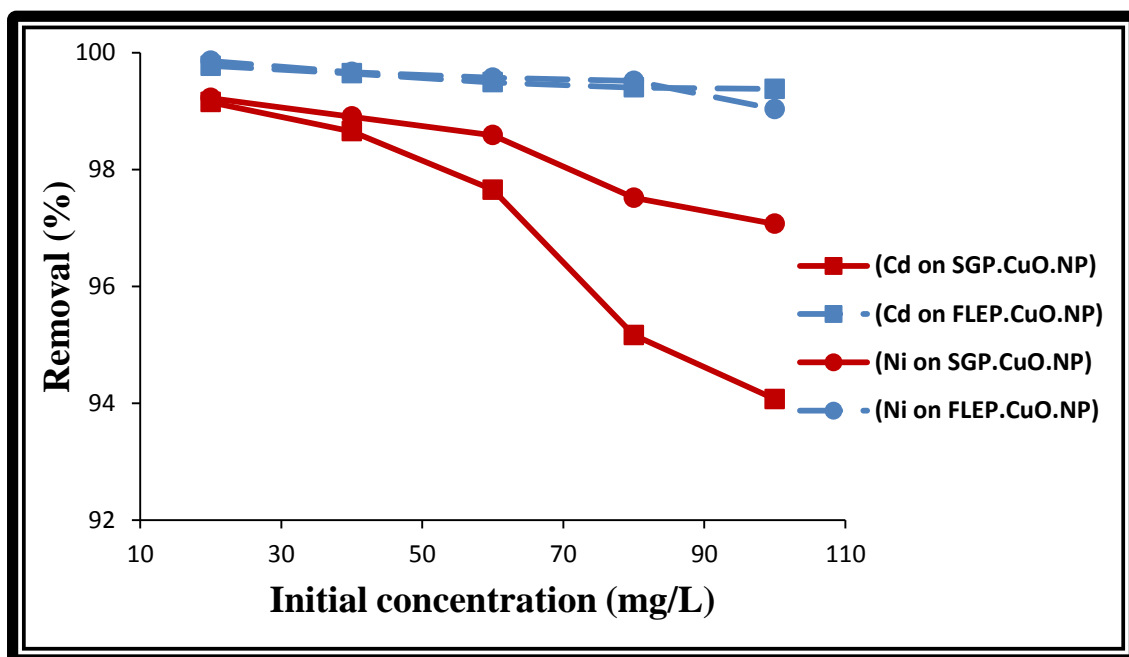
Figure (3.15): Effect of initial concentration on adsorption of Cd (II) and Ni (II) ions in binary system on the (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces at 298 K.

3.3. The adsorption isotherm

The adsorption of Cd (II) and Ni (II) ions from single and binary an aqueous solution on the (SGP.CuO.NP) and (FLEP.CuO.NP) at ideal condition, are shown in *Table (3.15)*:

Table (3.15): Ideal condition for adsorption.

No.	Conditions on two adsorbent	Value	
		Cd (II) ion	Ni (II) ion
1	pH	6	6
2	Temperature	298 K	298 K
3	Volume of metals Solution	Binary, 25mL Single,50mL	Binary,25mL Single,50mL
4	Contact time on (SGP.CuO.NP),(FLEP.CuO.NP)	30 (min) 15 (min)	30 (min) 15 (min)
5	Quantity of adsorbents	0.1 (g)	0.1(g)
6	Stirring speed	150 (rpm)	150 (rpm)

3.3.1. The adsorption isotherm of single metal ions systems

The adsorption isotherm studied of Cd (II) and Ni (II) single systems from an aqueous solution on (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces at ideal condition data are listed in *Table (3.15)*. The results are represented by the initial concentration $(C_\circ)$ of cadmium and nickel ions, and the equilibrium concentration (C_e) measured at equilibrium state and the adsorption capacity (Q_e) values are calculated from the experimental data by using equation **(2.2)**.

The adsorption capacity (Q_e) are plotted versus equilibrium concentration (C_e) to obtain general adsorption isotherm of Cd (II) ions removal which are describe in *Table (3.16)* and, *Figures (3.16)* and *(3.17)* by using (SGP.CuO.NP) and (FLEP.CuO.NP) and also adsorption isotherm of Ni (II) ions removal which are explain in *Table (3.16),* and *Figures (3.18)* and *(3.19)* by using (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces.

Table (3.16): Adsorption parameters values Cd (II) and Ni (II) ions of the single solution by (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces at ideal condition.

Metals	$C_\circ$ (mg/L)	SGP.CuO.NP						FLEP.CuO.NP					
		C_e (mg/L)	Q_e (mg/g)	log C_e	log Q_e	ln C_e	C_e/Q_e	C_e (mg/L)	Q_e (mg/g)	log C_e	log Q_e	ln C_e	C_e/Q_e
Cd (II) ions	20	0.151	9.924	-0.820	0.996	-1.897	0.015	0.032	9.984	-1.494	0.999	-3.442	0.003
	40	0.251	19.874	-0.600	1.298	-1.382	0.012	0.136	19.932	-0.866	1.299	-1.995	0.006
	60	0.511	29.744	-0.291	1.473	-0.671	0.017	0.245	29.877	-0.610	1.475	-1.406	0.008
	80	1.146	39.426	0.059	1.595	0.136	0.029	0.332	39.834	-0.478	1.600	-1.102	0.008
	100	1.977	49.011	0.296	1.690	0.681	0.040	0.474	49.763	-0.324	1.696	-0.746	0.009
Ni (II) ions	20	0.090	9.954	-1.044	0.998	-2.405	0.009	0.050	9.975	-1.310	0.998	-2.995	0.005
	40	0.227	19.886	-0.643	1.298	-1.481	0.011	0.100	19.950	-1.000	1.299	-2.302	0.005
	60	0.393	29.550	-0.405	1.470	-0.933	0.013	0.199	29.900	-0.701	1.475	-1.614	0.005
	80	0.770	39.614	-0.113	1.597	-0.260	0.019	0.250	39.875	-0.602	1.600	-1.386	0.006
	100	1.082	49.458	0.034	1.694	0.078	0.021	0.300	49.850	-0.522	1.697	-1.203	0.006
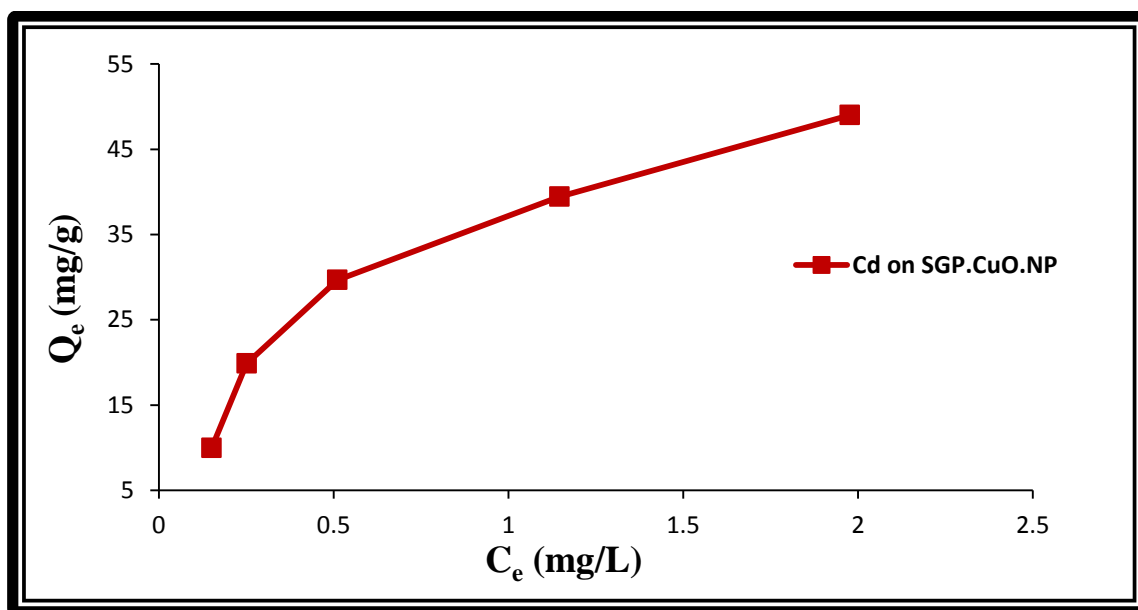
Figure (3.16): Adsorption isotherm of Cd (II) ions in single system by (SGP.CuO.NP) surface at various initial concentrations.
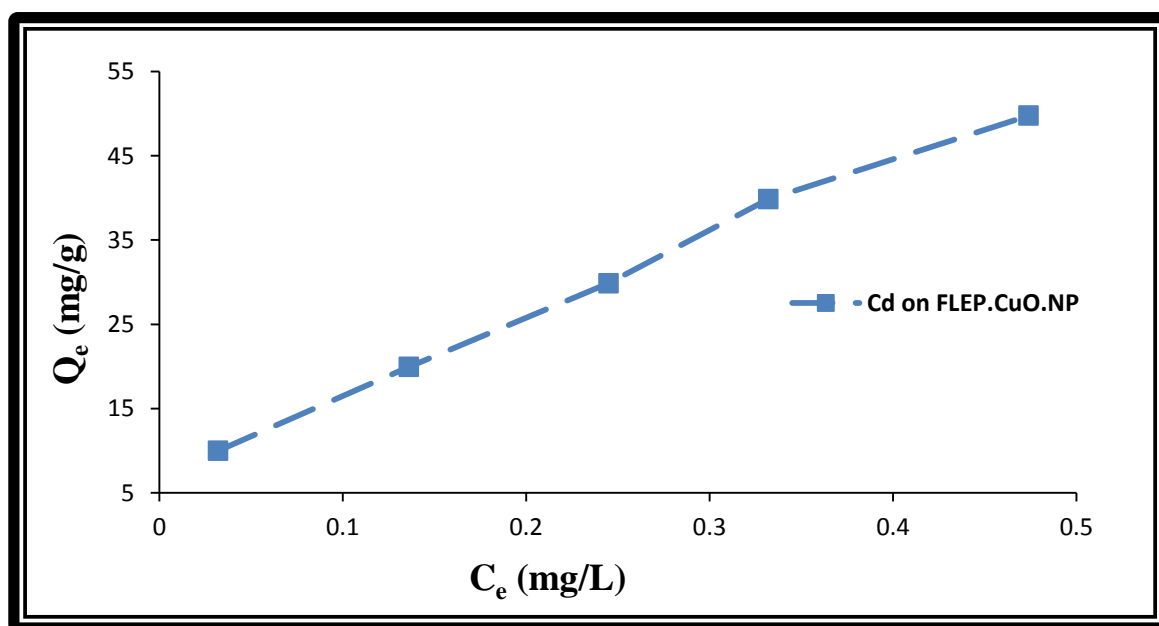
Figure (3.17): Adsorption isotherm of Cd (II) ions in single system by (FLEP.CuO.NP) surface at various initial concentrations.

Figure (3.18): Adsorption isotherm of Ni (II) ions in single system by (SGP.CuO.NP) surface at various initial concentrations.

Figure (3.19): Adsorption isotherm of Ni (II) ions in single system by (FLEP.CuO.NP) surface at various initial concentrations.

The results showed increase in adsorption capacities of the copper oxide nanoparticle prepared by sol-gel and *Fig* Leaves Extract with increase equilibrium concentration of solution, the general shape of adsorption isotherm of two surfaces is of (L) type on Giles Classification[69].

Increases in the initial metal concentration up to (100) mg/L results in an increase in the equilibrium uptake and a decrease in the adsorption yield of both components.

The initial concentration provides the necessary driving force to overcome the resistances to the mass transfer for Cd (II) and Ni (II) ions between the aqueous phases and solid phase. The increases in the initial concentration also enhance the interaction between the metal ions in the aqueous phase and surfaces.

3.3.1.1. Langmuir isotherm

Langmuir isotherm equation **(1.1)** was applied for adsorption of cadmium (II) and nickel (II) of single solution on the copper oxide nanoparticles prepared by sol-gel and *Fig* Leaves Extract at various initial concentrations. Adsorption isotherm data for Ni and Cd single solution removals are presented in *Table (3.16)* and plotted in *Figures (3.20) – (3.23)*.The values of the Langmuir isotherm constant **(a)** which is the monolayer adsorption capacity and **(b)** which is a constant related to the energy of adsorption are calculated from the slope and intercept of the plots **(C_e/Q_e)** versus **(C_e)** and are shown in *Table (3.17)*.
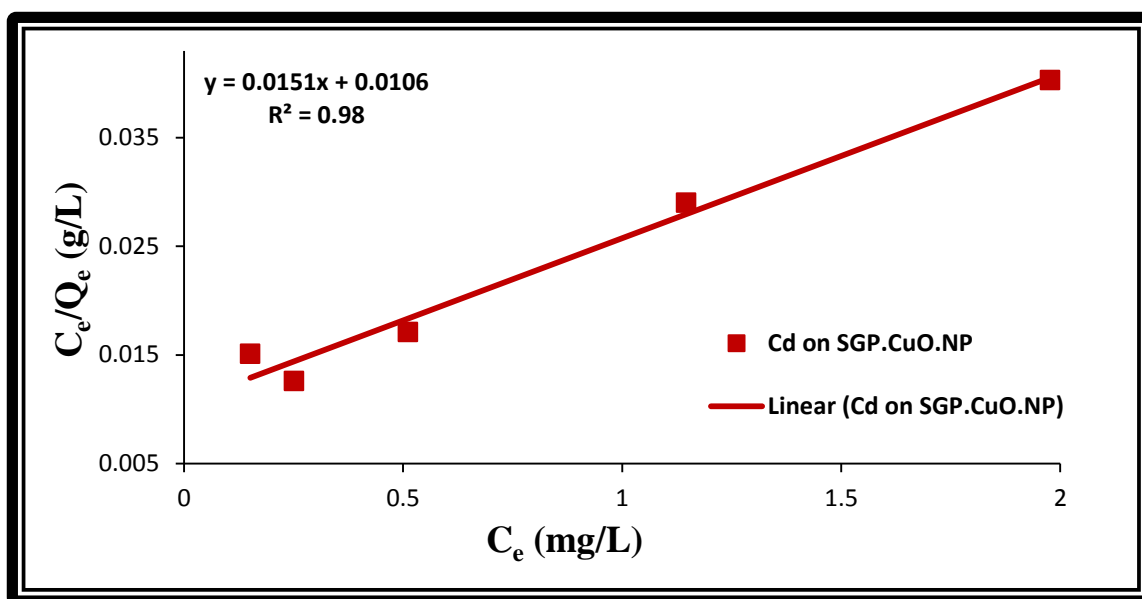
Figure (3.20): Linear Langmuir isotherm of Cd (II) ions in single system adsorption on (SGP.CuO.NP) surface at various initial concentrations.
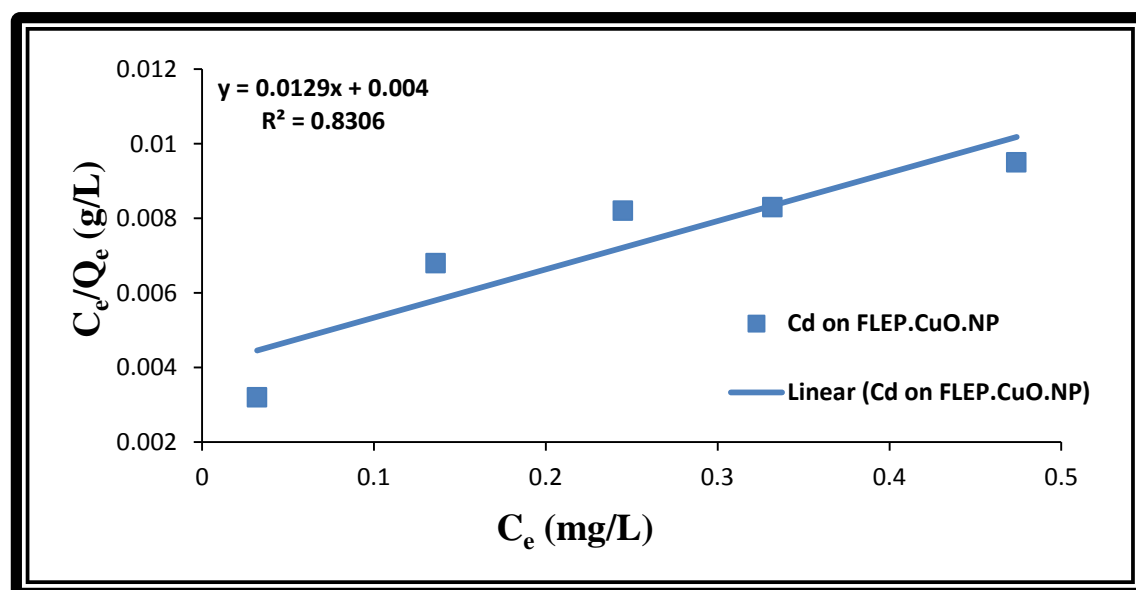
Figure (3.21): Linear Langmuir isotherm of Cd (II) ions in single system adsorption on (FLEP.CuO.NP) surface at various initial concentrations.
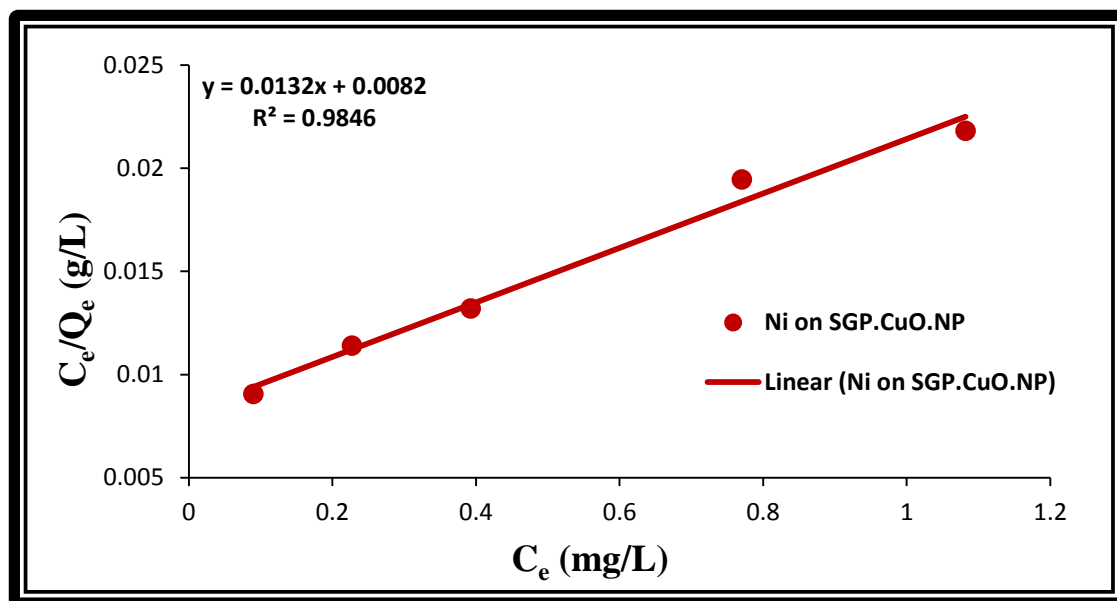
Figure (3.22): Linear Langmuir isotherm of Ni (II) ions in single system adsorption on (SGP.CuO.NP) surface at various initial concentrations.
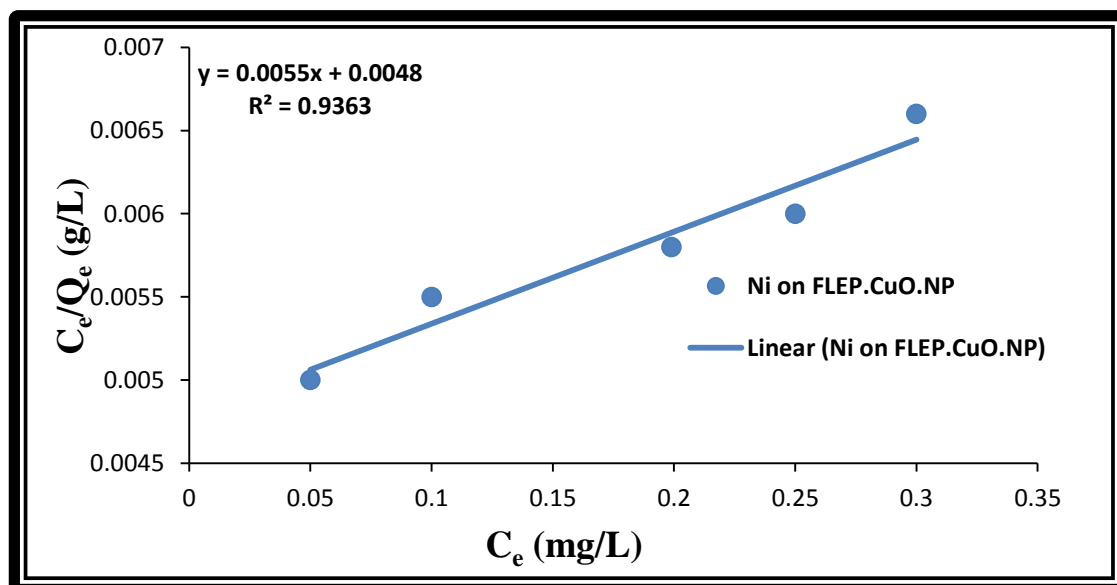
Figure (3.23): Linear Langmuir isotherm of Ni (II) ions in single system adsorption on (FLEP.CuO.NP) surface at various initial concentrations.

3.3.1.2. Freundlich isotherm

Freundlich isotherm equation **(1.3)** was applied on adsorption of Cd^{+2} and Ni^{+2} ions single system on the copper oxide prepared by sol-gel and *Fig* leaves extract surface. Adsorption isotherm data for (Cd and Ni ions) were plotted and shown in ***Tables (3.16)*** and ***Figures (3.24) − (3.27).*** The Freundlich isotherm constant **(K_f)** which is the adsorption capacity of the adsorbent, and **(n)** is the adsorption intensity being calculated from the slope and intercept of the plot of **(log Q_e)** versus **(log C_e)**, with the results are shown in ***Table (3.17)***.
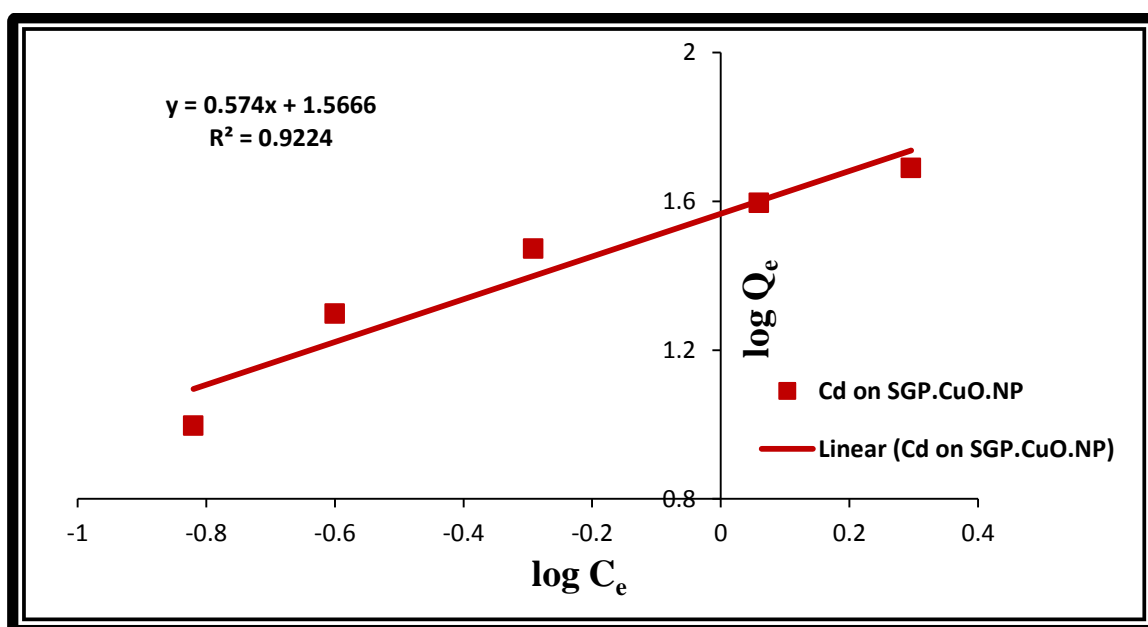
Figure (3.24): Linear Freundlich isotherm of Cd (II) ions in single system adsorption on (SGP.CuO.NP) surface at various initial concentrations.
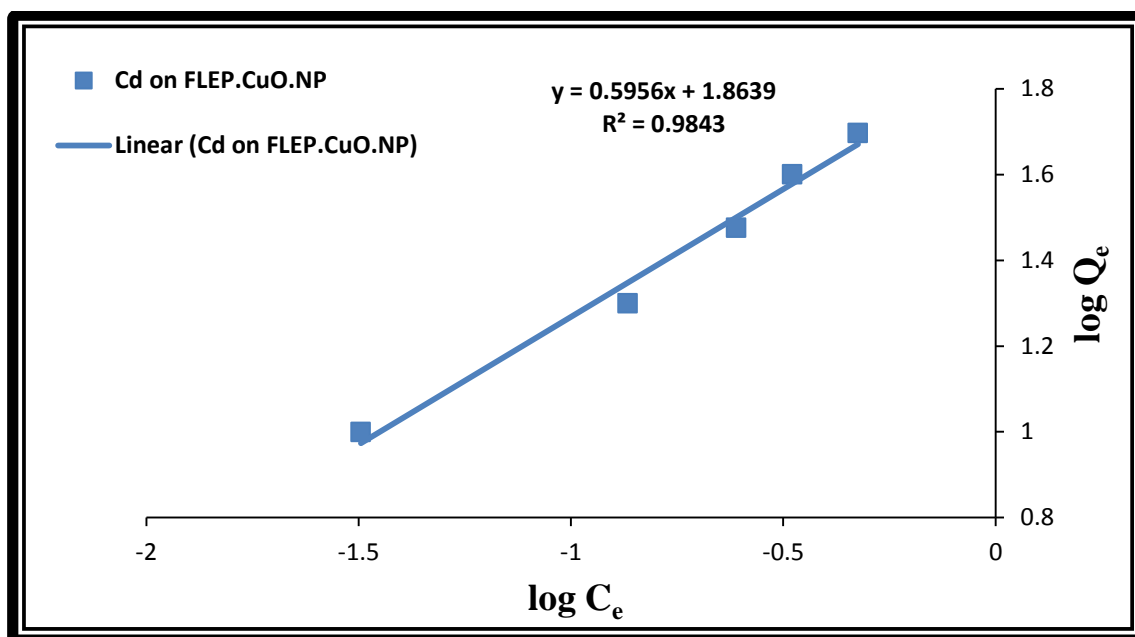
Figure (3.25): Linear Freundlich isotherm of Cd (II) ions in single system adsorption on (FLEP.CuO.NP) surface at various initial concentrations.
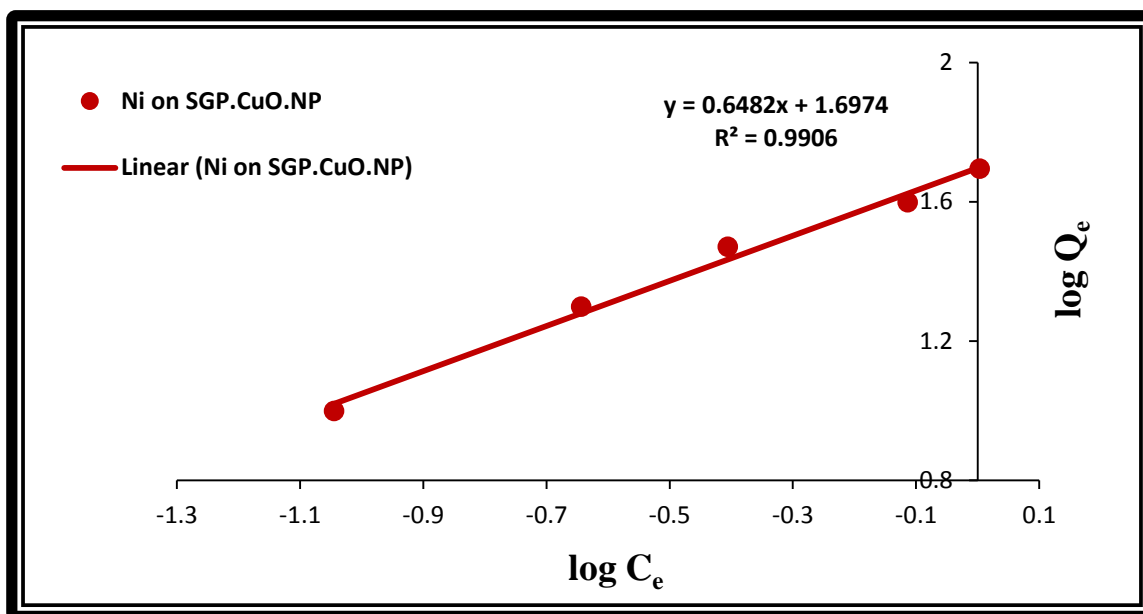
Figure (3.26): Linear Freundlich isotherm of Ni (II) ions in single system adsorption on (SGP.CuO.NP) surface at various initial concentrations.
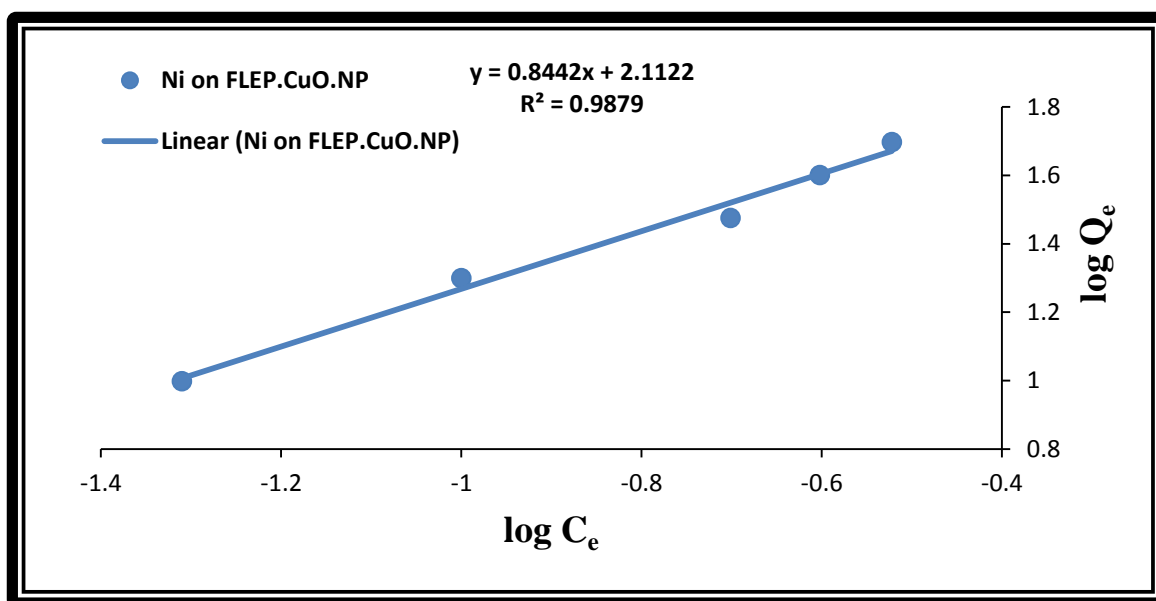
Figure (3.27): Linear Freundlich isotherm of Ni (II) ions in single system adsorption on (FLEP.CuO.NP) surface at various initial concentrations.

3.3.1.3. Temkin isotherm

Temkin isotherm equation **(1.6)** model was applied on the adsorption of Cd (II) and Ni (II) ions in single system on the (SGP.CuO.NP) and (FLEP.CuO.NP). Adsorption isotherm data for cadmium and nickel ions were plotted and presented in *Table (3.16)* and *Figures (3.28) − (3.31).*

The Temkin isotherm constant **(A_T)**, which is the equilibrium binding constant (L/g) corresponding to the maximum binding energy, and **(B_T)** is related the adsorption heat, being calculated from the slope and intercept of the plots of **(Q_e)** versus **($\ln C_e$)** and the results are shown in *Tables (3.17).*
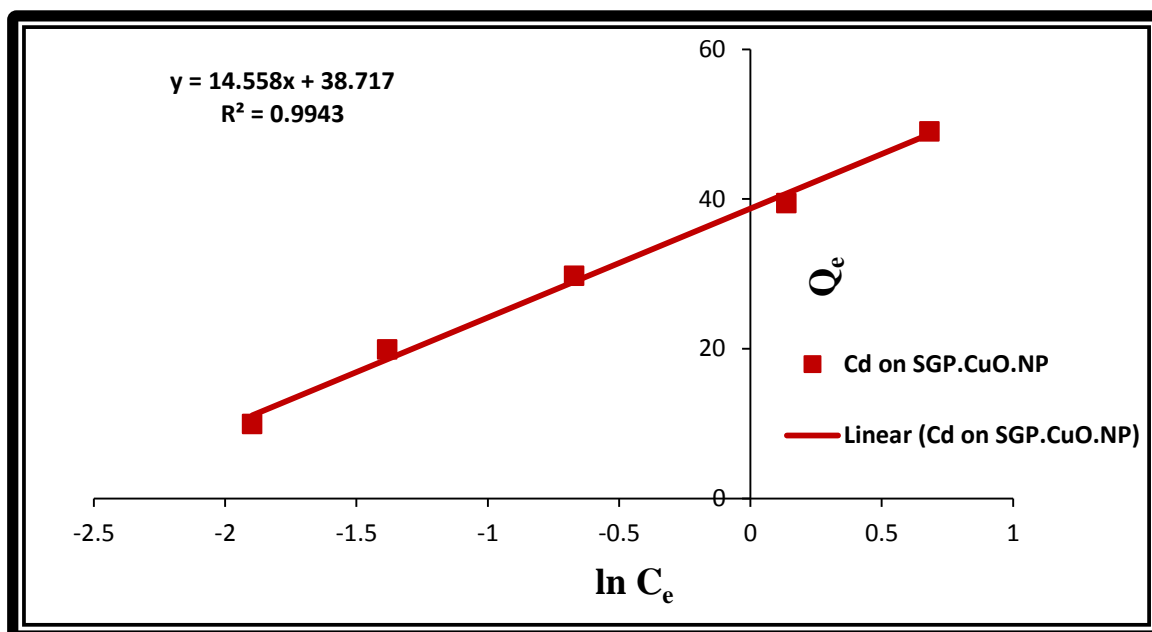
Figure (3.28): Temkin isotherm of Cd (II) ions in single system adsorption on (SGP.CuO.NP) surface at various initial concentrations.
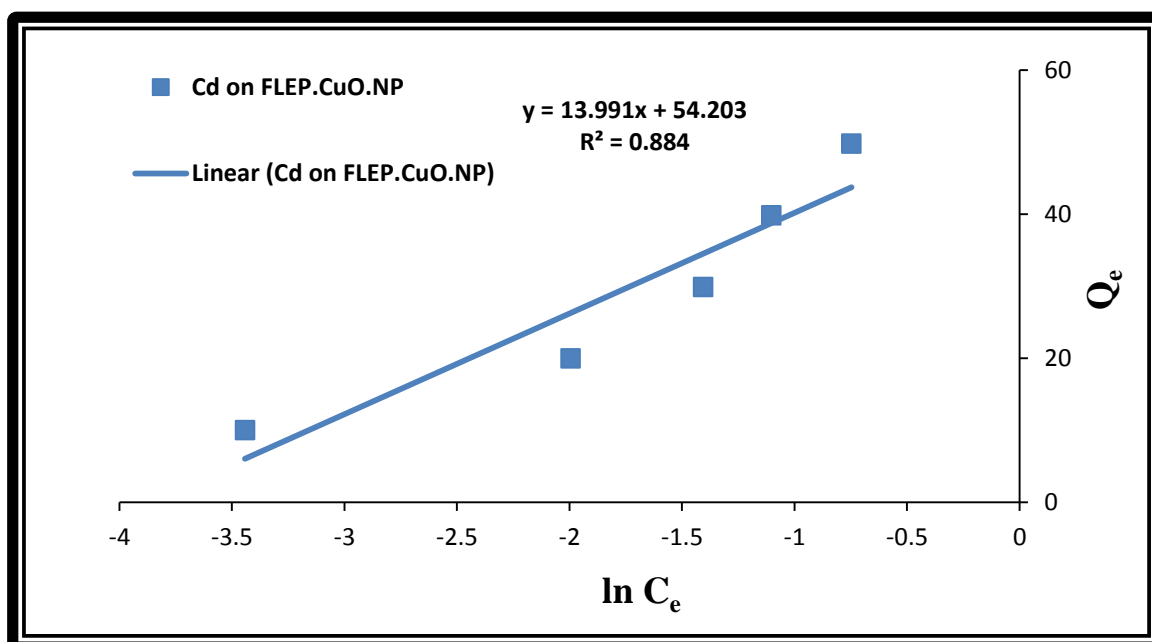
Figure (3.29): Temkin isotherm of Cd (II) ions in single system adsorption on (FLEP.CuO.NP) surface at various initial concentrations.
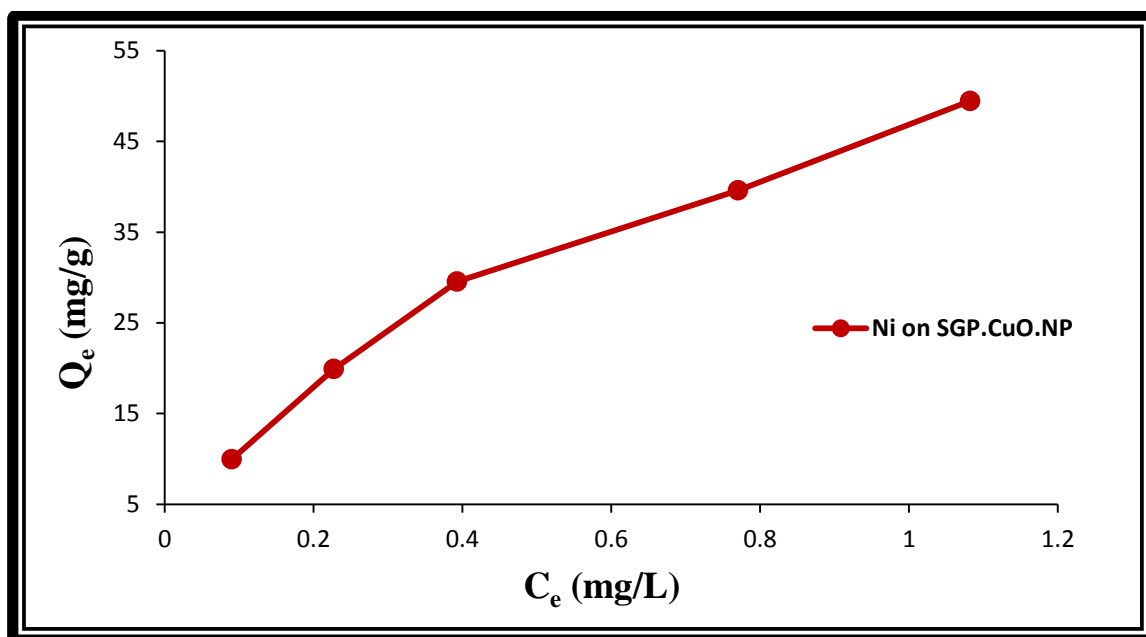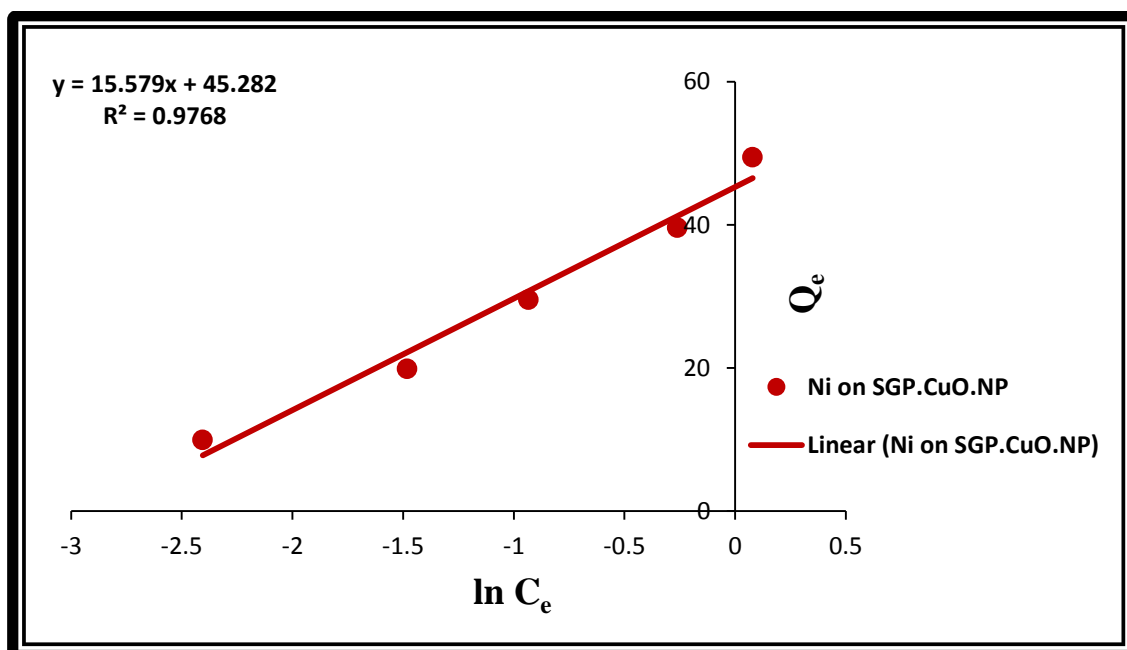
Figure (3.30): Temkin isotherm of Ni (II) ions in single system adsorption on (SGP.CuO.NP) surface at various initial concentrations.
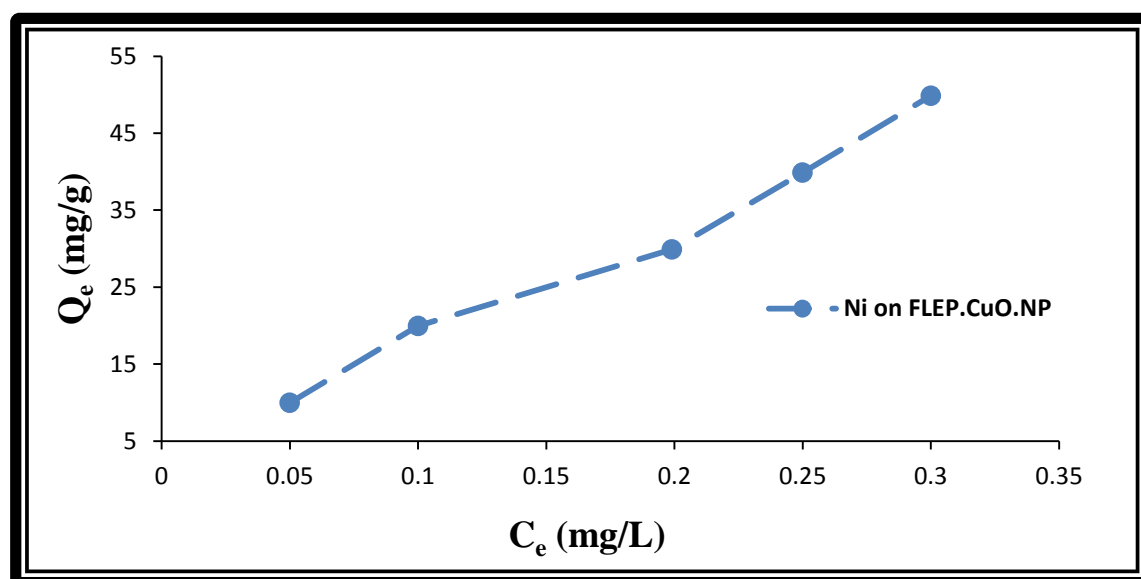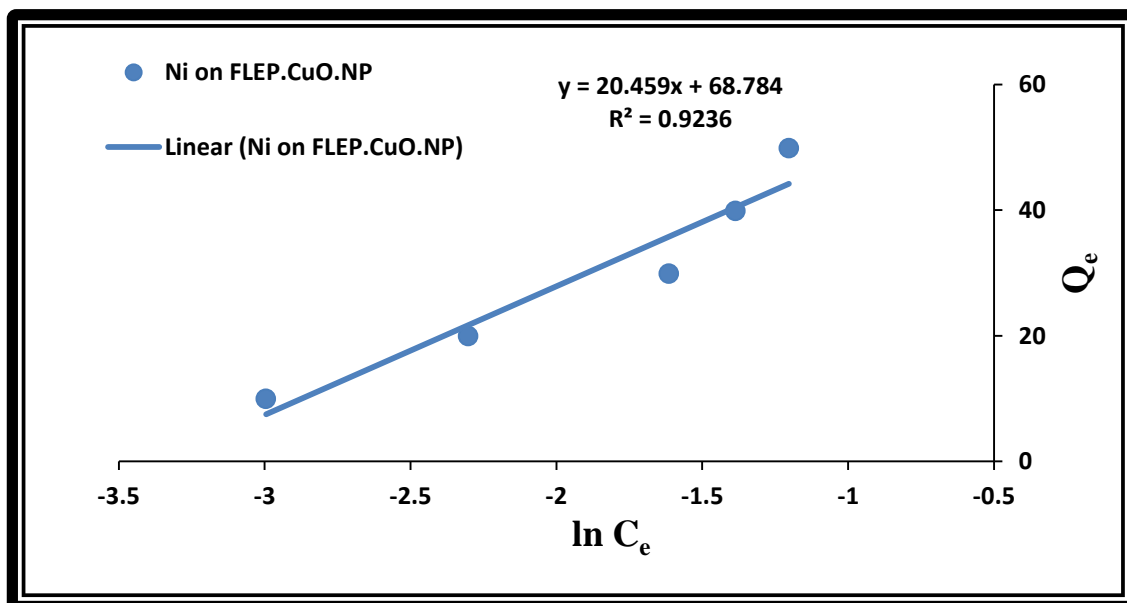

Figure (3.31): Temkin isotherm of Ni (II) ions in single system adsorption on (FLEP.CuO.NP) surface at various initial concentrations.

Table (3.17): Langmuir, Freundlich and Temkin constants for the adsorption of Cd (II) and Ni (II) ions in single system with (SGP.CuO.NP) and (FLEP.CuO.NP).

Models & Metals	SGP.CuO.NP			FLEP.CuO.NP		
Langmuir	**a (mg/g)**	**b (L/g)**	R^2	**a (mg/g)**	**b (L/g)**	R^2
Cd (II)	66.225	1.424	0.980	77.519	3.225	0.830
Ni (II)	75.757	1.609	0.984	181.818	1.145	0.936
Freundlich	**n**	**K_f (mg/g)**	R^2	**n**	**K_f (mg/g)**	R^2
Cd (II)	1.742	36.863	0.922	1.678	73.097	0.984
Ni (II)	1.542	49.819	0.990	1.184	129.419	0.987
Temkin	**A_T (L/g)**	**B_T (J/mole)**	R^2	**A_T (L/g)**	**B_T (J/mole)**	R^2
Cd (II)	14.341	14.558	0.994	48.140	13.991	0.884
Ni (II)	18.294	15.579	0.976	28.847	20.459	0.923

Table (3.17) present the adsorption data Cd (II) on (SGP.CuO.NP) which reach to follow Temkin regression as it fits better than that of the Laungmuir and Freundlich, this mean that heat of adsorption of all molecules in the layer decreases linearly with surface coverage, this is due to interaction of [Cd-(SGP.CuO.NP], while removal Cd (II) ions on (FLEP.CuO.NP) and Ni (II) ions on two surface fit well with Freundlich isotherm and this is because the adsorption take place on heterogeneous sites with different distribution of energy levels[142,143].

The values of **(n)** is higher than unity show the physical nature of the adsorption process on both adsorbents[144].

3.3.2. The adsorption isotherm of binary metal ions systems

The adsorption isotherm studies of cadmium (II) and nickel (II) (binary systems) from an aqueous solution on the copper oxide nanoparticles prepared by sol-gel and *Fig* Leaves Extract method at ideal condition mentioned in the ***Tables (3.15).***

The results are represented by initial concentration **(C₀)** of (Cd and Ni ions), and equilibrium concentration **(Cₑ)** measured at equilibrium state and values adsorption capacity **(Qₑ)** are calculated from the experimental data by using equation **(2.2)**. The adsorption capacity **(Qₑ)** are plotted versus equilibrium concentration to obtain general adsorption isotherm for Cd (II) ions removal by using (SGP.CuO.NP) and (FLEP.CuO.NP), with initial concentration varies (20, 40, 60, 80 and 100) mg/L at presence of Ni (II) with a constant initial concentration in each experimental ranges (20, 40, 60, 80, and 100) mg/L, as shown in ***Tables (3.18) – (3.22)*** and ***Figures (3.32)*** and ***(3.33)***, and the general adsorption isotherm of Ni (II) ions removal by using (SGP.CuO.NP) and (FLEP.CuO.NP), when it is initial concentration varies (20, 40, 60, 80 and 100) mg/L at presence of Cd (II) with a constant initial concentration in each experiment (20, 40, 60, 80, and 100) mg/L, as shown in ***Tables (3.18) – (3.22)*** and ***Figures (3.34)*** and ***(3.35).***

Table (3.18): Adsorption parameters values of Cd (II) ions removal in the presence [Ni] = 20 mg/L constant and values of Ni (II) ions in the presence [Cd] = 20 mg/L constant by (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces at ideal condition.

Metals	C_o (mg/L)	SGP.CuO.NP						FLEP.CuO.NP					
		C_e (mg/L)	Q_e (mg/g)	log C_e	log Q_e	ln C_e	C_e/Q_e	C_e (mg/L)	Q_e (mg/g)	log C_e	log Q_e	ln C_e	C_e/Q_e
Cd (II) ions	20	0.169	9.915	-0.771	0.996	-1.775	0.017	0.055	9.972	-1.259	0.998	-2.900	0.005
	40	0.357	19.821	-0.446	1.297	-1.028	0.018	0.139	19.930	-0.856	1.299	-1.973	0.006
	60	0.684	29.658	-0.164	1.472	-0.379	0.023	0.247	29.876	-0.607	1.475	-1.398	0.008
	80	1.304	39.348	0.115	1.594	0.265	0.033	0.403	39.798	-0.394	1.599	-0.908	0.010
	100	2.247	48.876	0.351	1.689	0.809	0.045	0.532	49.734	-0.274	1.696	-0.631	0.010
Ni (II) ions	20	0.155	9.922	-0.808	0.996	-1.864	0.015	0.028	9.986	-1.552	0.999	-3.575	0.002
	40	0.390	19.804	-0.408	1.296	-0.939	0.019	0.123	19.938	-0.910	1.299	-2.095	0.006
	60	0.690	29.654	-0.160	1.472	-0.370	0.023	0.202	29.899	-0.694	1.475	-1.599	0.006
	80	1.108	39.445	0.044	1.596	0.102	0.028	0.294	39.853	-0.531	1.600	-1.224	0.007
	100	1.826	49.086	0.261	1.690	0.602	0.037	0.379	49.810	-0.421	1.697	-0.970	0.007

Table (3.19): Adsorption parameters values of Cd (II) ions removal the presence [Ni] = 40 mg/L constant and values of Ni (II) ions in the presence [Cd] = 40 mg/L constant by (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces at ideal condition.

Metals	$C_\circ$ (mg/L)	SGP.CuO.NP						FLEP.CuO.NP					
		C_e (mg/L)	Q_e (mg/g)	log C_e	log Q_e	ln C_e	C_e/Q_e	C_e (mg/L)	Q_e (mg/g)	log C_e	log Q_e	ln C_e	C_e/Q_e
Cd (II) ions	20	0.220	9.889	-0.657	0.995	-1.513	0.022	0.065	9.967	-1.187	0.998	-2.733	0.006
	40	0.538	19.730	-0.268	1.295	-0.618	0.027	0.141	19.929	-0.850	1.299	-1.958	0.007
	60	1.212	29.393	0.084	1.468	0.192	0.041	0.258	29.871	-0.588	1.475	-1.354	0.008
	80	2.374	38.812	0.375	1.588	0.864	0.061	0.433	39.783	-0.363	1.599	-0.837	0.010
	100	3.877	48.061	0.588	1.681	1.355	0.080	0.545	49.727	-0.263	1.696	-0.606	0.010
Ni (II) ions	20	0.193	9.903	-0.713	0.995	-1.641	0.019	0.038	9.981	-1.420	0.999	-3.270	0.003
	40	0.461	19.769	-0.336	1.295	-0.773	0.023	0.133	19.933	-0.876	1.299	-2.017	0.006
	60	0.781	29.609	-0.107	1.471	-0.246	0.026	0.247	29.876	-0.607	1.475	-1.398	0.008
	80	1.206	39.396	-0.081	1.595	0.187	0.030	0.334	39.833	-0.476	1.600	-1.096	0.008
	100	1.870	49.065	0.272	1.690	0.626	0.038	0.516	49.742	-0.287	1.696	-0.661	0.010

Table (3.20): Adsorption parameters values of Cd (II) ions removal the presence [Ni] = 60 mg/L constant and values of Ni (II) ions in the presence [Cd] = 60 mg/L constant by (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces at ideal condition.

Metals	C_o (mg/L)	SGP.CuO.NP						FLEP.CuO.NP					
		C_e (mg/L)	Q_e (mg/g)	log C_e	log Q_e	ln C_e	C_e/Q_e	C_e (mg/L)	Q_e (mg/g)	log C_e	log Q_e	ln C_e	C_e/Q_e
Cd (II) ions	20	0.236	9.881	-0.626	0.994	-1.443	0.023	0.076	9.962	-1.119	0.998	-2.577	0.007
	40	0.562	19.718	-0.249	1.294	-0.575	0.028	0.141	19.933	-0.850	1.299	-1.958	0.007
	60	1.238	29.381	0.092	1.468	0.213	0.042	0.258	29.876	-0.588	1.475	-1.354	0.008
	80	2.488	38.756	0.395	1.588	0.911	0.064	0.433	39.833	-0.363	1.600	-0.837	0.010
	100	4.178	47.910	0.621	1.680	1.430	0.087	0.545	49.742	-0.263	1.696	-0.606	0.010
Ni (II) ions	20	0.228	9.885	-0.640	0.995	-1.474	0.023	0.076	9.962	-1.119	0.998	-2.577	0.007
	40	0.616	19.692	-0.219	1.294	-0.484	0.025	0.149	19.925	-0.826	1.299	-1.903	0.007
	60	0.846	29.576	-0.072	1.470	-0.166	0.028	0.256	29.872	-0.591	1.475	-1.362	0.008
	80	1.224	39.387	0.087	1.595	0.202	0.031	0.378	39.811	-0.422	1.600	-0.972	0.009
	100	1.877	49.061	0.273	1.690	0.629	0.038	0.807	49.596	-0.093	1.695	-0.214	0.016

Table (3.21): Adsorption parameters values of Cd (II) ions removal the presence [Ni] = 80 mg/L constant and values of Ni (II) ions in the presence [Cd] = 80 mg/L constant by (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces at ideal condition.

Metals	C_o (mg/L)	SGP.CuO.NP						FLEP.CuO.NP					
		C_e (mg/L)	Q_e (mg/g)	log C_e	log Q_e	ln C_e	C_e/Q_e	C_e (mg/L)	Q_e (mg/g)	log C_e	log Q_e	ln C_e	C_e/Q_e
Cd (II) ions	20	0.300	9.849	-0.522	0.993	-1.203	0.030	0.093	9.953	-1.031	0.997	-2.375	0.009
	40	0.870	19.565	-0.060	1.291	-0.139	0.044	0.198	19.901	-1.703	1.298	-1.619	0.009
	60	2.094	28.952	0.321	1.461	0.739	0.072	0.301	29.849	-0.521	1.474	-1.200	0.010
	80	3.868	38.066	0.587	1.580	1.352	0.101	0.462	39.769	-0.335	1.599	-0.772	0.011
	100	5.419	47.290	0.733	1.674	1.690	0.114	0.556	49.722	-0.254	1.696	-0.586	0.011
Ni (II) ions	20	0.424	9.787	-0.372	0.990	-0.856	0.043	0.095	9.952	-1.022	0.997	-2.353	0.009
	40	0.926	19.536	-0.033	1.290	-0.076	0.047	0.191	19.905	-0.721	1.298	-1.660	0.009
	60	1.413	29.293	0.150	1.466	0.345	0.048	0.295	29.852	-0.530	1.474	-1.220	0.009
	80	1.989	39.005	0.298	1.591	0.687	0.051	0.386	39.807	-0.413	1.599	-0.951	0.009
	100	2.839	48.580	0.453	1.686	1.043	0.058	0.940	49.530	-0.026	1.694	-0.061	0.018

Table (3.22): Adsorption parameters values of Cd (II) ions removal the presence [Ni] = 100 mg/L constant and values of Ni (II) ions in the presence [Cd] = 100 mg/L constant by (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces at ideal condition.

Metals	C_o (mg/L)	SGP.CuO.NP						FLEP.CuO.NP					
		C_e (mg/L)	Q_e (mg/g)	log C_e	log Q_e	ln C_e	C_e/Q_e	C_e (mg/L)	Q_e (mg/g)	log C_e	log Q_e	ln C_e	C_e/Q_e
Cd (II) ions	20	0.393	9.803	-0.405	0.991	-0.933	0.040	0.102	9.949	-0.991	0.997	-2.282	0.010
	40	1.101	19.449	0.041	1.288	0.096	0.056	0.214	19.893	-0.669	1.298	-1.541	0.010
	60	2.365	28.817	0.373	1.459	0.861	0.082	0.355	29.822	-0.449	1.474	-1.035	0.011
	80	3.974	38.012	0.599	1.579	1.379	0.104	0.486	39.757	-0.313	1.599	-0.721	0.012
	100	5.929	47.035	0.772	1.672	1.779	0.126	0.620	49.690	-0.207	1.696	-0.478	0.012
Ni (II) ions	20	0.513	9.743	-0.289	0.988	-0.666	0.052	0.105	9.947	-0.978	0.997	-2.253	0.010
	40	1.067	19.466	0.028	1.289	0.065	0.054	0.198	19.901	-0.703	1.298	-1.619	0.009
	60	1.479	29.260	0.170	1.466	0.391	0.055	0.298	29.851	-0.525	1.474	-1.210	0.009
	80	2.275	38.862	0.357	1.589	0.822	0.058	0.418	39.791	-0.378	1.599	-0.872	0.010
	100	2.929	48.535	0.466	1.686	1.074	0.060	0.965	49.517	-0.015	1.694	-0.035	0.019

Figure (3.32): Adsorption isotherm of Cd (II) ions [C₀ = 20 – 100] mg/L in the presence of increasing concentration of Ni (II) ions on (SGP.CuO.NP) surface at ideal condition.

Figure (3.33): Adsorption isotherm of Cd (II) ions [C₀ = 20 – 100] mg/L in the presence of increasing concentration of Ni (II) ions on (FLEP.CuO.NP) surface at ideal condition.

Figure (3.34): Adsorption isotherm of Ni (II) ions [C₀ = 20 – 100] mg/L in the presence of increasing concentration of Cd (II) ions on (SGP.CuO.NP) surface at ideal condition.

Figure (3.35): Adsorption isotherm of Ni (II) ions [C₀ = 20 – 100] mg/L in the presence of increasing concentration of Cd (II) ions on (FLEP.CuO.NP) surface at ideal condition.

The results showed increase in adsorption capacities of the copper oxide nanoparticle prepared by sol-gel and *Fig* Leaves Extract with equilibrium concentration of solution, the general shape of adsorption isotherm of two surfaces is of (L) type on Giles Classification[64]. It is seen that the equilibrium Cd (II) uptake increases with increasing initial Cd (II) concentration up to (100) mg/L at all Ni (II) ion concentration and also the observed equilibrium Ni (II) uptake increases with increasing initial Ni (II) concentration up to (100) mg/L at all Cd (II) ion concentration by using copper oxide sol-gel and *Fig* Leaves Extract.

The observed adsorption capacity of the binary metals on the (FLEP.CuO.NP) is better than the (SGP.CuO.NP). In general, the increase in the initial Ni (II) has non-effect on the individual adsorption yield of Cd (II) and the total adsorption yields for each experiment run and also the increase in the initial Cd (II) has non-effect on the individual adsorption of Ni (II) and total adsorption for experiment[28].

3.3.2.1. Langmuir, Freundlich and Temkin isotherms in binary systems

Langmuir, Freundlich and Temkin models are applied for equilibrium adsorption of Cd (II) and Ni (II) binary systems with (SGP.CuO.NP) and (FLEP.CuO.NP) at different initial concentration of each metals, to see the best isotherm that explain the adsorption phenomena presented in *Tables (3.18) – (3.22).*

The values of the Langmuir isotherm constant **(a)** which is the monolayer adsorption capacity and **(b)** which is a constant related to the energy of adsorption are calculated from the slope and intercept of the plots C_e/Q_e versus C_e .are shown in *Tables (3.23)* and *(3.24)* and *Figures (3.36) – (3.39).*The Freundlich constant **(K_f)** which is the adsorption capacity of the adsorbent, and **(n)** is the adsorption intensity being calculated from the slope and intercept of the plot of **($\log Q_e$)** versus **($\log C_e$)**, and the results are shown in *Tables (3.23)* and *(3.24)* and *Figures (3.40) – (3.43).* The Temkin isotherm constant **(A_T)**, which is the equilibrium binding constant (L/g) corresponding to the maximum binding energy, and **(B_T)** is related the adsorption heat, being calculated from the slope and intercept of the plots of **(Q_e)** versus **($\ln C_e$)** and the results are shown in *Tables (3.23) and (3.24)* and *Figures (3.44) – (3.47).*
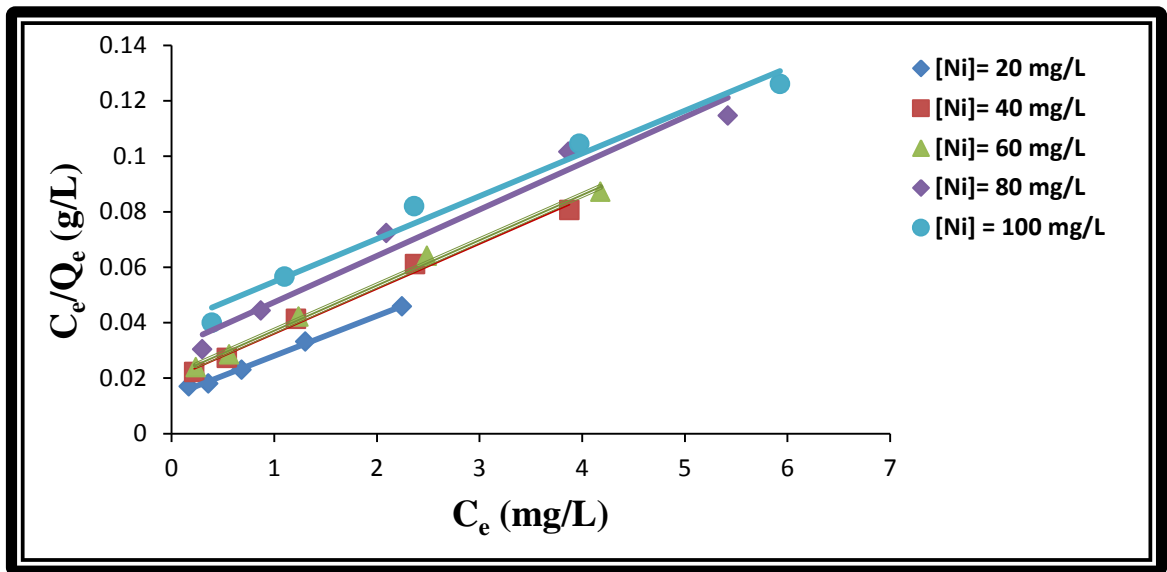
Figure (3.36): Linear Langmuir isotherm of Cd (II) ions [C₀ = 20 – 100] mg/L in the presence of increasing concentration of Ni (II) ions on (SGP.CuO.NP) surface at ideal condition.
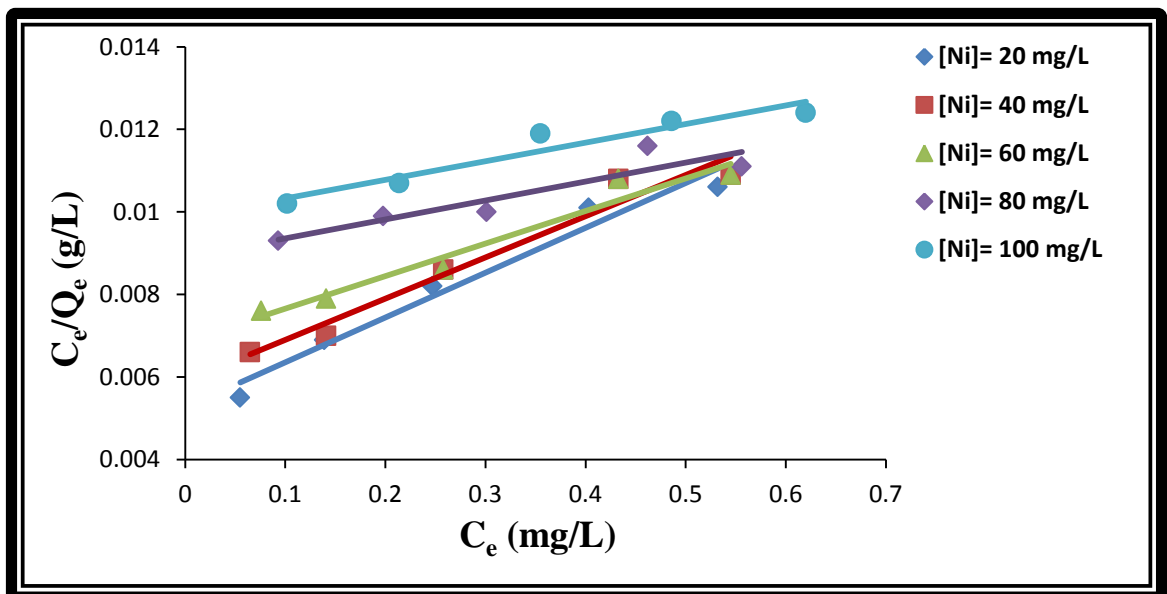
Figure (3.37): Linear Langmuir isotherm of Cd (II) ions [C₀ = 20 – 100] mg/L in the presence of increasing concentration of Ni (II) ions on (FLEP.CuO.NP) surface at ideal condition.
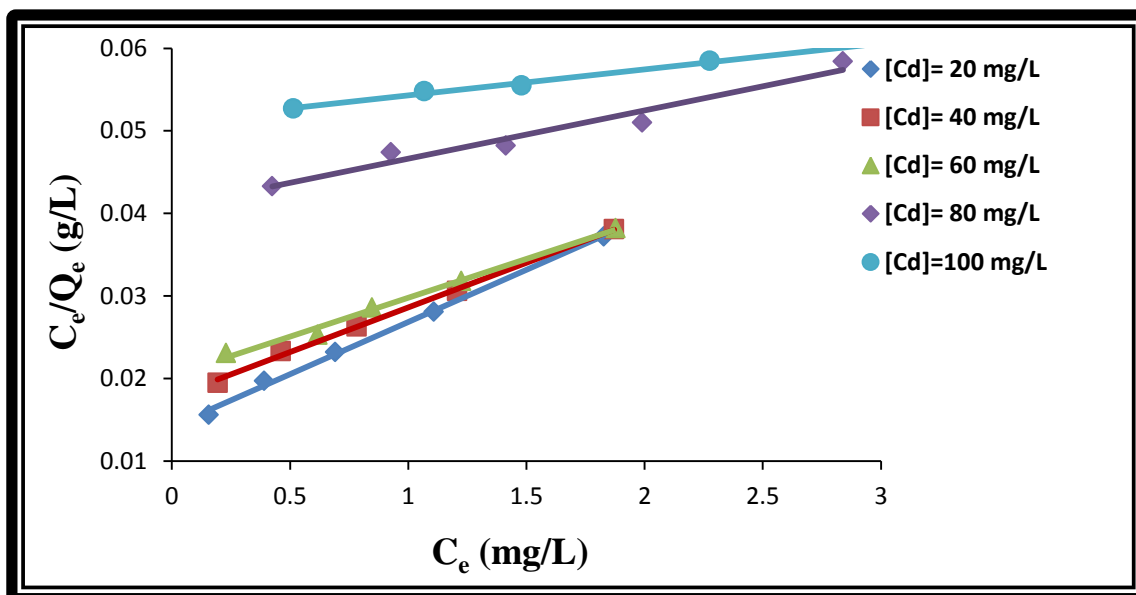
Figure (3.38): Linear Langmuir isotherm of Ni (II) ions [C₀ = 20 – 100] mg/L in the presence of increasing concentration of Cd (II) ions on (SGP.CuO.NP) surface at ideal condition.
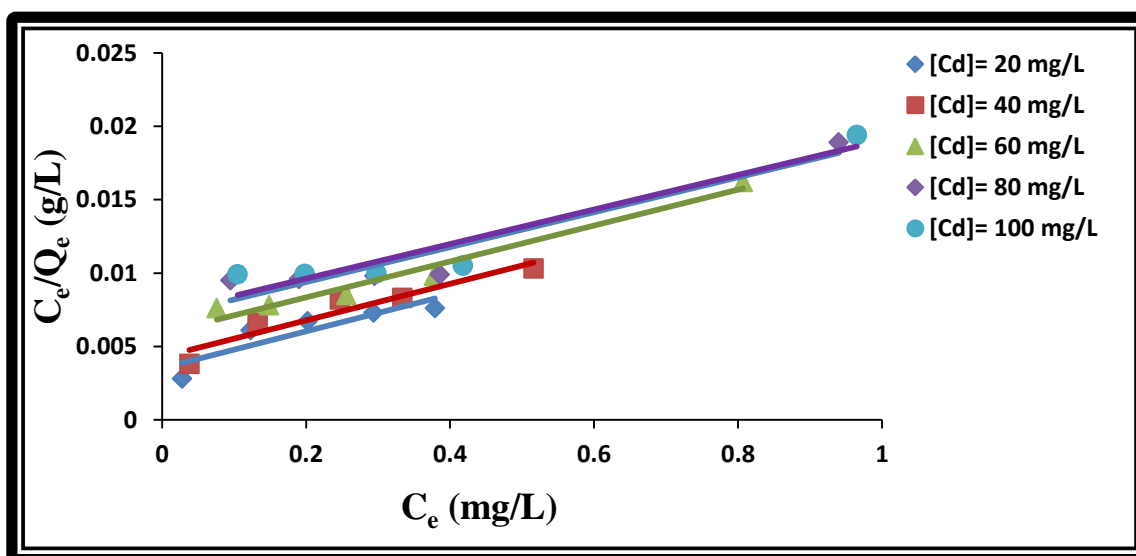
Figure (3.39): Linear Langmuir isotherm of Ni (II) ions [C₀ = 20 – 100] mg/L in the presence of increasing concentration of Cd (II) ions on (FLEP.CuO.NP) surface at ideal condition.
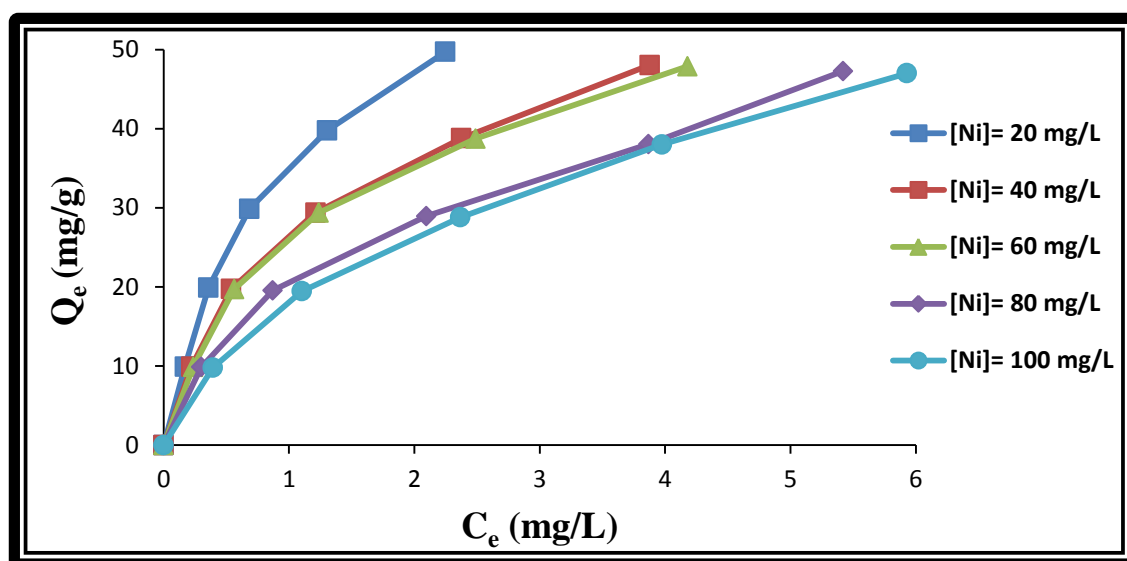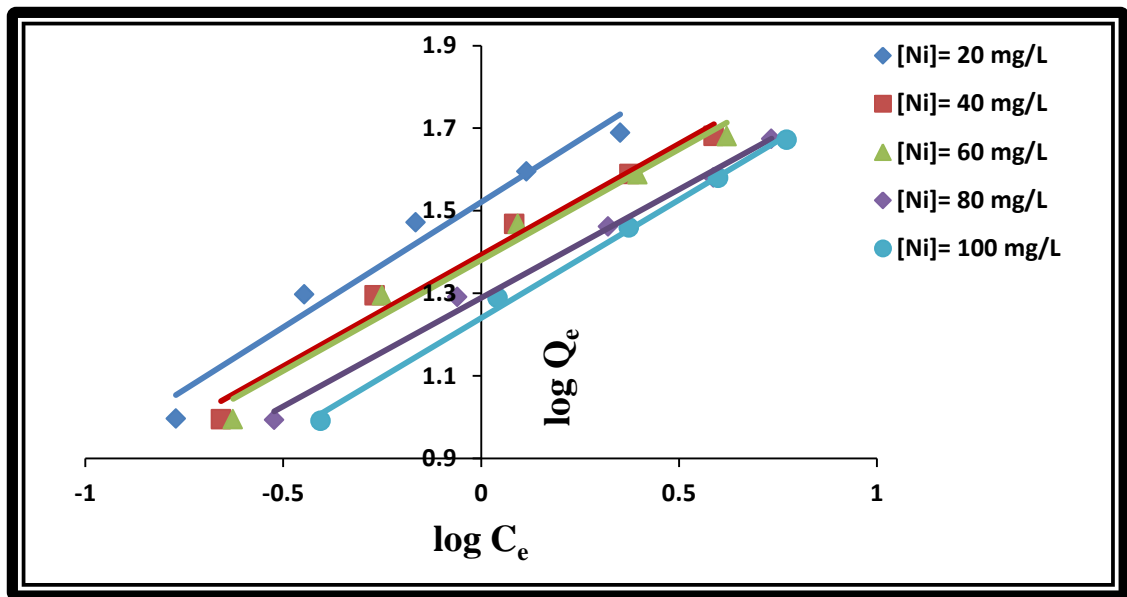
Figure (3.40): Linear Freundlich isotherm of Cd (II) ions [C₀ = 20 – 100] mg/L in the presence of increasing concentration of Ni (II) ions on (SGP.CuO.NP) surface at ideal condition.
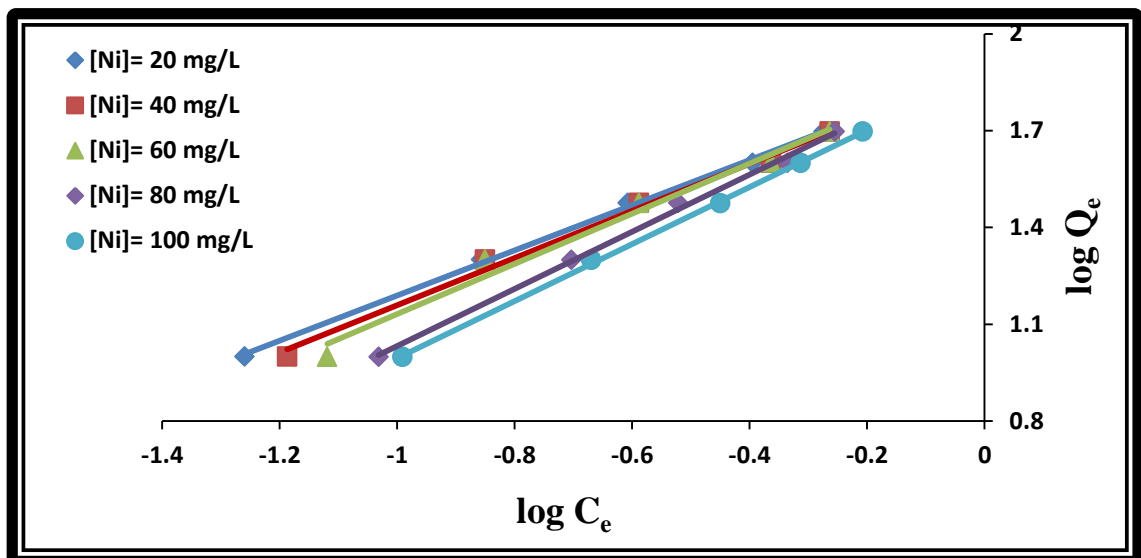
Figure (3.41): Linear Freundlich isotherm of Cd (II) ions [C₀ = 20 – 100] mg/L in the presence of increasing concentration of Ni (II) ions on (FLEP.CuO.NP) surface at ideal condition.
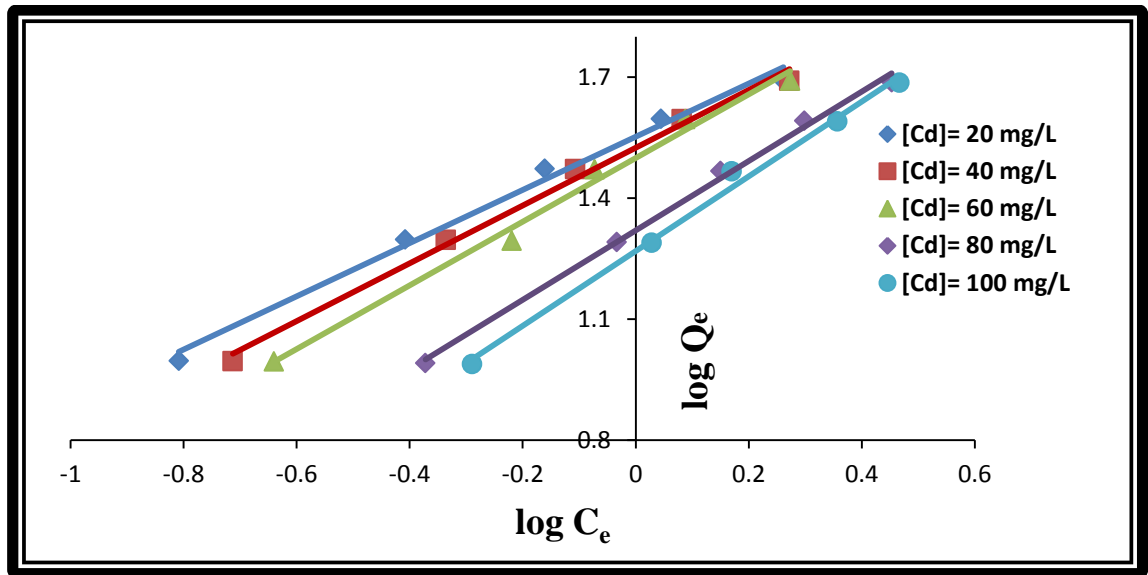
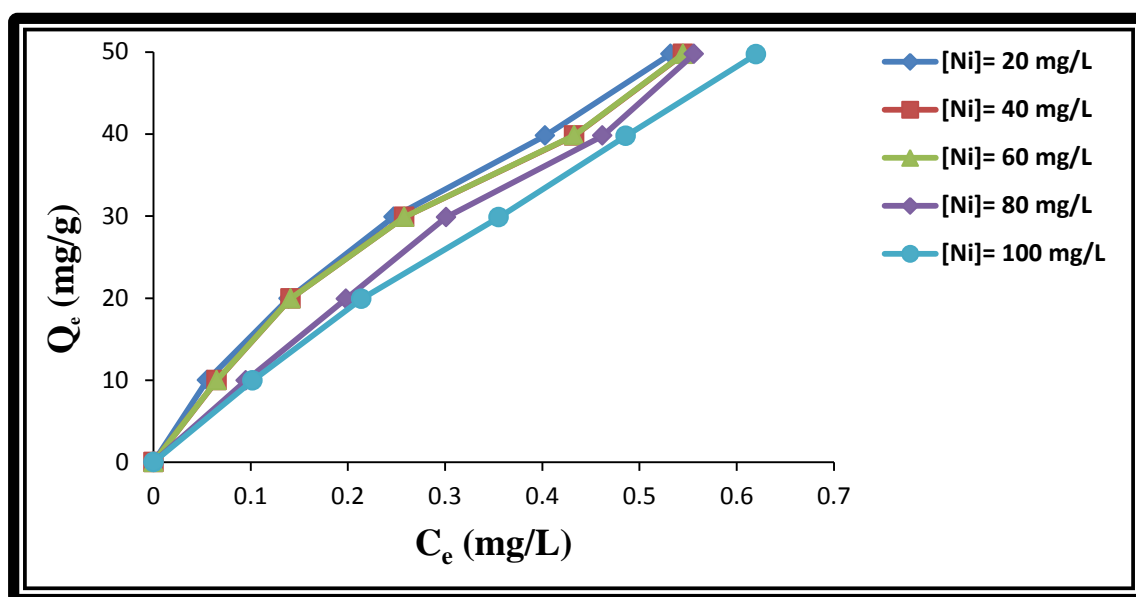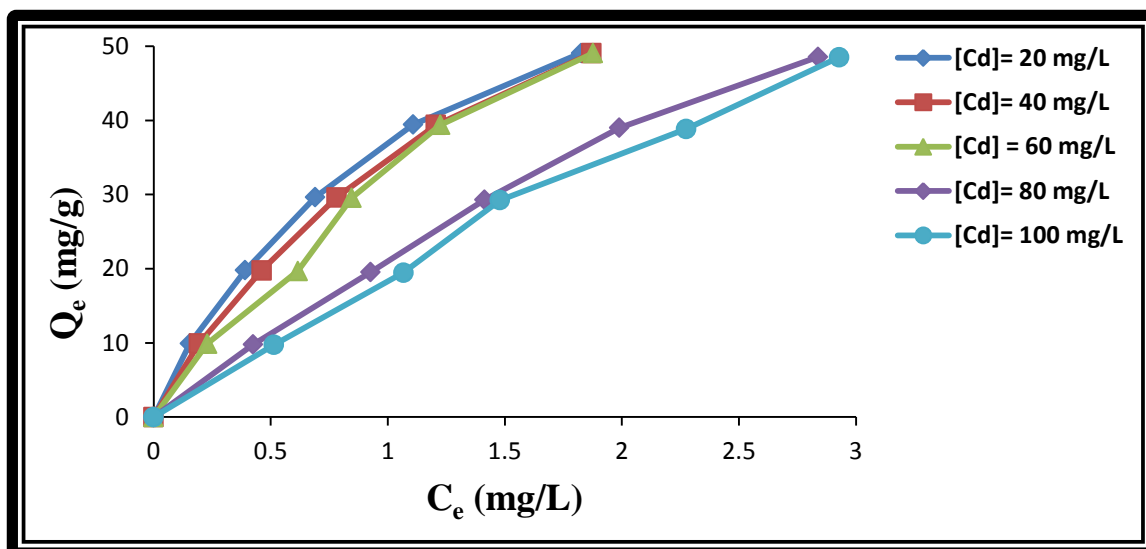*Figure (3.42): Linear Freundlich isotherm of Ni (II) ions [C₀ = 20 − 100] mg/L in the presence of increasing concentration of Cd (II) ions on (SGP.CuO.NP) surface at ideal condition.*
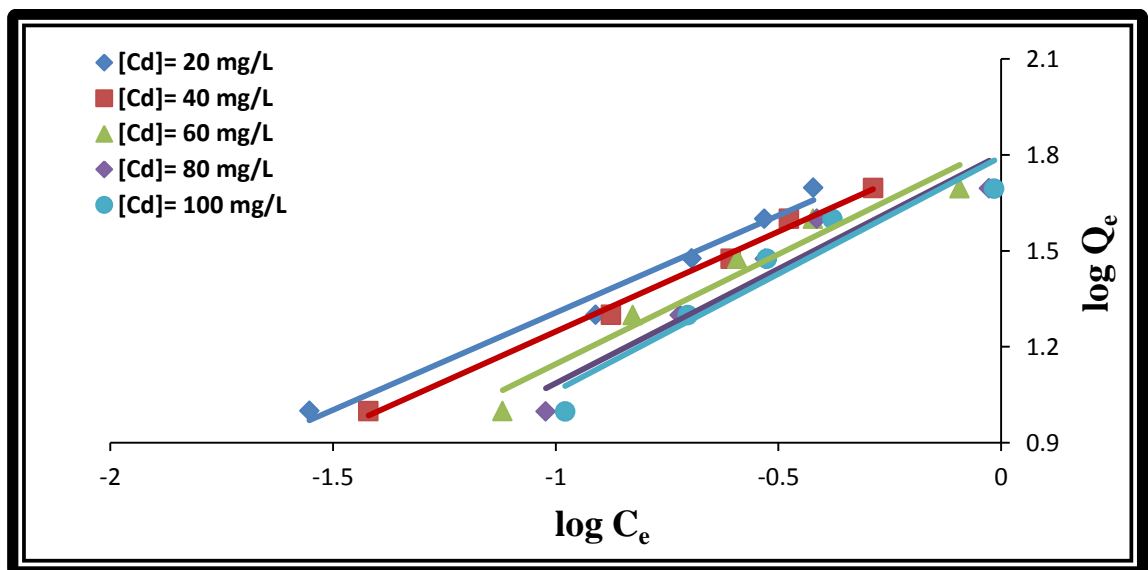
Figure (3.43): Linear Freundlich isotherm of Ni (II) ions [C₀ = 20 − 100] mg/L in the presence of increasing concentration of Cd (II) ions on (FLEP.CuO.NP) surface at ideal condition.
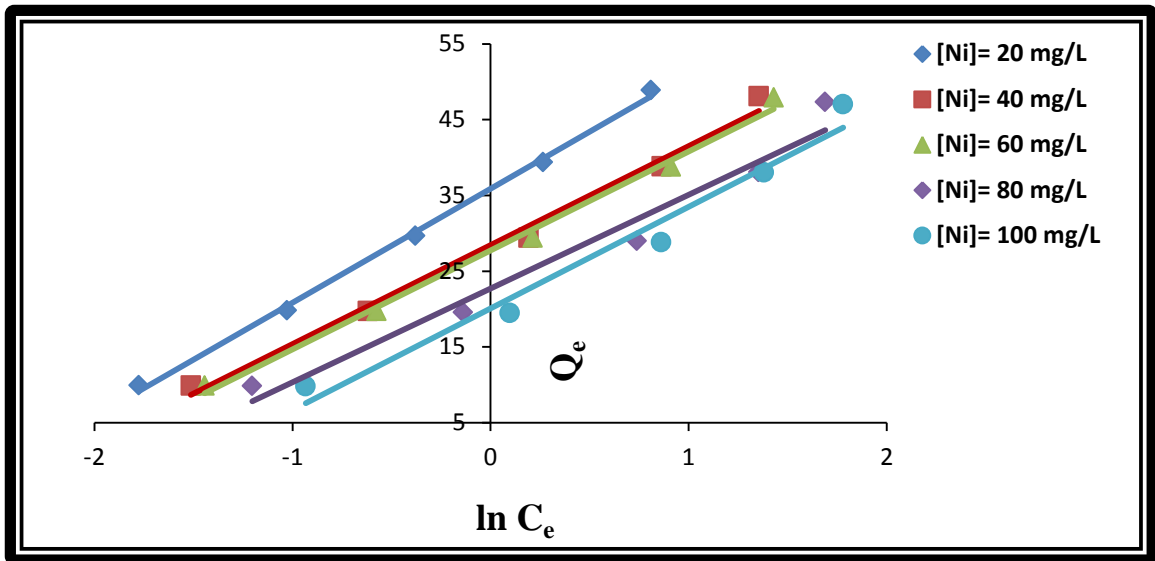
Figure (3.44): Temkin isotherm of Cd (II) ions [C₀ = 20 − 100] mg/L in the presence of increasing concentration of Ni (II) ions on (SGP.CuO.NP) surface at ideal condition.

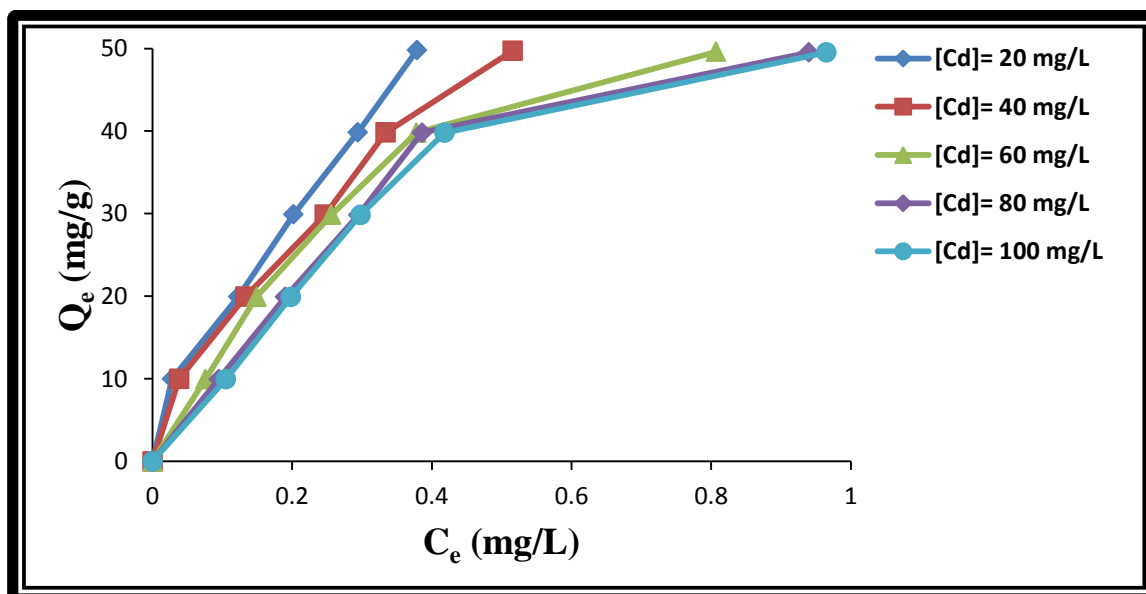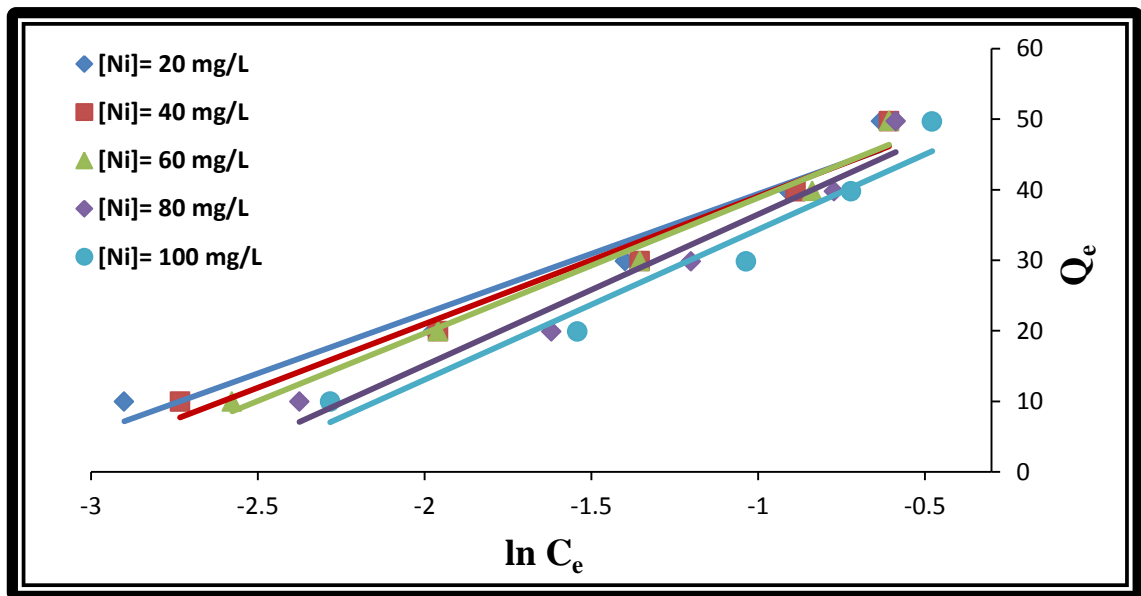
Figure (3.45): Temkin isotherm of Cd (II) ions [C₀ = 20 − 100] mg/L in the presence of increasing concentration of Ni (II) ions on (FLEP.CuO.NP) surface at ideal condition.
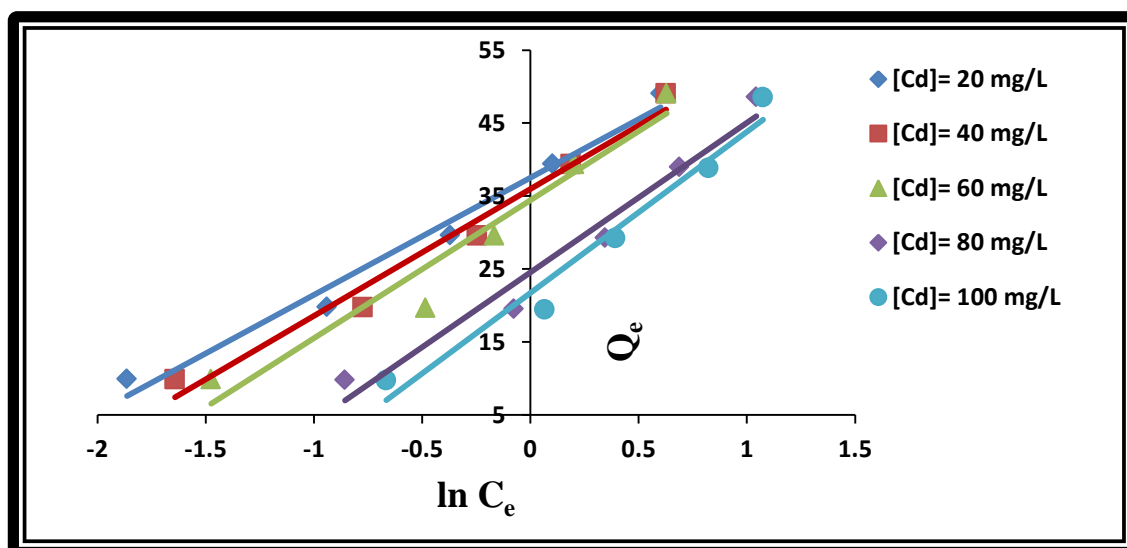
Figure (3.46): Temkin isotherm of Ni (II) ions [C₀ = 20 − 100] mg/L in the presence of increasing concentration of Cd (II) ions on (SGP.CuO.NP) surface at ideal condition.
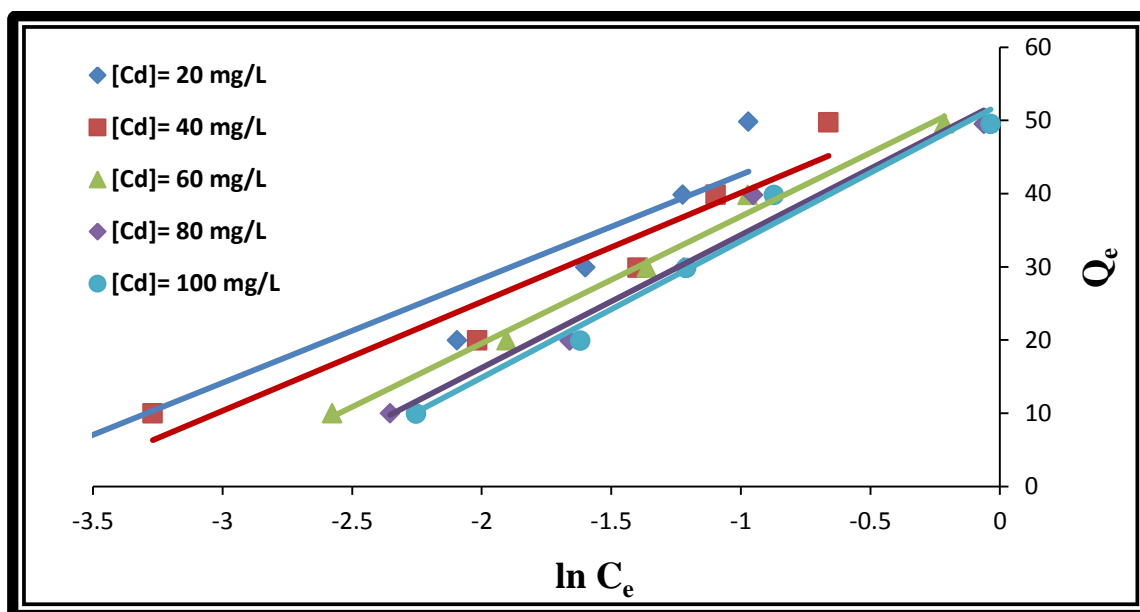
Figure (3.47): Temkin isotherm of Ni (II) ions [C₀ = 20 − 100] mg/L in the presence of increasing concentration of Cd (II) ions on (FLEP.CuO.NP) surface at ideal condition.

Table (3.23): Langmuir, Freundlich and Temkin constants and the correlation coefficients for the adsorption of cadmium ions by (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces in presence of variable initial nickel ions concentration.

surfaces	C_0 [Ni] (mg/L)	Langmuir			Freundlich			Temkin		
		a (mg/g)	b (L/g)	R^2	n	K_f (mg/g)	R^2	A_T (L/g)	B_T (J/mole)	R^2
SGP.CuO.NP	20	60.444	1.051	0.998	1.651	33.174	0.966	10.858	15.038	0.997
	40	61.728	0.814	0.992	1.857	24.694	0.980	8.809	13.073	0.990
	60	61.349	0.783	0.994	1.863	24.004	0.975	8.370	13.052	0.993
	80	61.880	0.542	0.993	1.902	19.451	0.992	6.280	12.362	0.995
	100	64.935	0.393	0.996	1.746	17.382	0.966	4.472	13.409	0.969
FLEP.CuO.NP	20	91.743	2.056	0.966	1.428	77.428	0.998	27.694	16.978	0.957
	40	100	1.694	0.961	1.367	77.553	0.992	23.539	18.089	0.969
	60	126.580	1.144	0.954	1.287	81.096	0.981	20.552	19.195	0.977
	80	217.390	0.582	0.845	1.130	82.660	0.997	14.950	21.406	0.952
	100	222.200	0.505	0.918	1.131	75.561	0.999	13.620	21.306	0.950

Table (3.24): Langmuir, Freundlich and Temkin constants and the correlation coefficients for the adsorption of nickel ions by (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces in presence of variable initial cadmium ions concentration.

surfaces	$C_\circ$ [Cd] (mg/L)	Langmuir			Freundlich			Temkin		
		a (mg/g)	b (L/g)	R^2	n	K_f (mg/g)	R^2	A_T (L/g)	B_T (J/mole)	R^2
SGP.CuO.NP	20	79.365	0.887	0.997	1.517	35.612	0.991	10.348	16.052	0.979
	40	92.592	0.606	0.997	1.396	33.481	0.993	7.921	17.384	0.921
	60	106.380	0.460	0.991	1.266	31.560	0.989	6.176	18.901	0.944
	80	169.490	0.144	0.998	1.162	20.878	0.996	3.306	20.525	0.965
	100	322.500	0.060	0.993	1.079	18.543	0.993	2.675	22.074	0.965
FLEP.CuO.NP	20	80.000	3.571	0.792	1.643	82.167	0.978	54.318	14.224	0.978
	40	80.000	2.906	0.904	1.600	74.524	0.994	40.239	14.891	0.998
	60	81.967	2.067	0.969	1.456	68.045	0.990	22.730	17.369	0.990
	80	84.033	1.700	0.913	1.397	63.314	0.968	18.049	18.140	0.968
	100	84.745	1.616	0.911	1.366	62.230	0.975	16.372	18.658	0.976

From ***Table (3.23)***, the correlation coefficients for the Laungmuir regression fits are larger than that for the Temkin and Freundlich isotherms at removal of Cd (II) ions by (SGP.CuO.NP) in presence different of initial nickel (II) ions concentration. Adsorption isotherms constant (R^2) showed that the uptake of Cd (II) on (FLEP.CuO.NP) in presence of different initial concentration Ni (II) ions at all experiment could be described by the Freundlich isotherm because adsorption processes happen on heterogeneous sites.

From ***Table (3.24)***, explains the values (R^2) for the Laungmuir preferred to describe the adsorption processes than that for the Freundlich and Temkin for removal of Ni (II) ions by (SGP.CuO.NP) in presence of variable initial cadmium (II) ions concentration at all experiment, which means that adsorption occurs at homogenous sites and forms a monolayer. The adsorption of Ni (II) ions on the (FLEP.CuO.NP) surface in presence of cadmium different initial concentration, Temkin isotherm was slightly best suited to describe adsorption than Freundlich one.

3.4. Thermodynamic study of binary metals ions systems

The Effect of temperature on removal of metals in binary system on adsorbents nanoparticles at various temperature (298, 308, 318 and 333) K was investigated .This study will help in evaluation the basic thermodynamic function (Change of free energy ΔG (kJ/mole), enthalpy ΔH (kJ/mole), and entropy ΔS (J/mole.K) of adsorption processes, equilibrium of adsorption constant, K is explains thermodynamically by Van 't Hoff equation below:

$$\ln K = -\frac{\Delta H}{R}(\frac{1}{T}) + \frac{\Delta S}{R} \quad \dots\dots\dots \textbf{(3.2)}$$

The equilibrium constant, K were calculated at any different temperature by below equation[82].

$$K = \frac{Qe \times m(g)}{Ce \times V \text{ (L)}} \quad \dots\dots\dots \textbf{(3.3)}$$

Where:

Q$_e$: The capacity adsorption of metals ion, **(mg/g)**.

m: The quantity of metal oxide nanoparticles, **(g)**.

C$_e$: The concentration of equilibrium after removal metals in binary system, **(mg/L)**.

V: Volume of aqueous solution contains cadmium (II) and nickel (II) ions, **(L)**.

Table (3.25) illustrates **(K)** values for adsorption Cd (II) and Ni (II) ions in binary system on (SGP.CuO.NP) and (FLEP.CuO.NP) at various temperatures.

Gibes free energy change can be calculated from relationship[64,119] :

$$\Delta G° = -RT \ln k \ldots\ldots \textbf{(3.4)}$$

Where:

ΔG°: The standard free energy change, **(kJ/mole)**.

R: The constant of gas general, **(8.314×10^{-3} J/mol.K).**

T: Temperature, **(K)**.

K: Constant of thermodynamic equilibrium.

Values **(ΔH)** and **(ΔS)** can be calculated from the slope and intercept at drawing **(LnK)** versus **(1/T)**[61,145], as shown *Figures (3.48)* and *(3.49),* and explain below equations:

$$\text{Slope} = -\Delta H/R \ldots\ldots \textbf{(3.5)}$$

$$\text{Intercept} = \Delta S /R \ldots\ldots \textbf{(3.6)}$$

It is observed a decreases in the a quantity of cadmium and nickel ions uptake onto copper oxide nanoparticle prepared by (sol-gel) and *Fig* Leaves Extract and with increasing temperature cause the adsorption reaction appeared exothermic, and *Table (3.26)* display the thermodynamic value of Cd (II) and Ni (II) ion removal on each adsorbents.

Table (3.25): Effect of temperature on thermodynamic equilibrium constant for the adsorption of Cd (II) and Ni (II) ions in binary system on (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces.

Surfaces	Metals	Temperature (K)	$1000/T(K^{-1})$	C_e (mg/L)	Q_e (mg/g)	K	ln K
SGP.CuO.NP	Cd (II) ions	298	3.355	4.367	47.816	21.897	3.086
		308	3.246	6.113	46.943	15.360	2.731
		318	3.144	7.110	46.444	13.064	2.569
		333	3.003	7.553	46.223	12.241	2.504
	Ni (II) ions	298	3.355	2.909	48.545	33.387	3.508
		308	3.246	2.954	47.941	32.852	3.492
		318	3.144	4.117	47.361	23.294	3.148
		333	3.003	5.277	49.869	17.952	2.887
FLEP.CuO.NP	Cd (II) ions	298	3.355	0.261	49.869	282.13	5.945
		308	3.246	0.758	49.621	130.92	4.874
		318	3.144	0.734	49.633	135.239	4.907
		333	3.003	0.658	49.671	150.97	5.017
	Ni (II) ions	298	3.355	1.547	49.226	63.681	4.153
		308	3.246	1.569	49.215	62.718	4.138
		318	3.144	3.961	48.019	24.241	3.188
		333	3.003	4.531	47.734	21.074	3.048
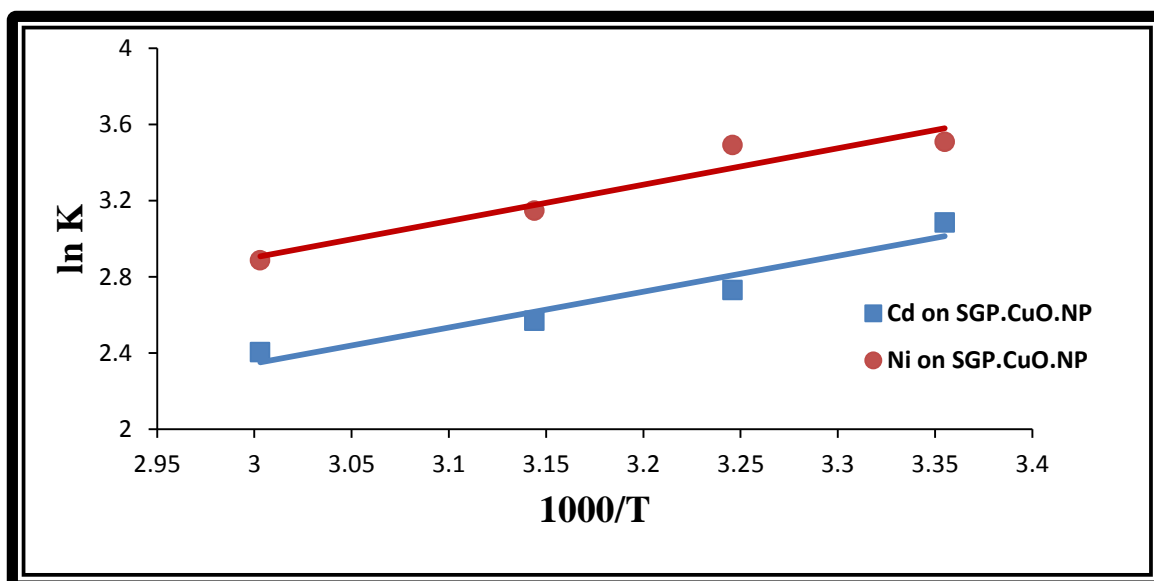
Figure (3.48): The Van 't Hoff Plot for adsorption of Cd (II) and Ni (II) ions in binary system by (SGP.CuO.NP) surface.
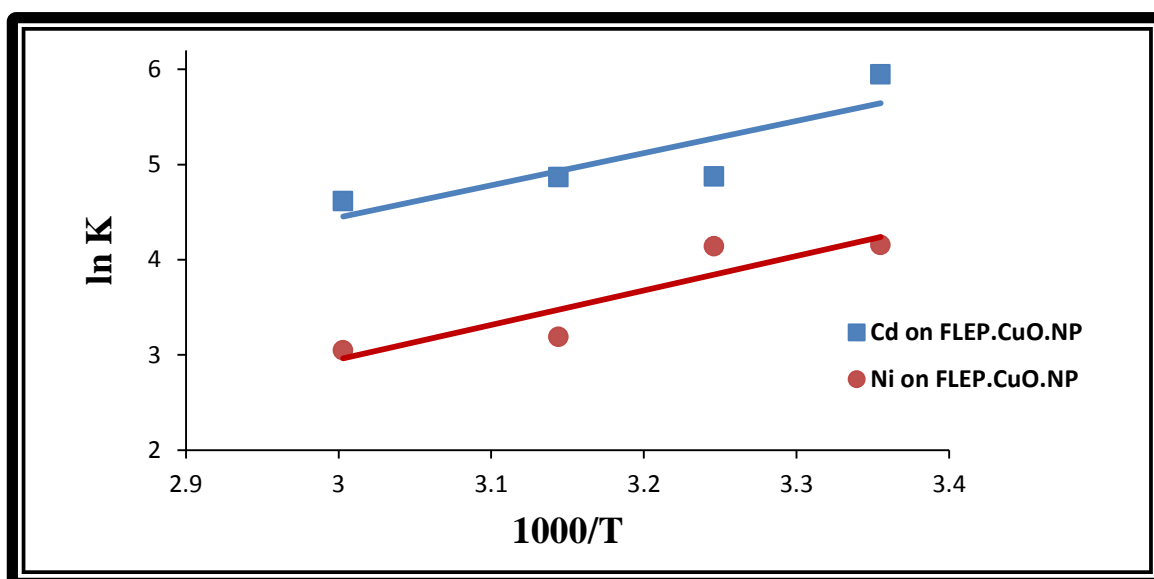
Figure (3.49): The Van 't Hoff Plot for adsorption of Cd (II) and Ni (II) ions in binary system by (FLEP.CuO.NP) surface.

Table (3.26): Values of thermodynamic function for the adsorption of Cd (II) and Ni (II) ions in binary system on (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces at different temperatures.

Surfaces	Metals	Temperature (K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol.K)
SGP.CuO.NP	Cd (II) ions	298	-7.645	- 0.0156	- 27.403
		308	- 6.993		
		318	- 6.792		
		333	- 6.932		
	Ni (II) ions	298	- 8.691	- 0.0158	- 23.533
		308	- 8.942		
		318	- 8.322		
		333	- 7.992		
FLEP.CuO.NP	Cd (II) ions	298	- 14.729	- 0.0281	- 47.397
		308	- 12.480		
		318	- 12.864		
		333	- 12.776		
	Ni (II) ions	298	- 10.289	- 0.0301	- 65.68
		308	- 10.596		
		318	- 8.428		
		333	- 8.438		

The ΔG value of the metals ion removal on two adsorbents being negative, indicated that the adsorption processes was spontaneous and ΔG values also determine the rate of the adsorption reaction, ΔG < 0 indicates physisorption process and indicated too favorable adsorption. The rate increases as ΔG increases. The value of ΔH were negative, indicating that the adsorption process was exothermic in nature, and ΔS negative indicates decreases in randomness at (solid - solution) interface through adsorption of Cd (II) and Ni (II) ions on both metal oxides nanoparticles[143,144].

3.5. Conclusions

We concluded from this study that:

1. The copper oxide nanoparticles can be prepared well by (sol-gel) and Fig Leaves Extract methods.

2. X-ray diffraction revealed that particle size obtained is about (21.11) nm for (SGP.CuO.NP) and (7.31) nm for (FLEP.CuO.NP), which agree fairly well with results of SEM and TEM one. From AFM the average particle size observed in the Nano scale, less (100) nm for both adsorbents.

3. The (SGP.CuO.NP) and (FLEP.CuO.NP) have a high capacity for removing the cadmium and nickel (ions) in (single and binary) systems from aqueous solution; however, (FLEP.CuO.NP) shows the highest ability to do so.

4. The percentage removal of (Cd^{+2} and Ni^{+2}) in binary system reach equilibrium in contact time (30) min and (15) min onto (SGP.CuO.NP) and (FLEP.CuO.NP) surfaces, respectively.

5. The (R %) of (nickel and cadmium ions) in binary system by (SGP.CuO.NP) and (FLEP.CuO.NP) increases with increase in adsorbent quantity and decrease slightly with increase in initial concentration of (Cd and Ni) ions concentration in a binary system.

6. Adsorption of cadmium (II) and nickel (II) ions on copper oxide nanoparticles prepared by (sol-gel) and *Fig* Leaves Extract surfaces increased when the pH of binary solution was increased from (2-6). For pH values above 6, the percentage removal of two metals ions decreased.

7. From the percentage removal (R%) of Cd (II) and Ni (II) in single on (SGP.CuO.NP) adsorbent at ideal condition is ($\approx$ 98 %), it is close to the percentage removal of two metals in the binary system, and percentage removal of cadmium and nickel ions in single system on

(FLEP.CuO.NP) adsorbent at ideal condition is ($\approx$ 99 %), it is also close to the percentage removal of two metals in the binary system.

8. The mixture of metals solution as pollution may exhibit three possible types of behavior. Synergism (the effect of the mixture is greater than that of each of the individual adsorbates in the mixture), antagonism (the effect of the mixture is less than that of each of the individual adsorbates in the mixture) and non-interaction (the mixture has non-effect on the adsorbates in the mixture).The combined effect of the two component Cd (II) and Ni (II) seems to have no effect.

9. In adsorption isotherm Cd (II) ion uptake in single system on (SGP.CuO.NP) is Temkin regression fits is higher than that for the Langmuir and Freundlich one, while adsorption Cd (II) on (FLEP.CuO.NP) the Freundlich is more appropriate to describe adsorption. Removal Ni (II) on two adsorbents is best fit with Freundlich model which described adsorption processes.

10. Isotherm of metals removal in binary system observed that removal of Cd (II) ions in presence different initial concentration of Ni (II) ions on (SGP.CuO.NP) in all experiment and Ni (II) ions in presence different initial concentration of Cd (II) on (SGP.CuO.NP) with the R^2 for the Laungmiur regression are larger than that for the Freundlich and Temkin, and at uptake of Cd (II) ions in binary system on (FLEP.CuO.NP) in presence Ni (II) with various initial concentration in all experiment , the Freundlich isotherm is better describe it than other models in this study. For the removal of Ni (II) ion in binary system in presence Cd (II) ion with various initial concentrations on (FLEP.CuO.NP), the Temkin isotherm is best described adsorption processes.

11. The negative values of the thermodynamic values ΔG, ΔH and ΔS for the adsorption of cadmium and nickel ions in binary system on two adsorbents prepared indicates that the adsorption processes is spontaneous, exothermic and less randomness at (solid– solution) interface.

3.6. Future studies

1. Using the copper (II) oxide nanoparticles prepared by using (sol-gel) and *Fig* Leaves Extract in removal of other various heavy metals in binary and ternary systems such as ; Cu-Zn, Cd-Ni-pb,…. etc.

2. Preparation of copper (II) oxide nanoparticles using another biomaterials.

3. Preparation of other metal oxides nanoparticles using (sol-gel) and *Fig* Leaves Extract and used them in removal of cadmium and nickel ions in binary system from aqueous solution.

4. Calculation the removal percentage of nickel (II) and cadmium (II) in binary system onto copper (II) oxide nanoparticles at temperature below 298 K.

5. Studying of kinetics on cadmium (II) and nickels (II) ions in binary system onto copper (II) oxide prepared in two different methods.

6. Trying other adsorbent like clay, alumina, kaolinite, and plant waste in removal of other heavy metals system.

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الملخص

في هذا البحث تم تحضير أوكسيد النحاس النانوي بأستخدام طريقة (المحلول - جل) والطريقه البسيطة بأستخدام مستخلص أوراق شجرة التين. أستخدم طيف حيود الاشعة السينية ، المجهر الألكتروني الماسح، المجهرالألكتروني النافذ ومجهر القوة الذرية لتشخيص هذه الأكاسيد حيث أظهرت نتائج قياس (XRD) أن حجم الجسيمات كانت (21.11) نانومتر و (7.31) نانومتر على السطحين (SGP.CuO.NP) و(FLEP.CuO.NP) على التوالي. وهذا ماأكدته نتائج قياسات (SEM، TEM) التي تم أجرائها وحيث شخص تركيب السطح بأستخدام تقنيات (SEM، TEM، AFM).

أن تلوث المياه بالعديد من المعادن الثقيلة يشكل ضرراً كبيراً على البيئة لذلك أستخدم أوكسيد النحاس النانوي المحضرتطبيقياً بطريقتين لإزالة أيونات النيكل والكادميوم الثنائية في النظام الثنائي من المحاليل المائية المخففة . وفي هذا المجال ، تم دراسة عدد من العوامل التي تؤثر على نسبة إزالة المعادن في النظام الثنائي على المواد المازة (النانوية). حيث وجد أن الزمن اللازم لإزالة أيونات الكادميوم والنيكل في النظام الثنائي والوصول الى حالة الأتزان هو (30) دقيقة على أوكسيد النحاس النانوي المحضر بطريقة (المحلول - جل) و (15) دقيقة على أوكسيد النحاس النانوي المحضر بأستخدام مستخلص أوراق شجرة التين. لقد تبين ان إزالة أيونات الكادميوم والنيكل تقل بزيادة تركيز المادة الممتزة وتزداد بزيادة وزن السطح الماز. وعند دراسة إزالة الفلزين في النظام الثنائي عند قيم مختلفة للدالة الحامضية (2، 4، 6، 8) ظهر ان أفضل أمتزاز لأيونات الفلزين الثقيلين على السطحين المحضرين كان عند الدالة الحامضية 6، أما تأثير درجة الحرارة على أمتزاز كل من الفلزين في النظام الثنائي فقد أشار ان نسبة الإزالة تقل بزيادة درجة الحرارة ممماأتضح ان العملية باعثة للحرارة. وعند حساب قيم الدوال الثرموديناميكية لعملية الأمتزاز (ΔS, ΔH, ΔG) تبين أن عملية الأمتزاز هي تلقائية، باعثة للحرارة ، وأقل عشوائية عند تداخل أيونات الفلزين الثنائية مع أكاسيد الفلزات النانوية المحضرة ، وكذلك نلاحظ ان قابلية أمتزاز أوكسيد النحاس النانوي المحضر بأستخدام مستخلص أوراق شجرة التين لأيونات المعادن الثقيلة أعلى من أوكسيد النحاس النانوي المحضربطريقة (المحلول - جل) علما أن السطحين أظهرا كفاءة عالية للأمتزاز.

قد وجد أيزوثيرم تمكن هو الأفضل لوصف عملية إزالة أيونات الكادميوم الثنائية على أوكسيد النحاس النانوني المحضر بطريقة (المحلول - جل)، وأيزوثيرم فرندلش هو الأفضل لوصف إزالة أيونات الكادميوم الثنائية على أوكسيد النحاس النانوي المحضر بأستخدام مستخلص أوراق شجرة التين في النظام الاحادي. كما ظهر أن أفضل أيزوثيرم لإزالة أيونات النيكل الثنائية على المادتين المازتين في النظام الاحادي هو فرندلش وهذا ما نلاحظه من قيم معامل الارتباط.

أن إزالة أيونات الكادميوم الثنائية بوجود تركيز أبتدائي مختلف من أيون النيكل الثنائية على سطح (SGP.CuO.NP) في جميع تجارب الأيزوثيرم للنظام الثنائي وأزالة أيونات النيكل الثنائية بوجود تركيز أبتدائي مختلف من أيون الكادميوم على سطح (SGP.CuO.NP) بينت أن معادلة لانكماير هي الافضل لوصف عملية الأمتزاز مقارنة مع أيزوثيرمات فرندلش وتمكن في حين ان أمتزاز أيونات الكادميوم الثنائية في النظام الثنائي على (FLEP.CuO.NP) بوجود تركيز مختلف من أيونات النيكل في جميع تجارب الأيزوثيرم للنظام الثنائي كان أيزوثيرم فرندلش هو الأفضل لوصف عملية الأمتزاز مقارنة مع الأيزوثيرمات الأخرى في هذه الدراسة أما عند أمتزاز أيونات النيكل الثنائية على سطح (FLEP.CuO.NP) بوجود تركيز أبتدائي مختلف من أيونات الكادميوم الثنائية فقد وجد أن أيزوثيرم تمكن هو الافضل لوصف عملية الامتزاز.

وزارة التعليم العالي والبحث العلمي

جامعــــة ديــــــالى

كليــــــة العلــــــوم

قســـم الكيميـــــاء

إزالة أيونات الكادميوم والنيكل من أنظمتها الثنائية بأمتزازها على أوكسيد النحاس النانوي

رســـالة مقدمـــة الى

مجلس كلية العلوم / جامعة ديالى

وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قبل الطالبة

ســـالي كامـــل سعـــدي

بكالوريوس في علوم الكيمياء ٢٠١٤

كليــــــة العلــــــوم – جامعــــة ديالـــــى

بأشراف

أ.د. كريم هنيكش حسن   م. د. أريج علي جار الله

١٤٣٩هجرية   العراق   ٢٠١٨ ميلادية