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Adsorption of Cd(II) and Cu(II) on CoMo/γ.Al_2O_3 Nano Catalysts in Single and Binary Systems

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

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

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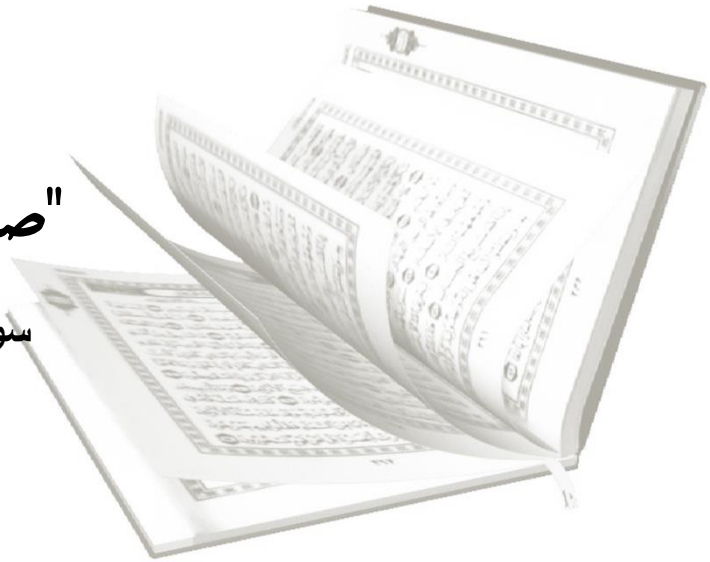

"صدق الله العظيم"

سورة الإسراء - الآية ٨٥

Dedication

To my dear Father

To the symbol of goodness ,kindness and sacrifice, My mother, To the luminous stars who shine in my dark night.

To my lovely Husband Ahmed and his family

To my strength in life my dearest brothers.

To the kind hearts, to the lovely people with whom I spent the most precious moments in my life. My teachers and my friends.

I dedicate my work

Ethar

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I am grateful to Allah, who granted me life, the power, peace and courage to finish this study.

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I express my deep thanks to my mother brothers and wives of my brothers and my husband Ahmed for all his love and support .

Finally, I would thanks everyone who helped me directly or indirectly in this work.

Ethar

Supervisor Certification

I certify that this thesis (**Adsorption of Cd(II) and Cu(II) on CoMo/γ.Al_2O_3 Nano Catalysts in Single and Binary Systems**) 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 (**ETHAR NASSHA JAWAD**).

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Abstract

In this study, the Nano $\gamma.Al_2O_3$, support was prepared by Co-Precipitation method from Aluminium Chlorides hexahydrate (source of Aluminum) and calcination at temperature off 550 ºC. Then Nano $CoMo/\gamma.Al_2O_3$ Catalyst was prepared by impregnation method were Cobalt nitrate (source of Cobalt) and ammonium hepta Molybdate (source of Molybdate) on the prepared Nano of $\gamma.Al_2O_3$ support with Calcination at a temperature 550 ºC.

They are characterized by X-ray diffraction spectrometry (XRD) and energy-dispersive X-ray spectrometry (EDX). Field Emission Scanning Electron (FESEM). Atomic force microscope techniques (AFM). XRD spectrum reveals that particle size obtained is about (4.33) nm for ($\gamma.Al_2O_3$) and (5.2) nm for prepared ($CoMo/\gamma.Al_2O_3$), which agreed fairly well with AFM.

Water pollution with many heavy metals is a major damage for environment, therefore the $CoMo/\gamma.Al_2O_3$ nanoparticles prepared are used to remove cadmium and copper 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 into adsorbents, the time required to remove Cd^{+} and Cu^{+2}) ions, in binary system to reach equilibrium was studied and showed that contact time were (15) min for removal of two metals of on $CoMo/\gamma.Al_2O_3$ surfaces. The removal of cadmium (II) and copper (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 Copper ions in binary systems, at different values of pH (2, 4, 6 and 8) indicated

that the best adsorption of two heavy metals on 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 at 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.

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List of Symbols and Abbreviations

Symbols or Abbreviations	Definitions
Q_e	*Adsorption capacity of the adsorbent at equilibrium time*
AAS	*Atomic absorption spectrophotometer*
AFM	*Atomic force microscope*
BET	*Brunauer, Emmett, and Teller*
C_t	*Concentration of adsorbate after any time*
R^2	*Correlation coefficient*
D	*Crystallite size*
DLS	*Dynamic light scattering*
EDX	*Energy dispersive X-ray spectroscopy*
ΔH	*Enthalpy change*
ΔS	*Entropy change*
A_T	*Equilibrium binding constant*
C_e	*Equilibrium concentration of adsorbate*
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 change*
IR	*Infrared spectroscopy*
C_0	*Initial concentration of adsorbate*
a	*Langmuir constant related with adsorption capacity*
b	*Langmuir constant related with energy of adsorption*

R%	***Percentage removal of adsorbale***
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***
K	***Thermodynamic equilibrium constant***
UV	***Ultraviolet - visible spectroscopy***
v	***Volume of solution***
m	***Mass of adsorbent***
XRD	***X-ray diffraction***
EDXA	***Energy Dispersive X-ray Analysis***
FESEM	***Field Emission Scanning Electron Microscope***

Chapter One

(Introduction)

1.1. Introduction

Adsorption is one of a common treatment applied in the heavy metal removal involves adsorbents such as undoubtedly activated carbon. However, the production and regeneration of activated carbon are very costly and tend to encourage people to find another alternative [30]. Recently, studies of low-cost adsorbent are intensively gain attention to the scientist were usually waste product from industrial, agricultural and food production which produced abundantly. Adsorption is one of the important and most popular physico-chemical method in removing contaminants [69]. It is an efficient process and economical way to remove ions from wastewaters; In order for the adsorption process to be good, there must be choice of the type of adsorbent that have good properties such as compatibility with adsorb ate, high surface area, high adsorption capacity, quick response of adsorption capacity to temperature change, high mass diffusivity and thermal stability.

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins, and water purification [4]. Among these methods, adsorption is currently considered to be very suitable for wastewater treatment because of its simplicity and cost-effectiveness. Adsorption is a commonly used technique for the removal of metal ions from various industrial effluents. Activated carbon is the most widely used adsorbent [37]. It is a highly porous, amorphous solid consisting of micro crystallites with a graphite lattice, usually prepared in small pellets or a powder. It can remove a wide variety of toxic metals.

Environmental pollution, particularly from heavy metals and minerals in the wastewater, is the most serious problem. Due to extensive anthropogenic activities such as industrial operations particularly mining, agricultural processes, and disposal of industrial waste materials; their concentration has increased to dangerous levels [24].

The problems of the ecosystem are increasing with developing the technology. Heavy metal pollution is one of the main problems. Toxic metal compounds coming to the earth's surface not only reach the earth's waters (seas, lakes, ponds, and reservoirs) but can also contaminate underground water in trace amounts by leaking from the soil after rain and snow [5]. Therefore, the earth's waters may contain various toxic metals. Drinking water is obtained from springs which may be contaminated by various toxic metals. One of the most important problems is the accumulation of toxic metals in food structures. As a result of accumulation, the concentrations of metals can be more than those in water and air. Contaminated food can cause poisoning in humans and animals. Although some heavy metals are necessary for the growth of plants, after certain concentrations heavy metals become poisonous for both plants and heavy metal microorganisms [35]. Another important risk concerning contamination is the accumulation of these substances in the soil in the long term. It has been determined that various metal ions hinder various enzymes responsible for the mineralization of organic compounds in the earth. Therefore, studies on the removal of heavy metal pollution are increasing. The purpose of this study was to investigate the removal of some toxic heavy metals from aqueous solution by adsorption, to determine the optimum removal condition by using different types of adsorbents [55]. Activated carbon is widely used as an adsorbent in the industry due to its high adsorption capacity.

This capacity is related to the pore structure and chemical nature of the carbon surface in connection with preparation conditions. The "Ceramic Membrane Filtration System" is a reliable technology to produce clean water by removing the turbidity, bacteria, and cryptosporidium and other protozoa contained in raw water sources such as surface water and groundwater [40]. Using a unique ceramic membrane as a filter, this system is a low cost and long life filtration system. Therefore it can enable a water supply system to meet recent demands for safe and tasty water. In recent years; there is an increased interest in using non-chemical and low-cost adsorbent to remove heavy metals from wastewater. Mesoporous silica materials have attracted attention because of their utilities in adsorption, selective separation and catalysis, one of the important mesoporous nanomaterials has excellent periodicities in the mesoporous channels, larger BET surface area, high porosities, and narrow pore sizes [23]. Initial studies of the self-assembled silica having a two-dimensional hexagonal ordering of cylindrical mesopores stimulated activities on the preparation of several mesoporous materials using alkyl trimethyl ammonium surfactants of varying alkyl chain length as structure-directing agents. Metal ion adsorbents have been prepared by grafting thiol functional groups as a monolayer onto the inner surface. Thiol functionalized was proved to be efficient adsorbents for mercury and heavy metal ions [57]. A few other reports are available on synthesis thiol and amine-functionalized mesoporous materials and use of the functionalized as adsorbents for removal of heavy metal ions. In the present work, the others try to find the best removal for heavy metals and low cost with a high percent of adsorbent

1.2. Heavy metal

The term “heavy metal” is collectively applied to a group of metals (and metal-like elements) with a density greater than 5 g/cm3 and atomic number above 20. Electroplating, battery manufactures, painting, paper, pigments, fuels, photographic materials, explosive manufacturing, and metalworking industries discharge large amounts of heavy metals [49]. Heavy metals are major pollutants in the environment due to their toxicity and threat to creatures and a human being at high concentrations. Several processing techniques are available to reduce the concentrations of heavy metals in wastewater, including precipitation, flotation, ion exchange, solvent extraction, adsorption, cementation onto iron, membrane processing, and electrolytic methods [34]. Adsorption is one of the alternatives for such causes the tendency of molecules from an ambient fluid phase to adhere to the surface of a solid. It has advantages over other methods are the simple design, sludge-free and can involve low investment in terms of both the initial costs and land.

Heavy metals in industrial effluent include nickel, chromium, lead, zinc, arsenic, cadmium, selenium and uranium. So far, a number of efficient methods have been reviewed for the removal of heavy metals such as chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, nanofiltration, coagulation, flocculation, floatation [37]. However, these methods have several disadvantages such as high reagent requirement, unpredictable metal ion removal, and generation of toxic sludge. Adsorption process being very simple, economical, effective and versatile has become the most preferred methods for removal of toxic contaminants from wastewater. This various readily available natural materials as adsorbents of heavy metals from industrial wastewater [72]. Various low-cost adsorbents reviewed

includes sand, waste tea leaves eggshell, rice husk, activated carbon, zeolites, olive stones, wood sawdust.

Heavy metal poses an impact on serious environmental problem due to their characteristic that accumulates in a living organism, causing various disease and disorder which is given (Table 1.1) [25]. Heavy metal that can be found in the landfill leachate such as iron, aluminum, arsenic, cadmium, copper, iron, manganese, mercury, nickel, silver, and zinc [67]. Heavy metal is not easy to break down and easy to enrich in different ambient mediums. It has been proven that heavy metal of leachate may lead to secondary pollution.

Industrial uses of metals and other domestic processes have introduced substantial amounts of potentially toxic heavy metals into the atmosphere and into the aquatic and terrestrial environments. In small quantities, certain heavy metals are nutritionally essential for healthy life. Some of these are referred to as the trace elements (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products. Heavy metals are also common in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel, and mining, refining ores, fertilizers industries, paper industries and so forth [35]. Many of these products are in our homes and actually add to our quality of life when properly used. However, high concentrations of heavy metals are known to produce a range of toxic effect and also have a potentially damaging effect on human physiology and other biological systems. For example, lead can cause encephalopathy, cognitive impairment, behavioral disturbances, kidney damage, anemia, and toxicity to the reproductive system [30]. At high exposure level, cadmium can cause nephrotoxic effect, while after long term exposure it can cause

bone damage. Other study reported that copper can cause weakness, lethargy, anorexia, and gastrointestinal tract.

Table (1.1): Sources and Effects of Heavy Metals[64]

Heavy Metal	Sources	Effects
Copper	**Water pipes, Copper water heaters, Frozen frees and canned greens using copper to produce an ultra-green color, alcoholic beverages from copper brewery equipment, instant gas hot water heaters, hormone pills, pesticides, insecticides, fungicides, copper cooking pots**	**Mental disorder, anaemia, arthritis, hypertension, nausea/vomiting, hyperactivity, schizophrenia, insomnia, autism, stuttering, postpartum psychosis, inflammation and enlargement of liver, heart problem, cystic fibrosis.**
Nickel	**Effluents of silver refineries, electroplating, zinc base casting and storage battery industries.**	**Dermatis, myocarditis, encephalopathy, pulmonary fibrosis, cancer of lungs, nose and bone, headache, dizziness, nausea and vomiting, chest pain, rapid respiration.**
Chromium	**Steel and textile industry**	**Skin rashes, respiratory problems, haemolysis, acute and renal failure, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer, and pulmonary fibrosis.**
Lead	**Industries such as mining, steel, automobile, batteries and paints. Pollutant arising from increasing industrialization.**	**Nausea, encephalopathy, headache and vomiting, learning difficulties, mental retardation, hyperactivity, vertigo, kidney damage, birth defects, muscle weakness, anorexia, cirrhosis of the liver, thyroid dysfunction, insomnia, fatigue, degeneration of motor neurons, schizophrenic-like behaviour.**
Cadmium		**Kidney damage, hypertension, human carcinogen, stomach problem, diarrhea and sometimes death.**

1.2.1. Definition of Heavy Metal and Human Effect

Heavy metals are naturally present in earth crust and rocks in the form of sulphides and oxide ores. These can be extracted as minerals from various ores such as sulphides of lead, iron, mercury, cadmium, arsenic or cobalt. Leaching of heavy metals into lakes, rivers and oceans, due to weathering of rocks and volcanic eruptions and mining processes, can cause serious pollution by affecting its surrounding areas via acid rains [72]. Several scientific data report that water, soil, vegetables, crops and dust in a close distance to the mining areas have been highly polluted by lead, arsenic, copper, chromium, zinc and cadmium. These heavy metals are the main toxicity-generating elements for living beings identified by World Health Organization (WHO).

A large number of commercial industries, municipal sewerage and wastewater irrigation systems release their heavy metals containing effluents into the environment by inappropriate means [37]. The release of heavy metals leads to contamination of soil and water, further used for agricultural purposes resulting in increased accumulation of heavy metals in food crops and vegetable plants and affecting food security throughout the world. It was observed that 90% of the total heavy metal uptake by human beings often occur by consuming vegetables grown in contaminated fields, and the remaining sources are contaminated through air inhalation or direct skin contacts [56]. It has been also reported that green leafy vegetables like lettuce are the major sources of heavy metal accumulation, without showing any morphological symptoms of toxicity by this accumulation. Other sources of metals, leaching from household pipelines, cook wares or utensils also contaminate food and water used by humans in daily routine. Milk and dairy products (main source of diet for infants and adults) are also affected via grazing of animals in fields contaminated by heavy metals, such as lead, cadmium, copper,

chromium, arsenic and zinc. Similarly, human beings are exposed to heavy metals by using industrial products, like electric batteries, paints, wires and pipes, to make up their routine needs [97]. These industrially prepared products require heavy metals as a part of manufacturing.

1.2.2. Heavy metals in industrial wastewater

The word of industrial wastewater mean any wastewater generated from any industrialization, processing institution, commercial, other process of agricultural ,or any operation that discharges other than domestic or healthful wastewater. In the process industries, many chemicals and different metals have been used, so large quantities of waste containing heavy toxic metals have been generated and their presence adversely affects the environment because they are not biodegradable [51]. Another source that, generates liquid waste is mining, metal processing. Many heavy metal have been used in electroplating and metal surface treatment that produce large quantities of contaminated wastewater containing heavy metals (cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver and titanium) [66].

In small quantities, certain heavy metals are nutritionally essential for a healthy life. Some of these are referred to as the trace elements (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products. Heavy metals are also common in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel, and mining, refining ores, fertilizers industries, paper industries [7]. Many of these products are in our homes and actually add to our quality of life when properly used.

Wastes of industrial processes varies from industry to another and from place to place. Some industries produce wastes containing a high proportion of organic matter, including food processing plants, dairy and meat products. Other industries discharge wastes with a low level of inorganic substance but high in toxic chemicals including: mining facilities, chemical plants, and textile factories [2]. Wastewater containing toxic compounds (dyes, heavy metals and pesticides) needs to be treated thoroughly before discharge into receiving water bodies. Many physical, chemical, physico-chemical and biological methods have been developed to remove pollutants from wastewater. Off these methods, flocculation, reverse osmosis, ion exchange and adsorption, chemical precipitation, ion-exchange, membrane separation, adsorption processes, electrolysis.

1.2.3. Treatment of heavy metals

Heavy metals are among the most detrimental pollutants in source and treated water, and are becoming a severe health problem. Since the damaging effects of heavy metals in the environment are known, many methods have been developed for the removal of heavy metals from waste discharges. Various chemical treatment methods have been developed for the removal and recovery of heavy metals from wastewater [41]. There are four major classes of conventional chemical separation technologies:

Chemical precipitation, electrolytic recovery, adsorption/ion exchange, and solvent extraction/liquid membrane separation [60]. These major classes involve various methods including chemical treatment with lime, caustic oxidation and reduction, ion exchange, adsorption, reverse osmosis, solvent extraction, membrane filtration, electrochemical treatment and evaporative recovery. In order to increase the performance

of the chemical precipitation process, many techniques of chemical precipitation were developed. As an alternative to hydroxide precipitation, numerous companies have developed and marketed chemical products which react with metal species to form insoluble compounds such as sulfides, carbonates, and carbamates [60]. Sodium decanoate, polymers, and other reagents can be used to precipitate metal ion. However, chemical precipitation is not very suitable when the pollutants are present in trace amounts. Another disadvantage of this method is generation on a large amount of sludge. Precipitation is accompanied by flocculation or coagulation, and one major problem is the formation of large amounts of sediments containing heavy metal ions. Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. In most cases, the term is used to denote the processes of purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineralic ion exchange materials [15]. Ion exchanged may facilitate an adsorption process. The exchange of ions occurs at the surface of the solid and ions are being transferred through interphase from the liquid to the surface of the solid. Exchange materials can be comprised of resins, membranes, minerals, and clays. The major disadvantage of ion exchange is that it is expensive in the capital and operating cost.

Nevertheless, the process of adsorption has become one of the preferred methods for removal of toxic contaminants from water as it has been found to be very effective, economical, versatile and simple. Adsorption has the additional advantages of applicability at very low concentrations, suitability for using batch and continuous processes, ease of operation, little sludge generation, the possibility of regeneration and reuse, and low capital cost [38]. Agricultural by-products and in some cases appropriately modified have shown to have a high capacity for

heavy metal adsorption. Toxic heavy metals such as Pb^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, Ni^{2+}, Cr^{3+}, and Cr^{6+}, as well as some elements from lanthanide and actinides groups have been successfully removed from contaminated industrial and municipal wastewaters using different agro-waste materials.

1.3 Adsorption Processes

Adsorption is a separation process where molecules tend to concentrate on the surface of the adsorbent as a result of Van der Waals force which exists between the molecules [29]. The adsorbability of a compound increases with: increasing molecular weight, a higher number of functional groups such as double bonds or halogen compounds, increasing polarizability of the molecules. Adsorption is a process where molecules of a gas or liquid contact and adhere to a solid surface. The adsorption process occurs at an interface between any two phases, such as, liquid-liquid, gas-liquid, gas-solid, or liquid-solid interfaces. The interface of interest in water and wastewater treatment is the liquid-solid interface. The adsorption of various substances on solids is due to the increased free surface energy of solids to their extensive surface [29]. According to the second law of thermodynamics, this energy has to be reduced. This is achieved by reduced the surface tension via the capture of extrinsic substance. From external surface of solids and liquids as well as from the internal surface of porous solid or liquids.

This phenomenon is applied for wastewater reuse. The adsorption force is the sum of all the interactions between all the atoms [3]. The short-range and addictive nature of these forces results in activated carbon having the strongest physical adsorption forces of any known materials. In this chapter, the fundamentals of gas phase and liquid phase adsorptions are considered. Gas-phase adsorption is a condensation

process where the adsorption forces condense the molecules from the bulk phase within the pores of the adsorbent [45]. The driving force for adsorption is the ratio of the partial pressure and the vapor pressure of the compound liquid phase adsorption is where the molecules move from the bulk phase to the pores of the adsorbent in a semi-liquid state. The driving force here is the ratio of the concentration to the solubility of the compound. Adorption is one of the most widely used methods for potable and wastewater treatment. By adsorption method most of the heavy metals are efficiently removed and depending on the type of bonding involved, adsorption can be classified as follows:

1. Physisorption

Physisorption or physical adsorption occurs as result of energy differences and/or electrical attractive weak forces such as the (Van der Waals forces), the adsorbate molecules (liquid contamination) are physically attached to the adsorbent molecules (solid surface) [43]. The reversibility of physisorption is dependent on the attractive forces between adsorbent and adsorbate. If these forces are weak, desorption is readily effected. The heat of adsorption for physisorption is at most a few Kcal/mole and therefore this type of adsorption is stable only at temperature below 150°C.

2. Chemisorption

Chemisorption or chemical adsorption occurs when a chemical compound is produced by the reaction between the adsorbent and the adsorbed molecule. Unlike physisorption, this procedure is one molecule thick and irreversible because energy is released to form the new chemical compound at the surface of the adsorbent and energy would be necessary to reverse the process. Both processes take place when the

molecules in the liquid phase are attached to the surface of solid as a result of the attractive forces at the adsorbent, overcoming the kinetic energy of the adsorbate molecules [43]. The substance that is being removed from liquid phase at the interface is call adsorbate or sorbent. The adsorbent or sorbate is the solid, liquid or gas phase onto which the adsorbate accumulate.

1.3.1. Applications of Adsorption Processes

The phenomenon of adsorption finds many applications, some of which are given below:

1. Pollution

The pollution of water due to the release of heavy metals are particularly problematic and supplies of clean water have become a major problem worldwide. The heavy metal ions can cause toxicities and serious side elects toward human health; therefore, these metal ions should be removed from water and wastewater [25]. A variety of strategies have been developed for ancient heavy metal removal from waters. Adsorption strategy plays a great important role in removing heavy metal ions due to their advantages. Nanomaterials are excellent adsorbents and extensive studies have been performed to remove heavy metals from wastewater by developing and using various nanomaterials. Recent developments for the heavy metals removal by various nanomaterials, mainly including carbon-based nanomaterials, iron-based nanomaterials and photocatalytic nanomaterials in batch.

2. Soil Sciences

Soil serves as a sink for some noxious elements known as heavy metals i.e. lead, chromium, cadmium, cobalt, and nickel where they persist in soil for a long period of times, caused detrimental effects on

health and quality of agricultural soils and crops [96]. Due to anthropogenic activities, they add harmful and toxic metals in the soil which indirectly affects human‟s health through the food chain. The upper 25cm surface layer of soil is mostly affected by the toxic metals where the roots of the plants or crops located. The anthropogenic activities which contribute pollution to water bodies are industrial and sewage effluents, domestic sewage, surface washing, organic matter of plants and animals, agrochemicals and treatment work‟s wastes [44]. Soils are the major sinks for heavy metals released into the environment by above mentioned anthropogenic activities and unlike organic contaminants which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation and their total concentration in soils persist for a long period of time after their introduction. Heavy metals are mainly originated from basic igneous rocks, in which the levels of metals are higher compared as compared to other rocks such as granites, gneisses, sandstones, and siltstones. Other factors such as proportion and composition of the clay and organic matter may also influence the levels of heavy metals in soils [25].

Heavy metals are very harmful due to their non-biodegradable nature. Soil organic matter that plays a key role in governing the metal mobility consists mainly of humic substances- humic and fulvic acids [93]. The heavy metals in soil cannot be destroyed like organic contaminants, but only be relocated from one place (contaminated site) to another place, e.g. landfill, which is, however, a very expensive procedure. Therefore, alternative strategies were developed to reduce risks and contamination which are associated with heavy metals in soils and to minimize potential impacts on plants, animals, water quality and consequently on human health. The increase of contaminants in soil can be hindered by soil stabilization techniques, which is based on an

application of suitable immobilizing agents. Adsorption of contaminants on mineral surfaces, the formation of stable complexes with organic ligands, surface precipitation, and ion exchange were identified as the main mechanisms responsible for the reduction of the metal mobility, leachability, and bioavailability [36].

3. Catalysis

A catalyst alters the rate of a chemical reaction without being consumed. Catalyzed reactions have a lower activation energy than uncatalysed reactions. The function of a catalyst is to split up the main reaction into two or more steps. The potential energy barrier in each step is reduced compared to a single step of the main reaction [76]. Hence catalyst helps to cross the barrier in two or more steps. A catalyst increases the rate of a reaction without modifying the overall standard Gibbs free energy change of the reaction. The initial and final states of the reaction energetically remain the same. The catalytic processes are classified into two types. In heterogeneous catalysis, the catalyst and reactants are in different phases. Typical example involves a solid catalyst with reactants as either liquids or gases. A homogeneous catalyst can function in the same phase of reactants [65].

Substances that increase the rate of reaction are called positive catalysts or simply catalysts, while substances that decrease the rate of reaction are called negative catalysts or inhibitors. In some reactions one of the reaction products is a catalyst for the reaction; this phenomenon is called self-catalysis or autocatalysis. Some substances that are not themselves catalysts but increase the activity of a catalyst when added with it; such substances are called promoters [53].

4. Chromotographic Analysis

The risks posed by heavy metals in nature are associated with toxicity and bioaccumulation in living beings. The contamination of water and soil is commonly caused by anthropogenic activity, being the industries the major source of such contamination [6]. Various paints used for printing in the graphic industry contain traces of heavy metals and, in the cleaning of printing machines, most of these compounds are dissolved and carried in the effluent. The graphic industries are located mainly in urban areas and the main destination of its effluents. Most paints used for printing in the graphic industry contain traces of heavy metals that are dissolved and carried in the effluent, and the risk posed by these contaminants in the environment is associated with toxicity and bioaccumulation in living beings. The evaluate of the adsorbent for the removal of heavy metals in wastewater from the graphic industry [47].

5. Medicine and Pharmacology

Heavy metal has proven to be a major threat and there are several medicine and health risks associated with it. The toxic effects of these metals, even though they do not have any biological role, remain present in some of the other form harmful for the human body and its proper functioning [16]. They sometimes act as a pseudo-element of the body while at certain times they may even interfere with metabolic processes. Few metals, can be removed through elimination activities, while some metals get accumulated in the body and food chain, exhibiting a chronic nature [84]. Various public health measures have been undertaken to control, prevent and treat metal toxicity occurring at various levels, such as occupational exposure, accidents, and environmental factors. Metal toxicity depends upon the absorbed dose, the route of exposure and duration of exposure, i.e. acute or chronic. This can lead to various

disorders and can also result in excessive damage due to oxidative stress induced by free radical formation. This review gives details about some heavy metals and their toxicity mechanisms, along with their health effects.

6. Industry

Industries have been evolving rapidly in the last few decades which have resulted in an increase in all kinds of pollution one of which is water pollution. The accessibility of water supply with regard to both quality and quantity is important to human survival. The environmental concern due to globalization and rapid industrialization are becoming a hindrance for a human being. Hence efficient and constructive methods are required specifically for process industries. Heavy metals accounted in wastewaters and industrial discharges are one of the major concerns of environmental pollution [52]. Heavy metals are normally contemplated as those whose density exceeds 5 g/cm3. Most of the components belonging to this grouping are extremely water-soluble, popularly-known toxins and carcinogenic agents.

1.3.2. Forces of the Adsorption

The forces of the adsorption process in solution are usually considered as follows: [11]

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 the Adsorption

Adsorption can be classified in two types which are physical adsorption or chemical adsorption depending on the nature of attractive powers present between the adsorbent and adsorbate forces called Vander Waals which are weak forces [1].

1. Physical adsorption:

When there are weak forces such as forces Vander walls which connecting adsorbate and adsorbent, the process is called (physical adsorption) or (physisorption).[46]

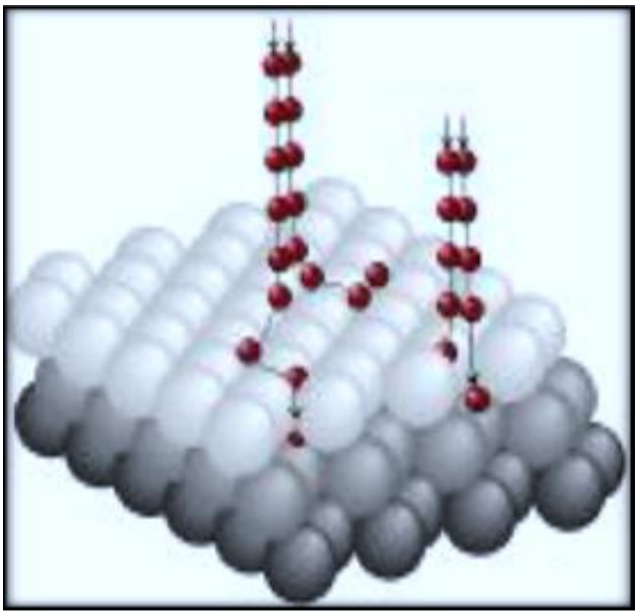

Figure (1.1): Physical adsorption

2. Chemical adsorption:

When there are chemical forces of attraction or chemical bond, which connect between adsorbate and adsorbent, the process is called (chemical adsorption) or (chemisorption)[87].

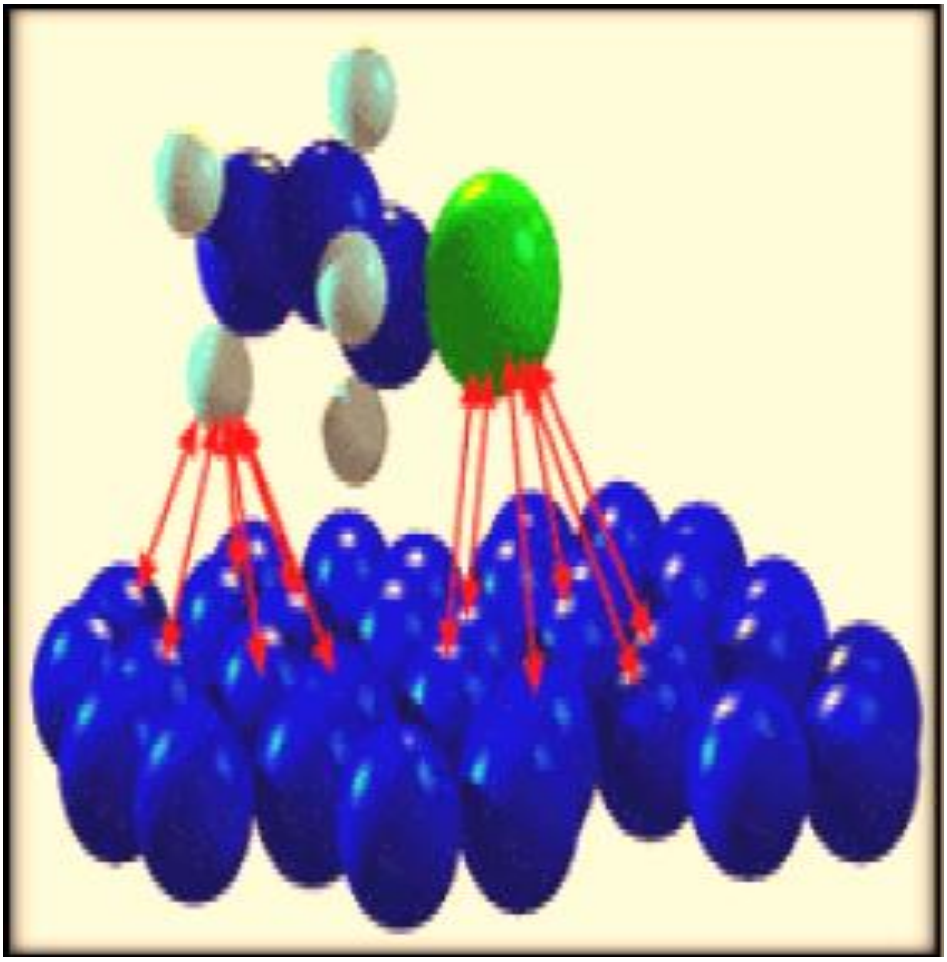

Figure (1.2): Chemical adsorption

3. The Difference between Physical and Chemical Adsorption

There are many differences between physisorption and chemisorptions which can be explained in, Table (1.2). [46,89]

Table (1.2): Comparison between physical and chemical adsorption.

NO.	Physical Adsorption	Chemical Adsorption
1	The forces operating between adsorbat and adsorbent are the weak Van Dar Waals forces	The forces operating between adsorbat and adsorbent are strong and similar to chemical bonds
2	The enthalpy of adsorption is low and ranges from 10 to 40 KJ mol^{-1}	The enthalpy of adsorption is high and ranges from 40 to 400 KJ mol^{-1}
3	No activation energy is involved	Significant activation energy is involved
4	Adsorption occurs more readily at low temperature and high pressure.	Chemisorption occurs more readily at high temperature and high pressure.
5	It is reversible in nature. The gas is desorbed on increasing the temperature or decreasing the pressure.	It is irreversible in nature. Desorption also separate some amount of the compound formed.
6	Multilayer formation is common.	Monolayer formation occurs.

1.3.4. Adsorption Mechanism from solution

Adsorption happens in three steps. First step that the adsorbate diffuses from the major body of the stream to the external surface of the adsorbent particle. Second step, the adsorbate migrates from the relatively small area of the external surface to the pores within each adsorbent particle [58]. The bulk of adsorption usually occurs in these pores because there is the majority of available surface area. Final step, the contaminant molecule adheres to the surface in the pore. This overall mechanism of diffusion and adsorption process[87].

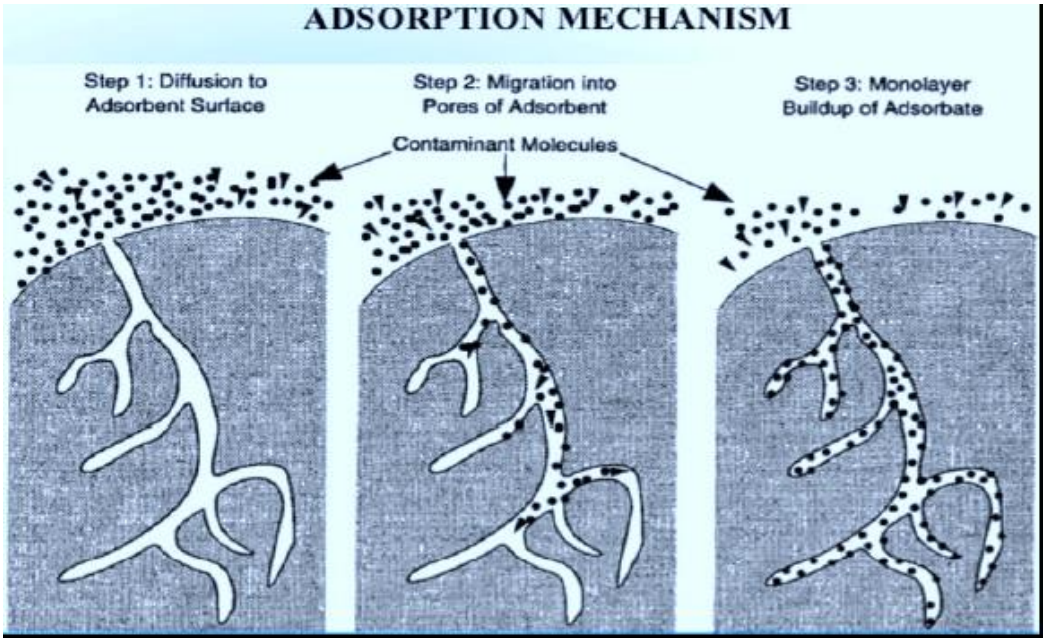

Figure (1.3): The mechanism of adsorption process

1.3.5. Factors of in flouncing adsorption processes

Adsorption occurs on the surface of almost all heavy metals. However, the extent of adsorption on the surface of a solid depends upon the following factors:

1. Contact time

The interaction of functional group between the solution and the surface of adsorbent results in the adsorption capacity if adsorbate into adsorbent. The specific time needed to maintain equilibrium interaction, therefore, the adsorption process undergo completion [33]. Removal achieve equilibrium contact time. However, for lead removal gain equilibrium contact time and thereafter, it's remain constant.

2. Nature of adsorbate

The interference between the adsorbent surface and the adsorbate particles affected by the nature of the adsorbate material shape, size, concentration, existence polar groups [73]. The increase in molecular weight and solubility of polar group and charges the interference between

the surface adsorbent and adsorbate particles which make the selective adsorption of one of the components.

3. Nature of adsorbent

There are some factors affecting on adsorption energy of an adsorbent which are[12,50]:

- **Surface Area:** Increase in the surface area of the adsorbent lead to increase the total amount of the adsorbate-adsorbed**.**
- **Homogeneous Systems:** The work with clean metal surfaces have accentuated the complexities that certainly occur when metal powders, chemically deposited metal films, oxides of metals and nonmetals are used as adsorbents.
- **Heterogeneous Systems:** The non-homogeneity of a surface is characterized using the presence of adsorption sites with different adsorption energies.
- **Polarity:** The polar surfaces tend to adsorb the more polar components in solution

4. Effect of the mixed solute

The effects of mixed solute on the shape of films formed on a heavy metals were investigated experimentally. The shape depended on the solvents used, and the mixing ratio. It was also found that the flow direction was dominated by solute-derived rather than solvent-derived Marangoni flows [75]. Consequently, the changes in the shape of the metals could not be explained.

5. Effect of the solvent

Solvent effects can significantly impact the reactivity ratios for given adsorption for heavy metals. More generally, the reaction medium can influence copolymerization processes as well as product copolymers.

Inhomogeneous copolymerizations, the continuous phase should be considered. However, for adsorption systems, the conditions at the reaction site are of primary import. Solvent effects are most often observed when the system contains ionizable comonomers, polar comonomers, or groups susceptible to hydrogen bonding [17]. In one of many discussions regarding solvent effects, Hagiopol summarized varying reactivity ratios for similar comonomers in different solvents and observed significant differences that could not be attributed to experimental error. These differences have been linked to electrostatic repulsion, variation in polarity, monomer complexing, hydrogen bonding (between comonomers and solvents), and dielectric constants of dissimilar solvents [28].

6. Effect of the temperature

Concerning the health hazard, heavy metals are among the most detrimental pollutants in source and treated water, and are becoming a severe health problem. Since the damaging effects of heavy metals in the environment are known, many methods have been developed for the removal of heavy metals from waste discharges [42]. Various chemical treatment methods have been developed for the removal and recovery of heavy metals from wastewater. There are four major classes of conventional chemical separation technologies: chemical precipitation, electrolytic recovery, adsorption/ion exchange, and solvent extraction/liquid membrane separation. These major classes involve various methods including chemical treatment with lime, caustic oxidation, and reduction, ion exchange, adsorption, reverse osmosis, solvent extraction, membrane filtration, electrochemical treatment and evaporative recovery. In order to increase the performance of the chemical precipitation process, many techniques of chemical precipitation

were developed [54]. As an alternative to hydroxide precipitation, numerous companies have developed and marketed chemical products which react with metal species to form insoluble compounds such as sulfides, carbonates, and carbamates. Sodium decanoate, polymers, and other reagents can be used to precipitate metal ion.

7. Effect of the PH

The number of adsorption sites is pH-dependent. Several studies have shown that cationic metal adsorption increases with pH. This as a matter of fact only occurs when the pH is greater than 7, the reason being partly due to preferential adsorption of the hydrolyzed metal in comparison to the free metal ion, nature of bonding and surface variable charges [94]. Also, the proportion of the hydrolyzed metals increases with pH as seen in the hydrolysis of Cu occurring at pH6, Cd at pH8 and Zn at pH5. PH also impacts on adsorption sites which are known to be pH-dependent. As pH reduces, the number of negative sites reduces. Also, as pH becomes more acidic, metal actions have to compete for available negatively charged sites with Al^{3+} and H^{+}.

The effect of pH on metal action adsorption is principally the result of changes in the net proton charge on particles [39]. As pH increases, the amount of H^{+} (and its associated positive charge) decrease and the electrostatic attraction of the adsorbent for a metal action is enhanced. PH is a very important parameter to control during batch experiments.

1.4. Adsorption Isotherms

Adsorption models are frequently used to describe the equilibrium between metal ions in solution and metal ions adsorbed on the surface. Equilibrium studies on adsorption give information about the capability

of the adsorbent to remove a unit gram of metal ions under specific system report conditions [68]. The three most commonly used equilibrium isotherms are the Langmuir isotherm model, the Temkin isotherm model, and the Freundlich isotherm model.

1.4.1. Langmuir isotherms

The Langmuir adsorption isotherm has been effectively applied to many pollutant adsorption processes and has been the most widely used isotherm for the adsorption of a solute from a liquid solution, on another word it has been employed to characterize the uptake of heavy metals by evaluating the adsorption capacities of the microorganisms [57]. It is also useful to describe the equilibrium conditions for adsorption in different systems. Basic assumptions of the Langmuir theory are:

1. The surface is homogeneous that is adsorption energy is unvarying overall sites.
2. Adsorption on the surface is localized that is adsorbed molecules or atoms are adsorbed at definite localized sites.
3. Every site can accommodate only one atom or molecule.

This model can be written in a non-linear form (Langmuir) as: [63,8]

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

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 = Langmuir constant which is a measure of adsorption maximum capacity (mg/g),

b = Langmuir constant which is a measure of energy of adsorption (L / mg).

1.4.2. Freundlich isotherms

The Freundlich model is the most popular adsorption model for a single solute system. The model has found broad acceptance because of its accuracy and broad applicability [59]. The Freundlich model assumes a heterogeneous adsorption surface and dynamic sites with different energy. The Freundlich model (Freundlich equation) is[63]

$$\log Q_e = \log K_F + \frac{1}{n}\log C_e \quad \ldots\ldots\ldots\ldots (1.2)$$

Where

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

K_F = Freundlich constant (mg/g).

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

n = adsorption process extent.

1.4.3. Temkin isotherms

This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption (a function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage [22]. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed Q_e against ln C_e and the constants were determined from the slope and intercept. The model is given by the following equation[27]

$$Q_e = B_T \ln A_T + B_T \ln C_e \quad \ldots\ldots\ldots\ldots\ldots \textbf{(1.3)}$$

A_T = Temkin isotherm equilibrium binding constant (L/g)

B_T = Temkin isotherm constant

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

1.5. Nanomaterials

In the last two decades, nanotechnology has developed with its applications in almost all branches of science and technology. With the rapid development of nanotechnology, there has been a great deal of interest in environmental applications of nanomaterials [85]. Nanomaterials are excellent adsorbents and catalysts. Since nanomaterials offer significant improvement with the extremely high specific surface area, numerous associated sorption sites, low-temperature modification, short intra-particle diffusion distance, tunable pore size, and surface chemistry compared to other materials, extensive research has been carried out to remove heavy metals from wastewater by developing and using various nanomaterials [83]. Nanometal and metal oxides were used as a photocatalyst to degrade the water-soluble organic pollutants and dyes and textile eluent under visible light condition.

The adsorption capacity and the desorption property are two key parameters to evaluate an adsorbent. The adsorption parameters, such as the amount of absorbent used, temperature, pH, ionic strength, metal ion concentration, and competition among metal ions, are often studied and optimized [26]. This study highlights recent developments for the removal of heavy metals by various nanomaterials, mainly including carbon-based nanomaterials, iron-based nanomaterials and photocatalytic nanomaterials in batch and offered systems. Finally, future perspectives are offered to inspire more exciting developments in this promising optimized.

Nanomaterials offer a common technology adoption and are widely studied as highly efficient adsorbents for heavy metal removal from aqueous solutions and wastewater. They presented advantages such as high capacity, fast kinetics, and preferable sorption toward heavy metals in water and wastewater and it has been demonstrated that the addition of nanomaterials aids to improvisation the efficiency of separations [74]. Nevertheless, to further promote the practical application of nanomaterial in the removal of heavy metal ions, there still exist drawbacks to being solved. For example, nanomaterials tend to aggregate into large-size particles and their adsorption capacity is reduced. The blocking and fouling problems in subsequent filtration steps exist due to their nanosized and finding approaches for better dispersion of nanomaterials need to be further explored, as well as such nanoparticles are not often fully recovered, secondary contamination could occur [32]. Also, an ancient, simple and cost-effective separation of the exhausted nanomaterials from water/wastewater still remains an interesting and challenging task. It seems that magnetic assistance-based separations would provide longterm benefits and magnetic separation system designs in the frontier area of research. The excessive pressure drop caused by nanomaterials should also be considered when column operation is performed [85]. Fortunately, fabrication of new carbon- and magnetic-based composite adsorbents seems to be an effective approach to respond to all the above technical problems. However, various issues need to be solved concerning the development of ancient and costly processes to obtain composite adsorbents. The type of interaction between the heavy metal ions and the supported nanomaterials, physicochemical properties of the composite adsorbents such as hydrophilicity, porosity, charge density, thermal and mechanical stability, the longterm performance of the composite adsorbents, high desorption,

regeneration, and reusability are great important parameters in heavy metal removal water treatment [85]. The potential effects of leached nanomaterials on the environment, nanomaterial leakage, and its environmental toxicity also need to be systematically investigated. Finally, there are very few reports existing on the large-scale production and industrial application and it is needed to evaluate the cost-effectiveness of large-scale membrane fabrication including the supplies of nanomaterials, additional procedures for nanomaterial incorporation and monitoring of the long-term stability of membranes under practical application conditions [92].

1.6. Literature Survey

(Desai and Kaler, 2008), Copper is an important essential element present in normal human serum at a concentration of 120 to 140 µg/g via binding to ceruloplasmin, albumin, and other molecules. Conversely, high levels of copper can cause adverse health effects such as liver and kidney damage, anemia and gastrointestinal irritation. Furthermore, copper is also associated indirectly with neurological disorders including Alzheimer's disease, Wilson's disease and prion disease.

(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 endothermi.

(Rahmanpour, et.al, 2012), studied a new method for synthesis of nano size (γ- Al2O3) by precipitation method under ultrasonic vibration mixing dehydration of methanol to dimethyl ether . The formed of alumina was characterized by using SEM, XRD, and BET techniques. The materials in nano-scale show different characteristics in comparison with their bulk state

(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 calculation.

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

(Ihab. A. Altameem et, al. 2013), Utilized a new simple method for the treatment of waste water effluent containing Cu(II) and Zn(II) which developed using dried Conocarpus erectusleavesas a low-cost natural adsorbent. Batch experiments were conducted to determine the effects of varying adsorbent weight, pH, contact time, metal ion concentration and temperature of adsorption. The adsorption of cu (II) was found to be maximum (94.7%) at pH9, at 25°C, metal ion concentration 100 ppm , contact time 60 min and speed Shake(185rpm) . adsorption capacity of Cu (II) and Zn were found maximum (94.7% and 93.3%)respectively at optimum conditions. The order of the removal of the efficiency of these metals was found Cu> Zn. Freundlich isotherm was found to be suitable for the adsorption of Cu(II),Zn(II),functional groups[(C-N), (C-O),(C=O),(O-H)] identification was given using FTIR spectrophotoscopy.

(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.

(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).

(M. K. Moftakhar, et. al, 2016), prepared, and their potential for separation of copper, lead, zinc, cadmium, cobalt and nickel ions from aqueous solutions was examined. The effect of parameters influencing adsorption efficiency including aqueous-phase pH, amount of adsorbent, stirring time and initial concentration of the metal ions was assessed and discussed. Although MNS1 and MNS3 removed lead ions efficiently, all adsorbents showed strong selectivity toward copper ions. It was shown that, under some circumstances, MNS3 decreased the amount of other ions, particularly cobalt, in the aqueous phase. The adsorbents were also applied for removal of copper and lead ions from real samples. Possible quantitative desorption of the metal ions loaded onto the adsorbents suggests their multiple uses in adsorption–desorption process. Investigation of temperature dependency of the process led to determination of the DH, DS and DG values. This investigation indicates that the adsorption of copper ions onto the all studied adsorbents and lead ions onto MNS1 and MNS3 is endothermic. The Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms were tested to describe the equilibrium data. Pseudo-first-order, pseudo-secondorder, Elovich and intra-particle diffusion equations were applied to study the kinetics of copper and lead adsorption onto the modified nanoparticles. This investigation indicates that the process for all adsorbents follows pseudo second-order kinetics and suggests a chemisorption mechanism for the adsorption processes by the studied adsorbents.

(Mohamed & Atta , 2016), prepared Nano γ- Al2O3 support by co-precipitation method using different calcination temperatures (550,650, and 750) ^{o}C and prepared Nano NiMo/ γ-Al2O3 catalyst by impregnation method with nickel carbonate and ammonium paramolybdate with Nano γ-Al2O3 support at calcination temperature of 550 ^{o}C . It was characterized by utilizing X-ray diffraction, X-ray fluorescent, AFM, SEM, BET surface area, and pore volume.

(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, 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.

(Tabesh, ,et.al,2017), prepared γ-Al2O3 by using modified sol–gel method In this study, the aluminium nitrate, ethylene glycol (EG), citric acid (CA) and triethanolamine (TEA) were used as an Al3+ source, gel, chelating and surfactant agents, respectively. Structural characterization using X-ray diffraction (XRD), scanning electron microscopy (SEM), thermo-gravimetric analysis (TGA) and infrared spectroscopy (IR). Then, the removal efficiency of heavy metal ions (lead and cadmium) in the adsorption process by the as-synthesized alumina nanoparticle has been investigated in PH (5) ,contact time of the 20 min and 30 min for Pb+2 and Cd+2 respectively.

(Jbara,et.al, 2017), prepared γ-Al2O3 by co-precipitation under annealing temperature effect, structural characterization using XRD analysis indicated that the particle diameter ranging from 6 to 24 nm of gamma phase of alumina .The surface area of the prepared nano powders is in the range of (109 to 367) m2/g. the morphology analysis indicates

that γ-Al2O3 nanopowders are consisted of grains almost spherical in shape.

(Nyairo, et.al, 2018), studied the adsorption of Cu (ll) ions by oxidized multiwalled carbon nanotubes/ polypyrrole composite from their aqueous solutions. The structure and the morphology of the oxidized multiwall carbon nanotube characterized by scanning electron microscopy, thermogravimetric analysis, Fourier transform infrared and raman spectroscopy and showed successful preparation of the multiwalled carbon nanotubes/polypyrrole composite. The influence of pH, contact time, and initial metal ion concentration on the adsorption for Cu+2 was studied. The adsorption processes fitted well with Langmuir isotherm and pseudo-second-order kinetic models. The maximum adsorption capacities for lead and copper were determined as 26.32 and 24.39 mg/g, respectively.

(Kour, et.al, 2018), studied the adsorption of Zn (ll) ions in industrial effluents, by using modified bio-sorbent prepared from Desmostachya bipinnata. The prepared biosorbent was characterized by (SEM, DR-FTIR, Elemental analyzer, XRD, Boem titration and point of zero charge), showing modificatios on the surface of the biosorbent. The result of removal of Zn+2 showed the interference of one metal ions with another, thereby reducing the adsorption capacities of both metal ions. Even though there is interference between two different metal ions, the modified bio sorbent proved quite efficient in removing complex mixtures of heavy metal ions from industrial effluents.

(Marton Czikkely, et.al, 2018), Heavy metal contamination of natural rivers and wastewaters is a problem for both the environment and human society. The accumulation and adsorption of heavy metals could happen with several organic and inorganic matters, but the most used adsorbents are (biological and chemical) organic compounds. This review

article presents the basics of heavy metal adsorption on several organic surfaces. There are many organic matters, which seem to be useful as agents for heavy metal adsorption. All of the cited authors and articles present the adsorption kinetics by the most used isotherm models (such as Langmuir and Freund lich isotherms). By comparing several research results presented by a pre-selected assortment of papers, we would like to give an overview of the microbiological, organic chemical, and other surface adsorption possibilities.

(Mingbao Feng, et.al, 2018), Heavy metals and radionuclides in water are a global environmental issue, which has been receiving considerable attention worldwide. Water-stable MOFs are green and recyclable materials to eliminate the environmental impacts caused by the hazardous heavy metal ions and radionuclides in water. This paper presents a systematical review on the current status of water-stable MOFs that capture and convert a wide range of heavy metal ions (e.g., As(III)/As(V), Pb(II), Hg(II), Cd(II), and Cr(III)/Cr(VI)) and radionuclides (e.g., U(VI), Se(IV)/Se(VI) and Cs(I)) in aqueous solution. Water-stable MOFs and MOF-based composites exhibit the superior adsorption capability for these metal species in water. Significantly, MOFs show high selectivity in capturing target metal ions even in the presence of multiple water constituents. Mechanisms involved in capturing metal ions are described. MOFs also have excellent catalytic performance (photocatalysis and catalytic reduction by formic acid) for Cr(VI) conversion to Cr(III). Future research is suggested to provide insightful guidance to enhance the performance of the MOFs in capturing target pollutants in aquatic environment.

(Khai M. Nguyen et. al. 2019), studied sludge from an iron-ore processing area and used as an adsorbent to remove As, Mn, Zn, Cd, and Pb from aqueous solutions. The adsorption capacity of target adsorbents

was investigated in batch experiments of both single- and mixed-metal solutions. The batch studies show that the maximum Langmuir adsorption capacities of the heavy metals onto the adsorbent occurred in the order Pb > As > Cd > Zn > Mn, and ranged from 0.710 mg/g to 1.113 mg/g in the single-metal solutions and from 0.370 mg/g to 1.059 mg/g in the mixed-metal solutions. The results of the kinetic experiments are consistent with pseudo-first-order and pseudo-second-order models, with a slightly better fit to the latter.

(Ifeoma Mary Ugwu et. al. 2019), Sorption of heavy metals plays a vital role in controlling environmental pollution. Here, we reviewed the sorption of heavy metals such as Ni, Co, Cu, Zn, V, Pb, Hg, In, As, Cd, Cr, Ga, Cs, Mn, V, Eu, Mo, Th, TI and Cr on metal oxides and clay minerals. The mechanism of association between these ions and the host minerals, and the factors controlling their sorption are discussed in detail. Both chemical and empirical methods of describing sorption mechanism are discussed. The sorption processes depend on the pH, metal concentration, ionic strength, temperature, time, adsorbent dosage, type of ion, surface area, type of adsorbent modification and nature of adsorbent. The review confirmed that both metal oxides and clay have capability of sequestering heavy metals, however, combination of both metal oxides and modified clay have enhanced capability of removing heavy metals from aqueous solution. These inorganic adsorbents have the regeneration and recycling potentials and can be used to remediate and sequester economic metals for commercial purposes, however, this needs future investigation.

(Gang Xiao. et. al. 2019), Water pollution caused by highly toxic Cd (II), Pb(II), and Cr(VI) is a serious problem. A green and low-cost adsorbent of g-C3N4 nanosheets was developed with superior capacity for both cationic and anionic heavy metals. The adsorbent was

easily fabricated through one-step calcination of guanidine hydrochloride with thickness less than 1.6 nm and specific surface area of 111.2 m2·g−1. Kinetic and isotherm studies suggest that the adsorption is an endothermic chemisorption process, occurring on the energetically heterogeneous surface based on a hybrid mechanism of multilayer and monolayer adsorption. The tri-s-triazine units and surface N-containing groups of g-C3N4 nanosheets are proposed to be responsible for the adsorption process. Further study on pH demonstrates that electrostatic interaction plays an important role. The maximum adsorption capacity of Cd (II), Pb(II), and Cr(VI) on g-C3N4 nanosheets is 123.205 mg·g−1, 136.571 mg·g−1, and 684.451 mg·g−1, respectively. The better adsorption performance of the adsorbent than that of the recently reported nanomaterials and low-cost adsorbents proves its great application potential in the removal of heavy metal contaminants from wastewater. The present paper developed a promising adsorbent which will certainly find applications in wastewater treatment and also provides guiding significance in designing adsorption processes.

(Khaled Elsherif. 2020), Look at the equilibrium and thermodynamics of the biosorption of Pb(II), Zn(II), Cu(II), and Cd(II) onto activated carbon prepared from olive branches under different parameters of pH, initial concentration, and temperature. The batch biosorption procedure was used to find the optimum conditions. The biosorption of each metal ion was found to be pH-dependent. The maximum metal ion biosorption was achieved at pH value 5 for Pb, Cu, and Cd ions and at pH 3 for Zn ions. The extent of the metal ion biosorption increased with temperature (indicating the endothermic character) and initial metal ion concentration. The experimental data of metal ion biosorption were analyzed by Freundlich and Langmuir isotherm models. For all metal ions, the Freundlich isotherm model gave

a better fit with higher correlation to equilibrium data than Langmuir model.

(Huaqing Qin. 2020), Biosorbent for heavy metals removal, for removal efficiency or economy efficiency limited, it has failed to make a substantial breakthrough in practical application. Thus, many improved methods based on biosorbents emerged. In this review, based on the literature and our research results, we highlight three types of novel methods for biosorbents removal of heavy metals: chemical modification of biosorbents; biomass and chemical materials combination; multiple biomass complex systems. We mainly focus on their configuration, biosorption performance, their creation method, regeneration/reuse, their application and development in the future. Through the comparative analysis of various methods, we think that intracellular autogenous nanomaterials may open up another window in biosorption of heavy metals area. At the same time, the combination of various treatment methods will be the development tendency of heavy metal pollution treatment in the future.

(Na Yao. 2020), Performed a comparative study on the adsorption of typical antibiotics (tetracycline and sulfadiazine) and heavy metals (Cu(II) and Zn(II)) onto graphene oxides (GO), a promising nano-adsorbent, from both experimental and theoretical viewpoints. Effects of solution chemistry parameters were studied. Interfacial interactions and geometries among contaminants and GO were clarified using experimental and computational tools. Interaction strength of contaminants towards GO followed the order of $Cu(II) > Zn(II)$ sulfadiazine (coordination of heavy metal-GO in sp3 regions; π-π stacking of antibiotic-GO in sp2 and H-bonding in sp3 regions). In the combined contaminants, heavy metals demonstrated enhancement effect for the adsorption capacities (Qe) for antibiotics, but antibiotics displayed

slight promotion to Qe for heavy metals. Through coordination, the combined contaminants formed complexes, which preferred to be adsorbed onto GO's sp3 regions with heavy metals acting like "bridges" and facing towards GO, instead of antibiotics directly interacting with GO. Coexisting salt ions, especially Ca2+, inhibited the adsorption. Humic acid provided more sites for heavy metal uptake but competed with antibiotics for adsorption. After six adsorption-release cycles, re-adsorption capacities still kept high, implying the feasibility of GO on such sort of combined contaminants removal.

1.7. Aim of the present study

1. Preparation of nano $\gamma.Al_2O_3$ using co-precipitation method and characterize it.
2. Preparation of nano Catalyst $CoMo/\gamma.Al_2O_3$ using impregnation method and characterize it.
3. Thermodynamic studies of adsorption processes of Cadmium (II) and Copper (II) ions on these adsorbent.
4. Determining the ideal Condition for the adsorption of Cd^{+2} and Cu^{+2} ions in binary system such as (Contact time, quantity adsorbent, pH, temperature, initial concentration).
5. Thermodynamic studies of adsorption processes of metals ion in binary system.

Chapter Two

(Experimental)

2.1. Materials used

2.1.1. The Chemical materials used

The properties of chemicals used in this work are shown in table 2.1.

Table (2.1): The chemicals used

No	Chemicals Name	Formula	Purity %	Molecular Mass	Origin
1	Aluminium Chloride hexahydrate	$AlCl_3.6H_2O$	99	241.42	CDH
2	Absolute ethanol	C_2H_5OH	99.9	45.069	GCC
3	Ammonium hepta molybdate	$(NH_4)_6Mo_7.O_{24}.4H_2O$	99	1235.86	CDH
4	Ammonium hydroxide solution	NH_4OH	25	34.05	BDH
5	Citric acid	$C_6H_8O_7$	99.9	192.124	Panreac Espane
6	Oxalic acid	$H_2C_2O_4$	99.9	90.04	Barceloa Espana
7	Hydrochloric acid	HCl	35.4	36.46	CDH
8	Sodium hydroxide	NaOH	99	40	Alpha chemical
9	Copper (II) Chloride dyhydrate	$CuCl_2.2H_2O$	99	170.48	BOH
10	Cadmium (II) chloride monohydrate	$CdCl_2.H_2O$	99	201.317	India

2.1.2. The adsorbate used

Copper and Cadmium heavy metals ions are used as adsorbate in this work based on its being strong pollutants which need to be removed from the waste-water and also used widely industry.

2.1.3. Adsorbents used in this study

Prepared CoMo/ $\gamma.Al_2O_3$ catalyst are used as adsorbent for heavy metal removal here.

2.2. Instruments and Apparatus

2.2.1. The instruments and tools used

The instruments and tools that are used in this study are tabulated with their details, origin, and location in table (2.2)

Table (2.2): The Instruments used in this study

No	Instrument	Details and Origin	Location
1	Electric balance	Kern Acjiacs , ACS 120-40, WB 12AEO308, Max 120g, d = 0.1 mg, (Germany) Binder	The Laboratories of Chemistry Department, College of Science, University of Diyala, Iraq
2	Oven	Hotline International (20-360 °C), (Germany)	
3	PH Meter	PH / Ion Benchtop WTW inolab PH Meter 7110 Benchtop Meter, (Germany)	
4	Hot plate magnetic stirrer	MS - H280-pro ISOLAB Laboratory GmbH, (Germany)	
5	Water bath with shaker	BS-11,230 VAC-50Hz, (KOREA)	
6	Centerifuge	Hermie Laborti Chink Type Z 200 A, 6000rpm, (Germany)	
7	Distillation device	Luzpe A viso Agua Insuficicente, (Germany)	
8	Electric furnace	Type - Nabentherm, Max Temperature 1300 °C, 400V, IS.OA, 50160 HZ, (Germany)	

2.2.2 Apparatus used

The apparatus used are shown in table (2.3) with their details, origin, and location.

Table (2.3): the Apparatus used in characterization

No	Apparatus Names	Details and Origin	Location
1	X-ray Diffraction spectroscopy (XRD)	XRD - 6000CU KA (1=1.5406A9) 220/50, HZ, Shimadzu, (Japan)	Lab. of X-Ray Diffraction Central Service Laboratory College of Education Ibn -al-Haitham University of Baghdad, Iraq
2	Atomic Absorption Spectrophotometer (AAS)	Shimadzu AA-7000, (Japan)	Lab, of atomic Absorption Central Service Laboratory, College of Education Ibn – al- Hitham, University of Baghdad, Iraq
3	Atomic Force Microscope (AFM)	Scanning Probe Microscope, AA 3000 SPM 220V Angstrom Advanced Inc, AFM Contact Mode, (USA)	The Special Laboratory of Dr. Abdul Kareem M.A. AL-Sammaraie, College of Science University of Baghdad, Iraq
4	Energy – dispersive X- ray (EDXA)	MIRA3 TESCAN, College of Sharif University of Technology, Tehran, Iran	
5	Field Emission Scanning Electron Microscope (FESEM)	MIRA3 TESCAN, College of Sharif University of Technology, Tehran, Iran	Image Topography of Materials

2.3. Preparation of adsorbent catalyst

2.3.1. Preparation of nano alumina ($\gamma.Al_2O_3$) using Co-precipitation method

Dissolved (47.0722g) of ($AlCl_3.6H_2O$) in (45 ml) of distilled water and then 150 ml of ethanol was added to get a transparent solution,

60 ml of ammonium hydroxide solution was added drop wise with the rate of 2.5 ml /min until the white precipitate as Al^{+3} gel hydroxides was formed. The gel thus formed is filtered, washed with deionized water several time to removed impurities and dried at 80°C for 10 hours in an oven, finally it is calcinated at 550°C for 4h where a white fine of γ. – alumina nano – powder was obtained.

2.3.2. Preparation of nano molybdenum oxide (MoO_3) nano particles using sol gel method

Molybdenum oxide nano particles was synthesized using the Citrate Sol-gel method. Ammonium molybdate powder (1.16g) was dissolved in de-ionzed water to which citric acid crystals (0.38g) was added. The mixture was then stirred carefully using a magnetic stirrer while ammonium hydroxide was added to obtain pH of 7. The mixture was then heated in a furnace to a temperature of 250°C for 1h where initially a zero gel and finally a powder was obtained. The powder was then heated to a temperature of 500°C for 90 min to obtain a pale yellow powder.

2.3.3. Preparation of nano cobalt oxide (Co_3O_4) nanoparticles by Sol. gel method

Metal Salt Solution (2.9) gm of $Co(No_3)_2.6H_2O$ was mixed in double distilled water (10ml) with continuous Stirring for 1 hour.

In another beaker take (0.9) gm of oxalic acid was mixed with (10 ml) double distilled water with continuous half an hour to prepare oxalic acid solution.

The oxalic acid Solution was then mixed with $Co(No_3)_2.6H_2O$ drop wise with Continuous stirring for three hours. The resultant light pink coloured precipitates thus obtained were washed with double

distilled water and then dried at 100°C in oven for 5 hours. Finally, it was put into the muffle furnace at 600ºC for 2 hours were black Colour Cobalt oxide nanoparticles were obtained.

2.3.4. Preparation of nano catalyst CoMo/γ. Al_2O_3

The CoMo/ γ. Al_2O_3 Catalyst composed of 3wt.% Co_3O_4 15% MoO_3 and 82wt.% Al_2O_3 was prepared.

The required amount of molybdenum oxide and cobalt Oxide were mixed with 10 ml of distilled water and placed on hot plate with mixing. This mixture was then added to (8.2) g of γ.Al_2O_3 being prepared with constant stirring and the mixture was placed in ultrasonic appartus for (1.5) h. Finally it is put in oven to dry and then calcined at 550ºC for 8 hours where CoMo/ γ. $A1_2O_3$ nano-powder was obtained.

2.4. Preparation of solutions used in adsorption processes

2.4.1. Hydrochloric acid

(0.1) M solution of HCl was prepared by transferring (0.83) 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 in to (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 solutions of Cu (II) ions

(1000) mg/L stock solutions of Cu(II) was prepared by using (2.6826) g of ($CuCl_2.2H_2O$) and dissolve it in deionized water and then dilute it to (1000) ml. A series of solutions with (20,40,60.80 and 100)

mg/L were prepared by adequate amount dilution of the above stock solution and deionized water.

2.4.4. Standard solutions of Cd (II) ions

To prepare a stock solution (1000) mg/L of cadmium, ions weight (1.791)g of ($CdCl_2.H_2O$) and dissolve it in deionized water and then dilute it to (1000) ml in a volumetric flask. A series of solutions with (20,40,60,80 and 100) mg/L were prepared by adequate amount dilution of the above stocks solution and deionized water.

2.5. Optimization of batch adsorption method

The solutions of Co (II) and Cd (II) single ion systems were analyzed by atomic absorption spectroscopy technique with absorbance of solutions measured at a wave length of (228.8)nm for cadmium and (230.0) nm for copper.

2.5.1. Effect of contact time

Six volumetric flasks with a volume of (100) ml containing (50) ml, (25) ml of Cu (II) ion 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 of (0.1) g of $CoMo/A_2O_3$ was added into each flask. It is the covered with glass stopper and placed in a water bath shaker at constant temperature (298) K, speed of (150) rpm at various contact time (15,30,45,60,75,90) min. It is then filtered before analysis to prevent nanoparticles interference with the analysis. The concentration of binary metal ions Cu (II) and Cd (II)

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 of $CoMo/\gamma$. Al_2O_3 on the removal of Cu^{+2} ions in

binary system using a fixed (25) ml of (100) mg/L Cu (II) solution and (25) ml of (100) mg/L of Cd (II) solutions, pH of (6), temperature of (298) K and stirring speed of (150) rpm. The contact time of Cu (II) and Cd (II) ions adsorption used was (15) min**.**

2.5.3. Effect of pH

Effect of pH was investigated at pH (2,4,6 and 8). It was adjusted by wise drop addition of (0.1 M) NaOH or (0.1 M) HCl at following conditions, (0.1) g of adsorbent, (25) ml of Cu (II) and (25) mL of Cd (II) solutions in binary systems with initial concentration of (100) mg / L, temperature of 298 K and stirring speed (150) rpm. The contact time used was (15) min for cadmium and copper. ions on adsorbent of CoMo/γ. Al_2O_3.

2.5.4. Effect of temperatures

The effect of temperature was studied at (298,308,318, and 333) K with following conditions, (0.1) g of adsorbent, (25) ml of (100) mg/L Cu (II) Solution and (25) ml Cd of (100) mg/L Cd (II) solution in binary system, pH of 6 and stirring speed of (150) rpm.

The contact time for the binary heavy metal ion removal used was (15) min on (CoMo/γ. Al_2O_3) adsorbent.

2.5.5. Effect of initial concentration

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

2.6 Calculation of percentage removal (R %)

The percentage metal removal (R%) was calculated using equation: [71, 81]

$$R\ \% = \frac{C_o - C_t}{C_o} \times 100 \quad \text{..... (2.1)}$$

where :

R % : The percentage metal removal

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

C_t : The concentration of metal ion (mg/L) after adsorption is at time, t.

2.7. Study of the adsorption isotherm

The adsorption isotherm for Copper (II) and cadmium (II) ions solution in single and binary systems on the nano catalyst CoMo/γ.Al_2O_3 at temperature (298) K, pH of 6, (0.1)g adsorbents and stirring speed (150) rpm. The contact time was (15) min for cadmium (II) and Copper (II) ions in single and binary systems on (CoMo/γ.Al_2O_3) surface.

In single system, (50) ml of Cd (II) or Cu (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 copper (II) ions with initial concentration of Cd (II) solution, varied (20-100) mg/L with presence increasing concentration of copper ions, in all binary metals isotherm experimental, and the copper (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**:** [71, 81]

$$Qe = \frac{(C_0 - C_e) \times v}{m} \quad \text{..... (2.2)}$$

Where :

Q_e: Adsorption capacity of the adsorbent at equilibrium, (mg/g). C_0: Initial concentration of adsorbate, (mg/L).

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

V: Volume of solution, (L).

m: Mass of adsorbent, (g).

Chapter Three

(Results & Discussion)

3.1. Characterization of prepared nanoparticles

The characterization of nanoparticle is important to confirm the shape, size, crystallity and purity. Nanoparticle characterization techniques such as FTIR, EDX, SEM, XRD and AFM were used to accurately determine particle size, size distribution and particle morphology. The primary results obtained from the study gives the clear indication regarding the size distribution, shape and yield. SEM images revealed the distribution and dispersion with extend of exfoliation, intercalation and orientation of nanoparticles.

3.1.1. Energy – dispersive X-ray Analysis Spectroscopy (EDXA)

The EDX spectra of CoO_3-NPs, Al_2O_3-NPs and MoO-NPs, nano Catalyst CoMo/γ.Al_2O_3-NPs were determined and shown in figures (3,1),(3,2),(3,3) and (3,4) respectively. EDX were used in order to determine the elements that present in the samples of CoO-NP_S. Result revealed in fig (3.1), that the EDX data was composed of Co (78.67%) and O (21.33%) were major. This results has confirmed that the CoO-NPs has high purity. Similar finding was also found in previous studies by Salavati-Niasari et al. (2009) that obtained strong peaks related to Co and O in cobalt oxide nanoparticles, Farhadi et al. (2013) has stated that the theoretical expected mass percent of cobalt and oxygen elements existed in the product with a Co/O atomic ratio was of obtained. Thus, the EDX result revealed that the synthesized CoO NPs were of high purity.

The Al_2O_3 nanoparticle elemental composition also shown in figure (3.2) The EDX data of Al_2O_3 nanoparticle reported that NPs composed of two elements oxygen is the present in the highest amount (47.06%) and Al (52.94%), Our results are strengthen by Koopi & Buazar, (2018), they synthesized aluminum oxide nanoparticles using the

macroalgae Sargassum ilicifolium, their results revealed that The chemical composition of the $\gamma.Al_2O_3$ NPs indicated only two peaks for the components aluminum (46.31%) and oxygen (53.69%), demonstrating the high purity of the similar results also reported by Atrak et al. (2018), they studied the elemental composition of Al_2O_3 NPs as (Al-52.94% & O- 47.6%).

In figure (3.3) the molybdenum oxide nanoparticle EDX results shown revealed that oxygen is (33.33%) and molybdenum is (66.67%) involve in composition of MoO_3-NPs. Similar findings were reported from the studies of Ragg et al. (2014). Figure and table (3,4) shows the EDX results of nano $CoMo/\gamma.Al_2O_3$-NPs. In which the Al (43.41%), O (44.23%), Mo (10.00%), Co (2.36%) are involve as major composition. Thus, the EDX result revealed that the synthesized CoO-NPs, MoO_3-NPs, Al_2O_3-NPs and nano Catalyst $CoMo/\gamma.Al_2O_3$-NPs were highly pure.

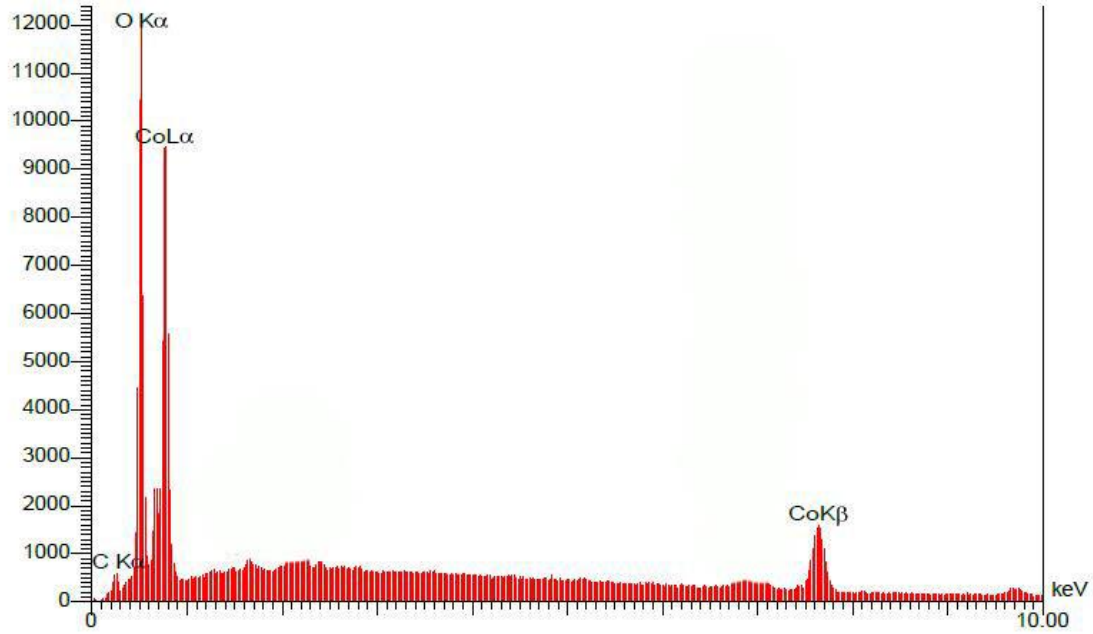

Figure (3.1): EDX of CoO_3-NPs

Table (3.1): Quantitative elemental composition of CoO_3-NPs obtained from EDX.

Element Name	Atomic Weight %
C	78.67
O	21.33
	100.00

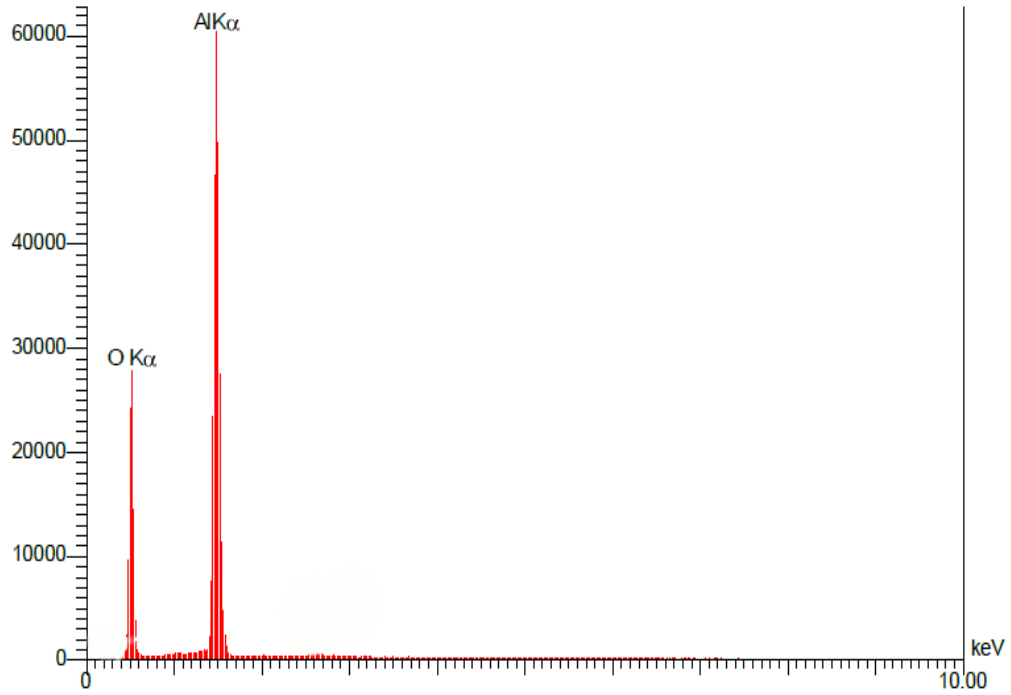

Figure (3.2): EDX spectrum of prepared nano Al_2O_3.

Table (3.2.): Quantitative Results of elemental composition of Al_2O_3-NPs in EDX

Element Name	Atomic Weight %
O	47.06
Al	52.94
	100.00

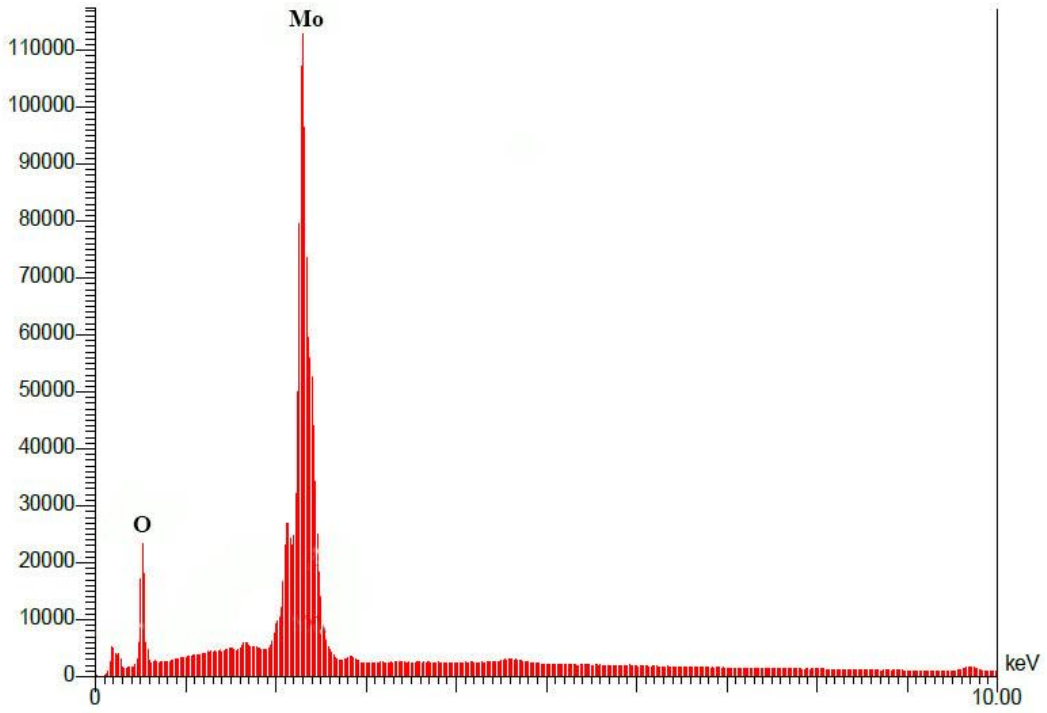

Figure (3.3): EDX of MoO_3-NPs

Table (3.3): Quantitative Results of elemental composition of MoO_3-NPs in EDX

Element Name	Atomic weight %
O	33.33
Mo	66.67
	100.00

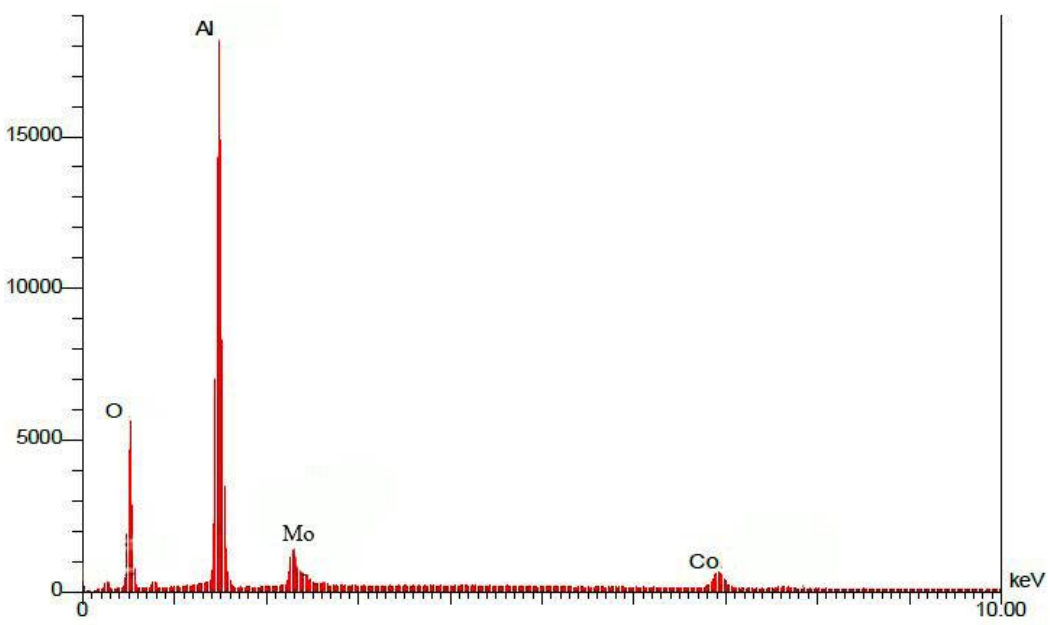

Figure (3.4): EDX of nano Catalyst CoMo/γ.Al_2O_3-NPs

Table (3.4): Quantitative Results of elemental composition of nano Catalyst CoMo/γ.Al_2O_3-NPs in EDX

Element Name	Atomic Weight %
Co	2.36
Mo	10.00
Al	43.41
O	44.23
	100.00

3.1.2. X-ray Diffraction Characterization

The XRD analysis of CoO-NPs, MoO-NPs and Al_2O_3-NPs was carried out to confirm the crystalline nature of the synthesized nanoparticles. Figure (3.5) to (3.7) show the XRD spectra of CoO-NPs, MoO-NPs and Al_2O_3-NPs, respectively. Figure (3.5) The X-ray diffractograms of MoO-NPs, at 2θ from 2°-80°, clearly indicate the crystallinity of the prepared samples as indicated by the broadening of Bragg's peaks. The Bragg's reflection angles of 26.08°, 37.06°, 50.73°, 53.61°, 60.28° and 66.72°, obtained for Mo-NPs, corresponding to the set of lattice planes, that is, (110), (060), (002), (170), (081) and (211) respectively, have been obtained at 2θ indicating the formation of face centred cubic (fcc). Crystalline structure of pure MoO_3 which is in good agreement to the data (JCPDS No. 05-0508) (Malakooti et al., 2014). The peak related to the lattice plane (110) is the most intense suggesting its most predominant orientation in addition to the crystalline nature of the synthesized Mo-NPs (Arafat et al., 2011). The XRD spectrum did not show any other crystallographic peak confirming the high purity of synthesized MoO-NPs. The XRD spectrum of CoO-NPs in Figure (3.6) showed distinct diffraction peaks around 19.09°, 31.31°, 36.86°, 44.67°, 55.44°, 59.37°, 65.24° and 77.57°, which are indexed by the (111), (220), (311), (222), (400), (422), (511), (440) and (533) respectively, of the cubic face-centered. The XRD results of CoO-NPs are of consistent with the standard value of (JCPDS Card file No. 74–1656) (Salavati-Niasari et al., 2009).

Figure (3.7) shows the XRD pattern of the synthesized Al_2O_3 NPs. The presence of intense peaks at different 2θ is indicative of the crystalline nature of the alumina NPs. Analysis of the crystal planes of the assigned alumina peaks at 26.06°, 37.08°, 49.59°, 53.57°, 60.28° and 66.72°, which are indexed by the (012), (014), (202), (116), (018) and

(300) respectively, indicated that the nanoparticles showed a rhombohedral structure (JCPDS 88-0826) Koopi et al. (2018). The same number of six peaks reported by Atrak et al. (2018). The XRD pattern exhibited no extra peaks, indicating the phase fineness of the γ.Al_2O_3 nanoparticle.

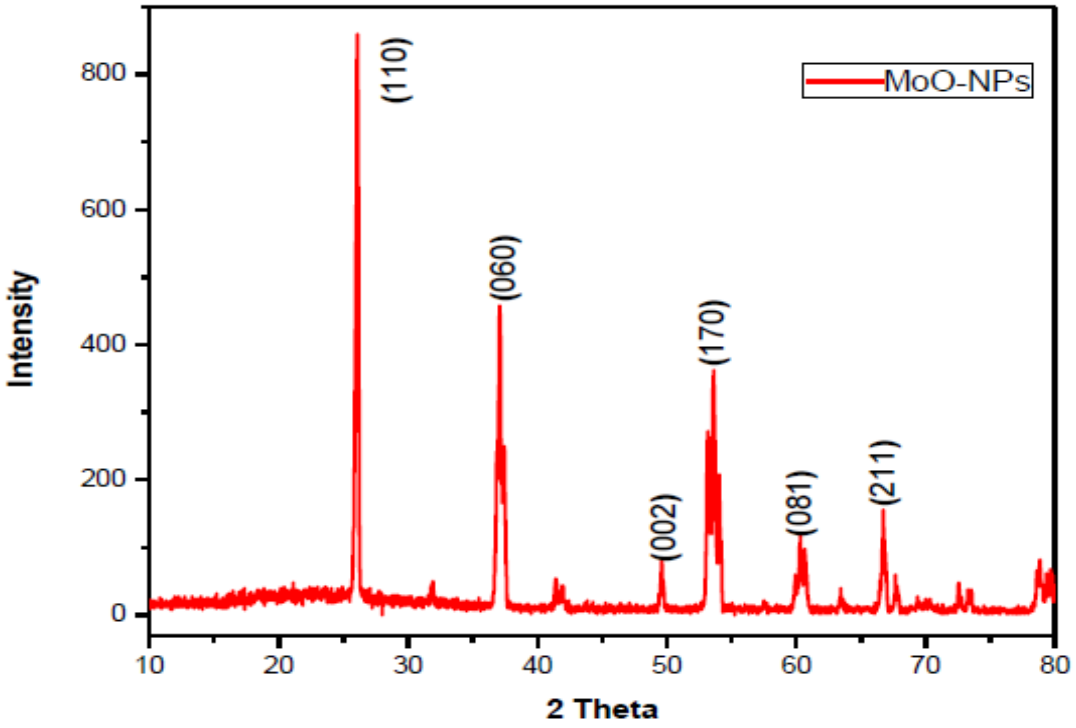

Figure (3.5): XRD spectrum of molybdenum oxide nanoparticles

Table (3.5): Three strongest peaks in XRD of MoO_3-NPs

No	2Theta(deg)	d(A)	FWHM (deg)	Intensity (Counts)	Integrated (Counts)
1	26.0898	3.41272	0.24780	550	7339
2	37.0614	2.42375	0.29060	305	4120
3	53.6111	1.70812	0.22890	269	3274

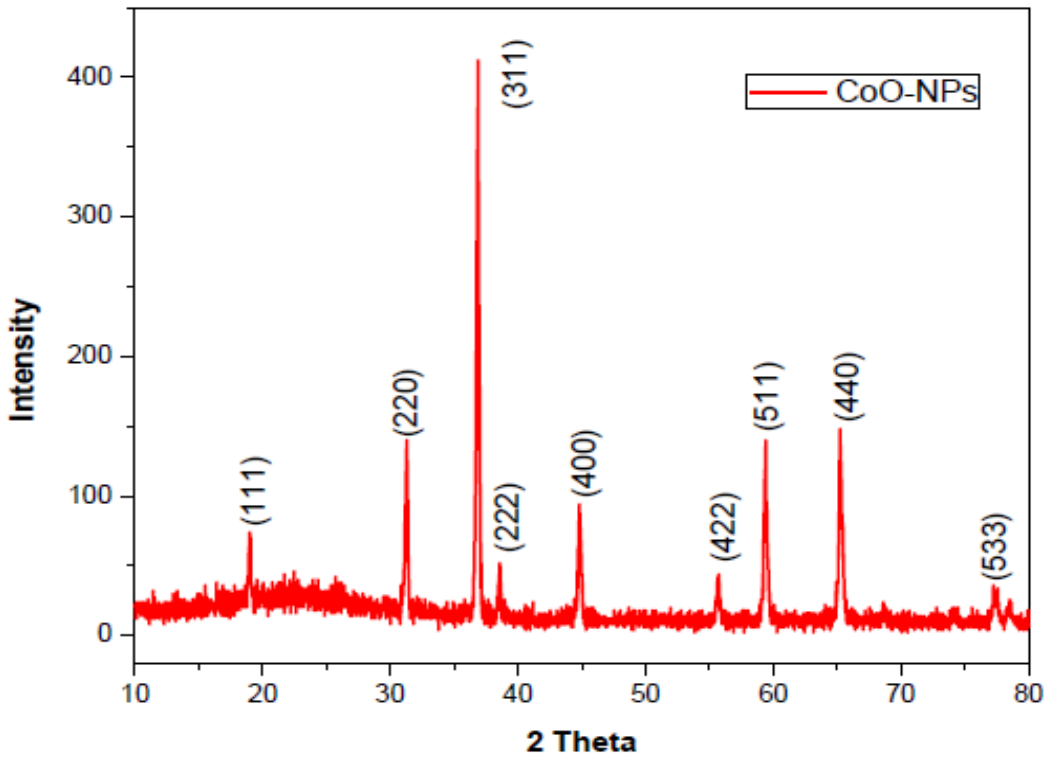

Figure (3.6): XRD spectrum of cobalt oxide nanoparticles

Table (3.6): Three strongest peaks in XRD of CoO-NPs

No	2Theta (degree)	d (A)	FWHM (degree)	Intensity (Counts)	Integrated (Counts)
1	36.8632	2.43633	0.21760	263	2796
2	65.2491	1.42878	0.21290	104	1239
3	59.3757	1.55530	0.22250	92	1151

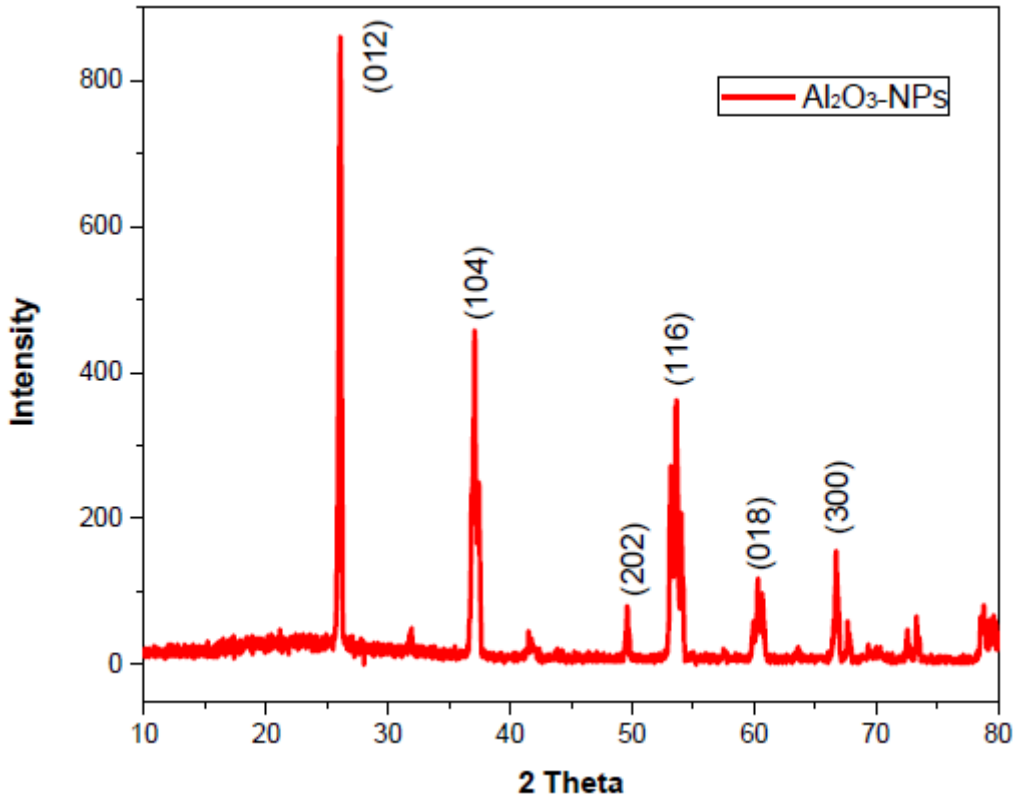

Figure (3.7): XRD spectrum of aluminum oxide nanoparticles

Table (3.7): Three strongest peaks in XRD of Al_2O_3-NPs

No	2Theta (deg)	d(A)	FWHM (deg)	Intensity (Counts)	Integrated (Counts)
1	26.0683	3.49297	0.06000	3	27
2	37.0859	2.40532	1.24000	13	845
3	53.5782	1.68817	0.22000	2	74

3.1.3. Field Emission Scanning Electron Microscopy

FESEM was used for the morphological assessment of obtained CoO-NPs, MoO-NPs, Al_2O_3-NPs and CoMo/γ.Al_2O_3 -NPs as depicted in Figure (3.8) to (3.11). As per the FESEM images, the nanoparticles predominantly appear to be spherical in shape with little shape variation. The high resolution images clearly show the tapering surface features where the nanoparticles distribution over the entire surface can be seen.

These extremely fascinating surface features allow nanoparticle to possess higher active sites compared to other morphologies. FESEM images revealed that average size of cobalt nanoparticle (27.01nm), molybdenum (30.50nm), aluminum oxide (27.07nm), and CoMo/γ.Al_2O_3 (26.64nm). Similar size (12-19nm) of cobalt nanoparticles reported by Ramachandran et al. (2020). Another study by (Cruz et al. 2019) synthesized cobalt nanoparticles, of 10 nm smaller size nanoparticle.

Our results are further supported also by Koopi and Buazar (2018), as they synthesized 35nm aluminum oxide nanoparticles using an extract of the algae Sargassum ilicifolium. Atrak et al. (2018) also synthesized small size (11nm) of amorphous and aluminum oxide nanoparticles by tragacanth gel. The findings of Li et al. (1999) also confirms our results, they reported molybdenum nanoparticles of 25nm.

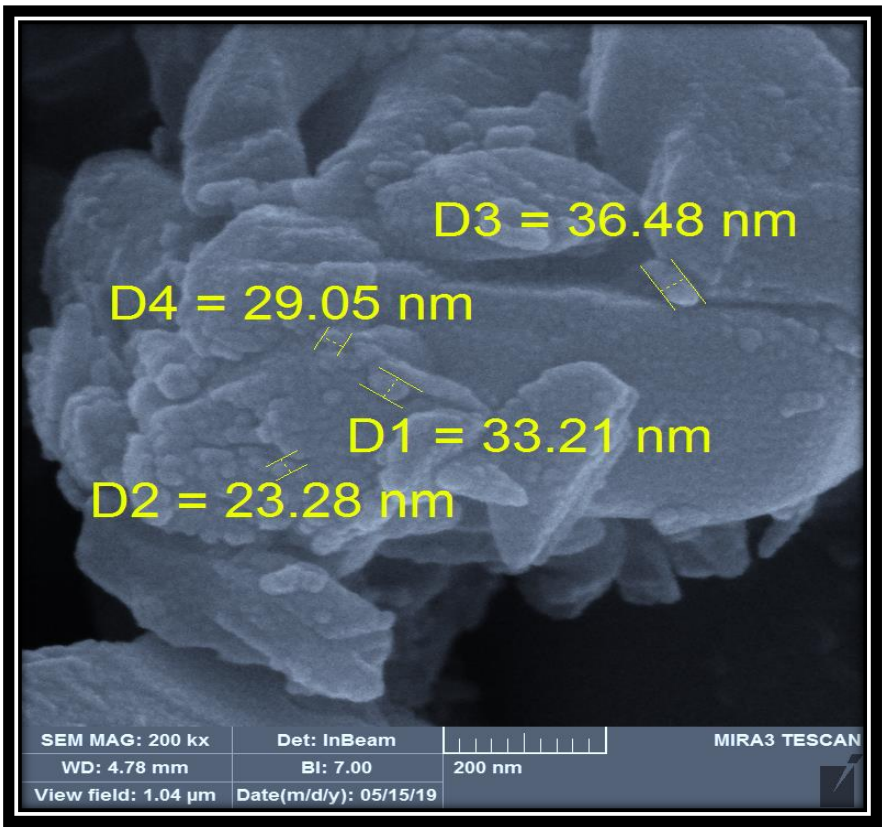

Figure (3.8): FESEM images of molybdenum oxide nanoparticles

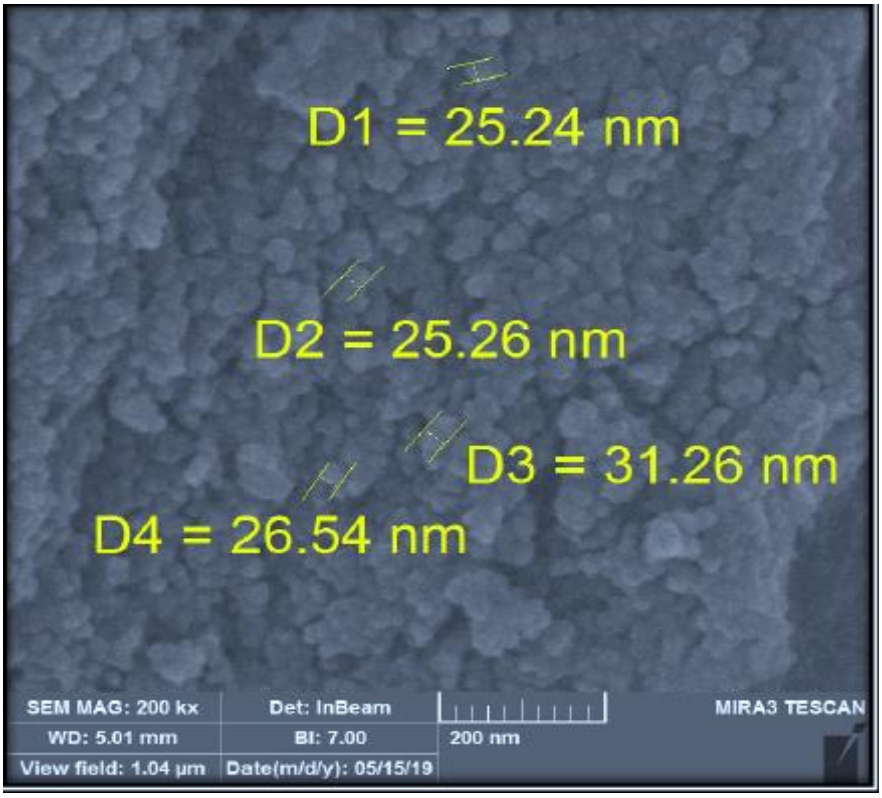

Figure (3.9): FESEM images of Al_2O_3 oxide nanoparticles

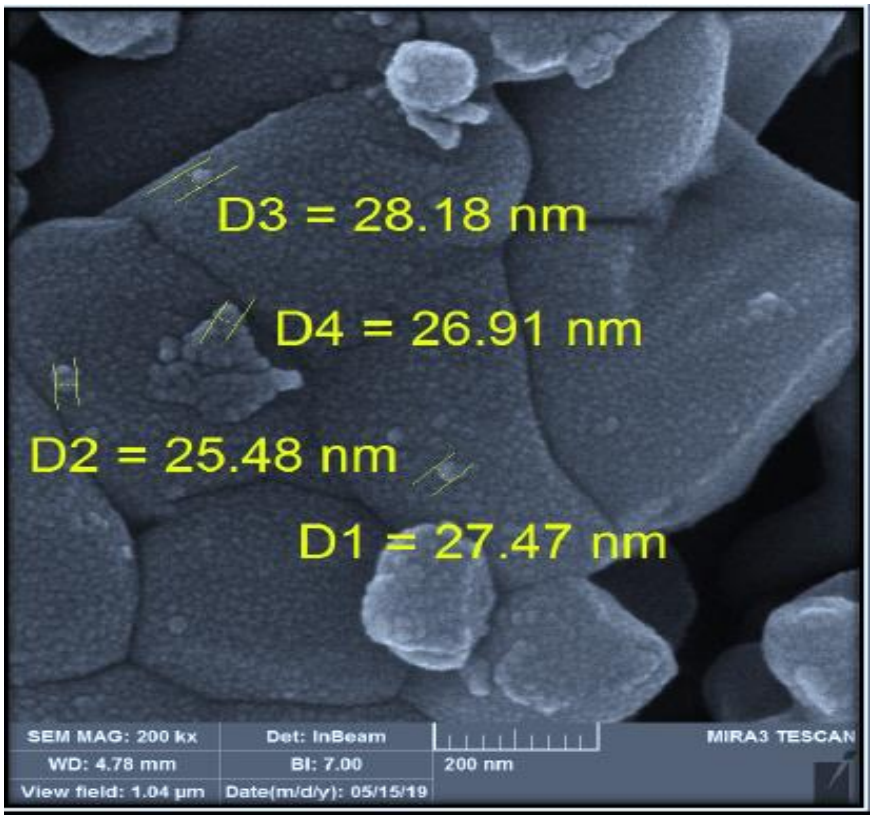

Figure (3.10): FESEM images of cobalt oxide nanoparticles

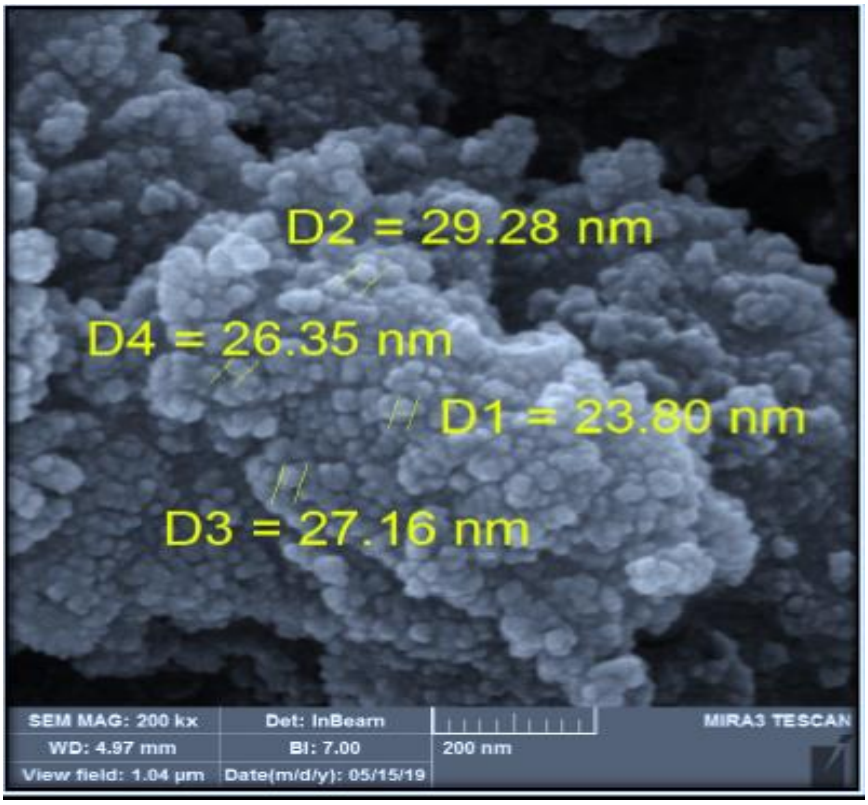

Figure (3. 11): FESEM images of CoMo/γ.Al_2O_3 nanoparticles

3.1.4. AFM Atomic Force Microscope Studies

The AFM is one of the foremost tools for merging, measurement and manipulation of data at nanoscale. Therefore, this technique is ideally suited for nanoparticle characterization (Bankura et al., 2012; Ramirez-Aguilar & Rowlen, 1998). Advantages of AFM for the applications are derived from the fact that the AFM is nondestructive technique and it has a very high 3-D spatial resolution (Song et al., 2009). Figure (3.12 - 3.15), show the AFM of CoO-NPs, Al_2O_3-NPs and MoO_3-NPs, CoMo/γ.Al_2O_3 -NPs.

The AFM 3D images indicate the formation of homogeneous distribution of CoO-NPs, MoO_3-NPs, Al_2O_3-NPs and CoMo/γ.Al_2O_3 -NPs and no agglomeration was observed while the particles shape and size were indicated. AFM shows the Granularity Accumulation Distribution (GAD), which gives the particles size distribution. The average particle diameter of the synthesized MoO_3-NPs, CoO-NPs, Al_2O_3-NPs and CoMo/γ.Al_2O_3 -NPs are 32.82 nm, 52.72 nm, 66.52 nm and (76.60 nm) respectively, size image of AFM (1762.20nm X 1758.00nm), and pixel (420,419). Figures (3.16) to (3.19) and tables (3.8) to (3.11) show the granularity cumulating distribution and average diameter data for the all prepared nanoparticles which prove that all have a nanoparticle size is AFM images in two dimensions (2D), it is found that average roughness are (2.12) nm and the root mean square (RMS) is (2.52) nm.

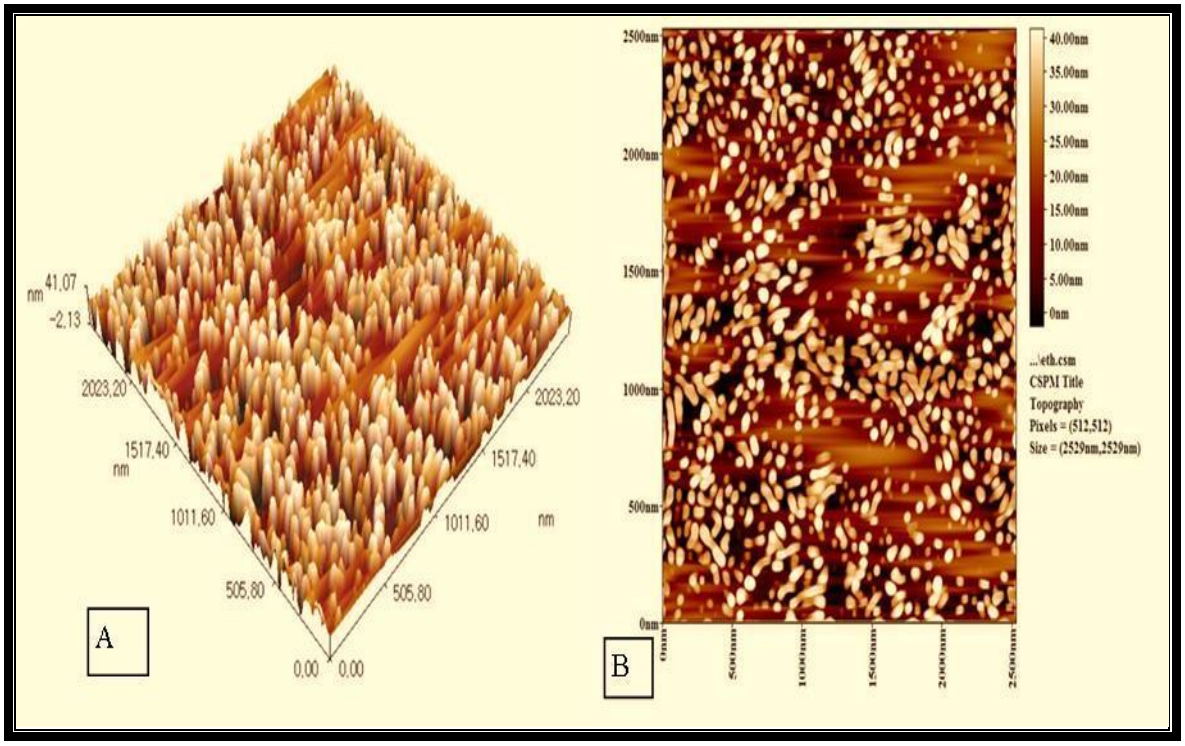

Figure (3. 12): (A) 3D AFM images and (B) 2D AFM images of prepared cobalt oxide nanoparticles

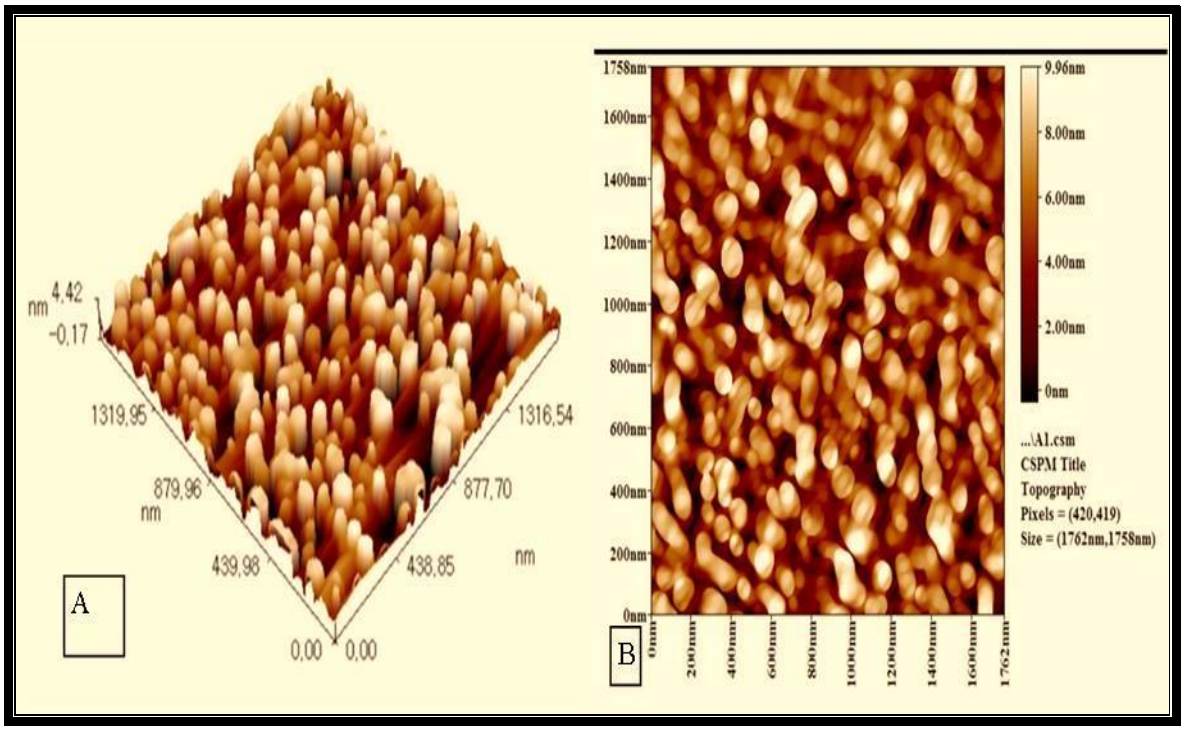

Figure (3.13): (A) 3D AFM images and (B) 2D AFM images of prepared Al_2O_3-NPs

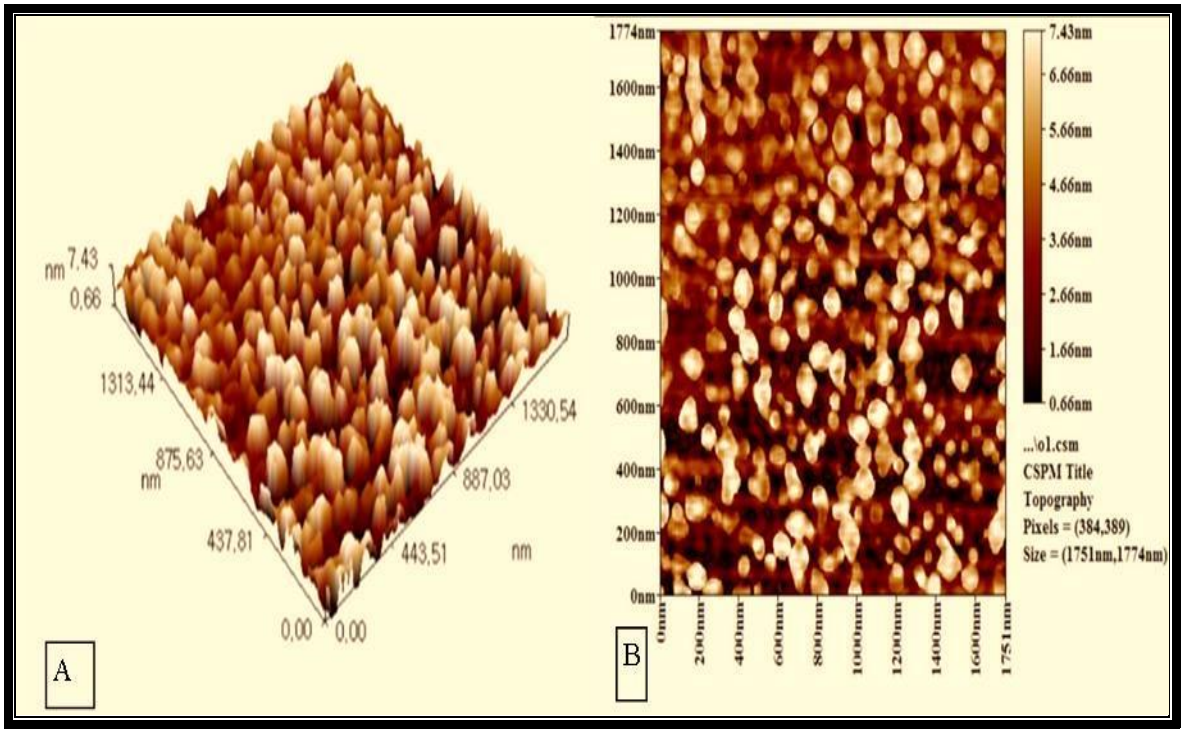

Figure (3.14): (A) 3D AFM images and (B) 2D AFM images of prepared Molybdenum Oxide-NPs

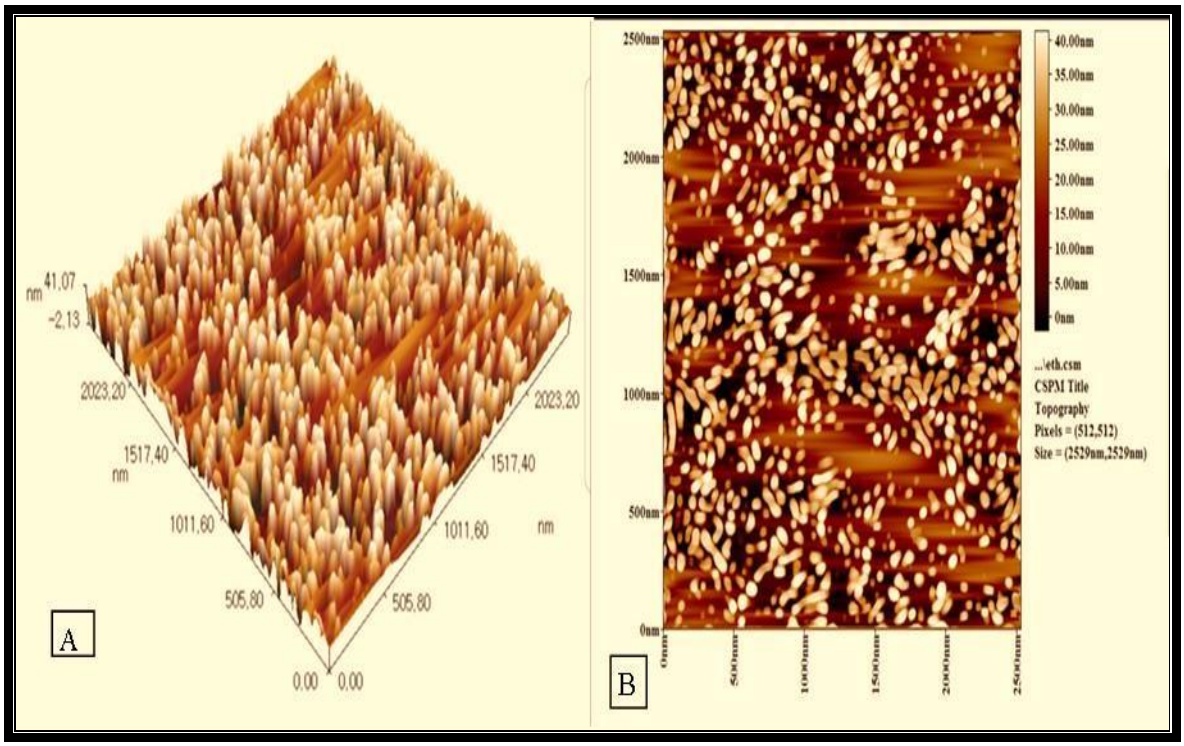

Figure (3.15): (A) 3D AFM images and (B) 2D AFM images of prepared CoMo/γ.Al_2O_3 -NPs

Table (3.8): Granularity cumulating distribution and average diameter of cobalt oxide nanoparticles,

Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)
30.00	5.76	5.76	50.00	9.88	45.68	70.00	7.41	81.89
35.00	9.05	14.81	55.00	8.64	54.32	75.00	9.88	91.77
40.00	11.11	25.93	60.00	9.47	63.79	80.00	8.23	100.00
45.00	9.88	35.80	65.00	10.70	74.49			

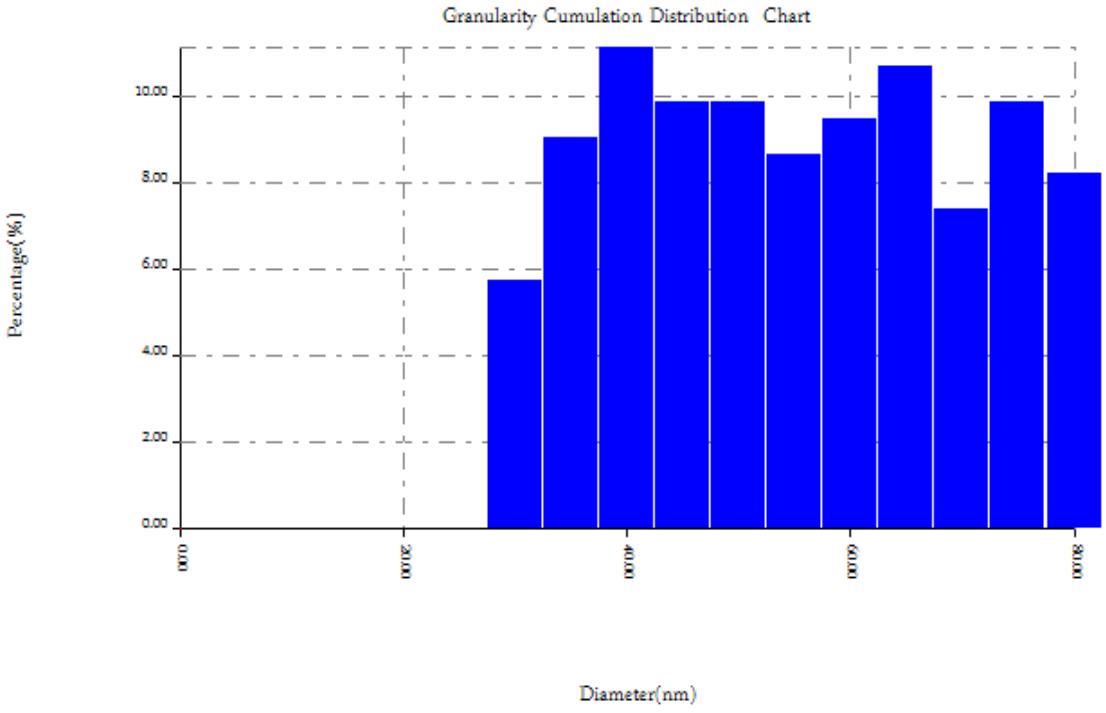

Figure (3.16): Granularity cumulating distribution of (CoONPs).

Table (3.9): Granularity cumulating distribution and average diameter of prepared molybdenum oxide nanoparticles,

Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)
24.00	7.47	7.47	34.00	7.91	58.46	44.00	7.91	94.07
26.00	12.53	20.00	36.00	8.57	67.03	46.00	3.52	97.58
28.00	9.89	29.89	38.00	8.35	75.38	48.00	2.42	100.00
30.00	8.35	38.24	40.00	4.62	80.00			
32.00	12.31	50.55	42.00	6.15	86.15			

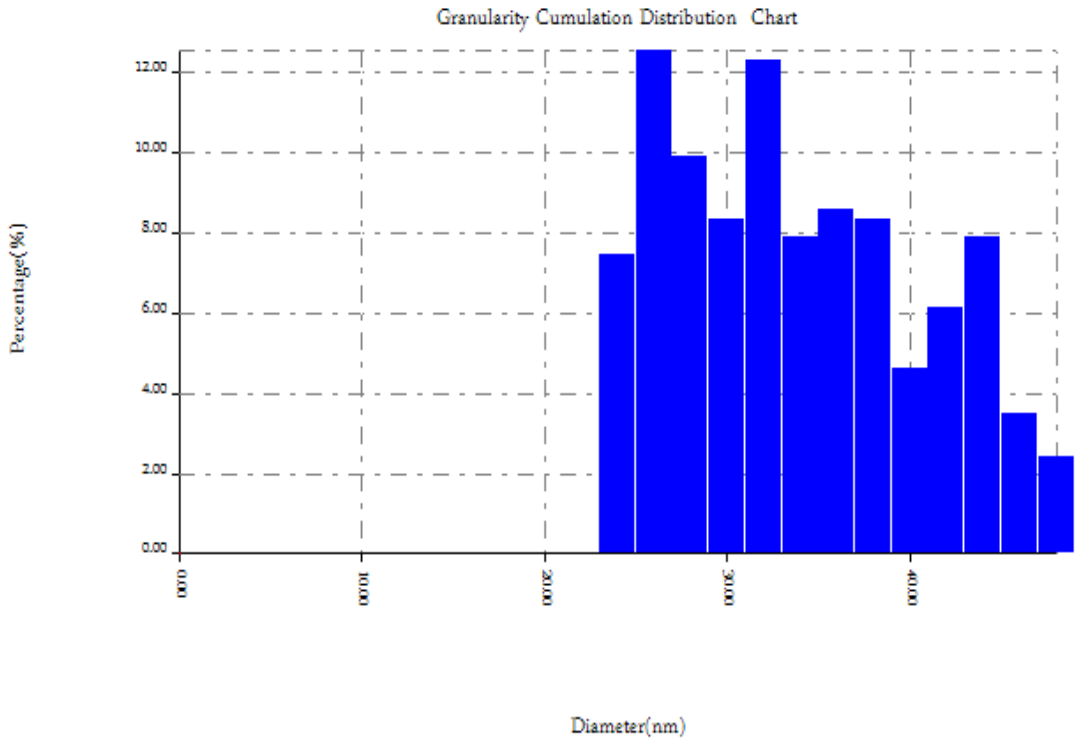

Figure (3.17): Granularity cumulating distribution of (MoO-NPs).

Table (3.10): Granularity cumulating distribution and average diameter of Al_2O_3-NPs,

Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)
45.00	9.02	9.02	65.00	13.53	48.12	85.00	9.02	85.71
50.00	10.53	19.55	70.00	11.28	59.40	90.00	11.28	96.99
55.00	7.52	27.07	75.00	7.52	66.92	95.00	3.01	100.00
60.00	7.52	34.59	80.00	9.77	76.69			

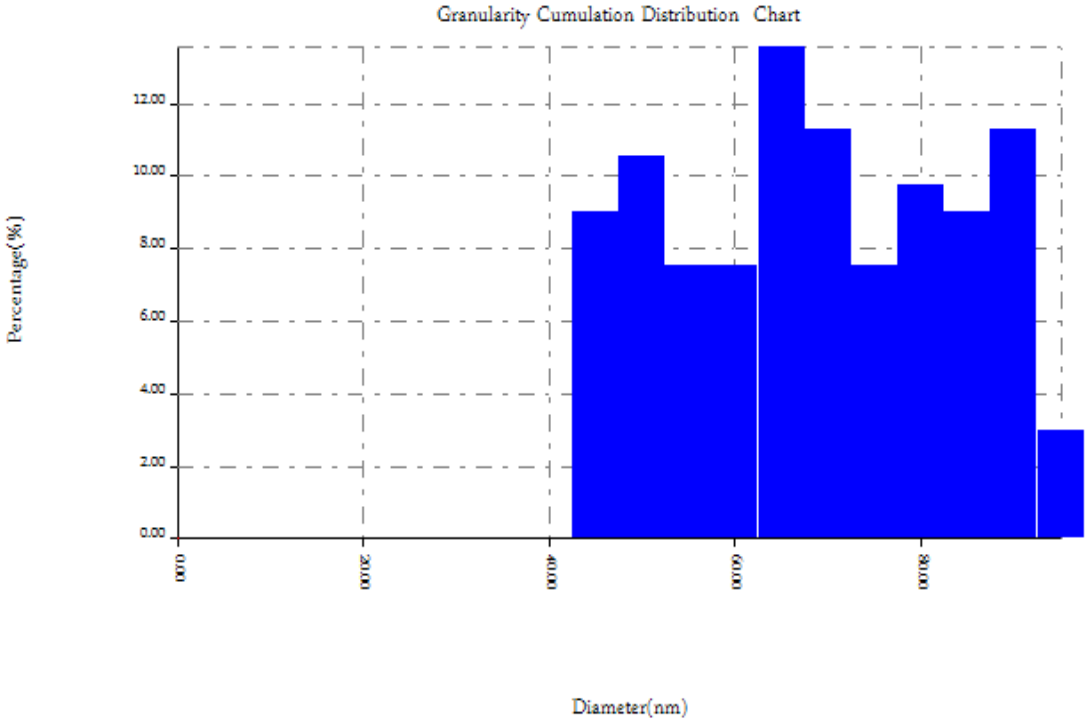

Figure (3.18): Granularity cumulating distribution of (Al_2O_3-NPs).

Table (3.11): Granularity cumulating distribution and average diameter of CoMo/γ.Al_2O_3-NPs,

Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)
60.00	3.77	3.77	80.00	11.32	61.01	100.00	4.40	96.23
65.00	20.13	23.90	85.00	11.32	72.33	105.00	3.77	100.00
70.00	11.95	35.85	90.00	12.58	84.91			
75.00	13.84	49.69	95.00	6.92	91.82			

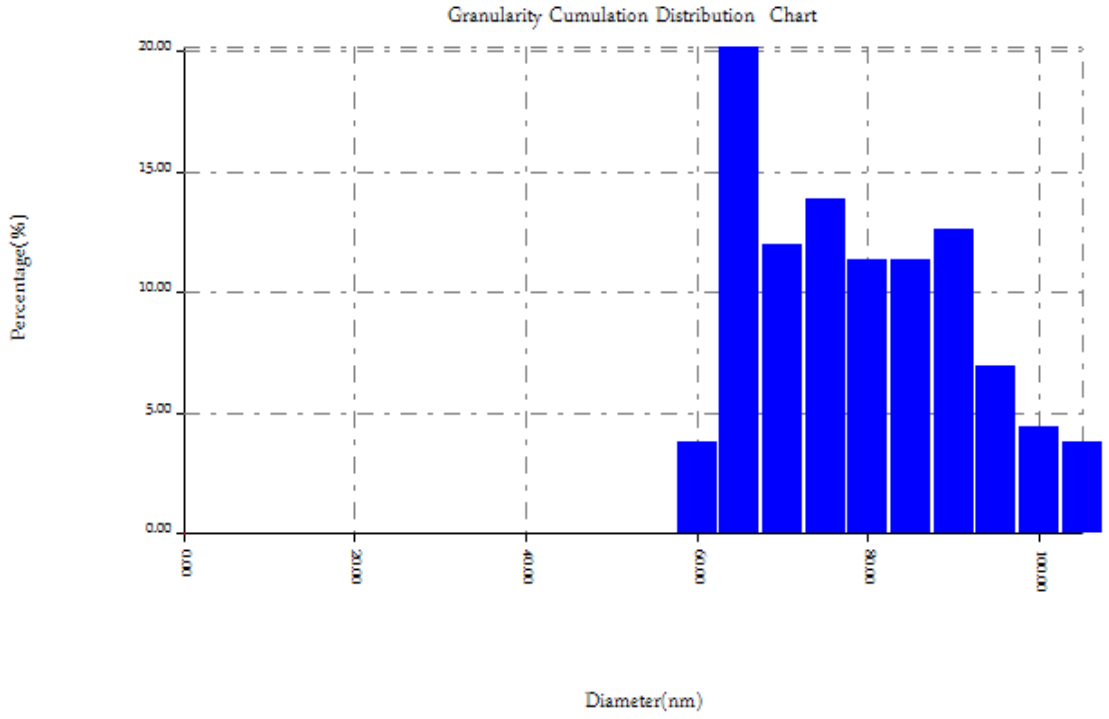

Figure (3.19): Granularity cumulating distribution of (CoMo/γ.Al_2O_3-NPs).

3.2. Adsorption of Cadmium (II) and Copper (II) ions in binary system on the nano catalyst (CoMo/γ.Al_2O_3) surfaces

3.2.1. Effect of contact time on adsorption

It is the covered with glass stopper and placed in a water bath shaker at constant the effect of contact time on adsorption Cd (II) and Cu (II) ions in binary system on the nano catalyst (CoMo/ γ.Al_2O_3) 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.

It is then filtered before analysis to prevent nanoparticles interference with the analysis. The concentration of binary metal ions Cu (II) and Cd (II).

Tables (3.12) explain the change of the percentage removal if Cu (11) and Cd (11) ions with contact time. As seen the equilibrium time required for the adsorption of both are almost 15 min. The effect of contact time on the adsorption of Cu (II) and Cd (II) ions in binary system on nano catalyst (CoMo/ γ.Al_2O_3) surfaces are also explained in Figure (3.20) which showed increasing in the percent removal at the beginning of contact time of nano catalyst (CoMo/ γ.Al_2O_3) for both cadmium (II) and Copper (II) ions, then there was a gradual decline in the percentage removal of Cd^{+2} and Cu^{+2} ions 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. 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.

Table (3.12): Effect of contact time on the adsorption of Cd (II) and Cu (II) ions in binary system on (CoMo/ γ.Al_2O_3) surface at 298 K.

Time (min)	Contact time Cd (II) ions		Cu (II) ions	
	C_t (mg/L)	R%	C_t (mg/L)	R%
15	0.330	99.670	0.986	99.014
30	0.393	99.607	1.098	98.908
45	0.375	99.625	1.093	98.907
60	0.368	99.632	1.113	98.887
75	0.487	99.513	1.237	98.763
90	0.447	99.553	1.257	98.743

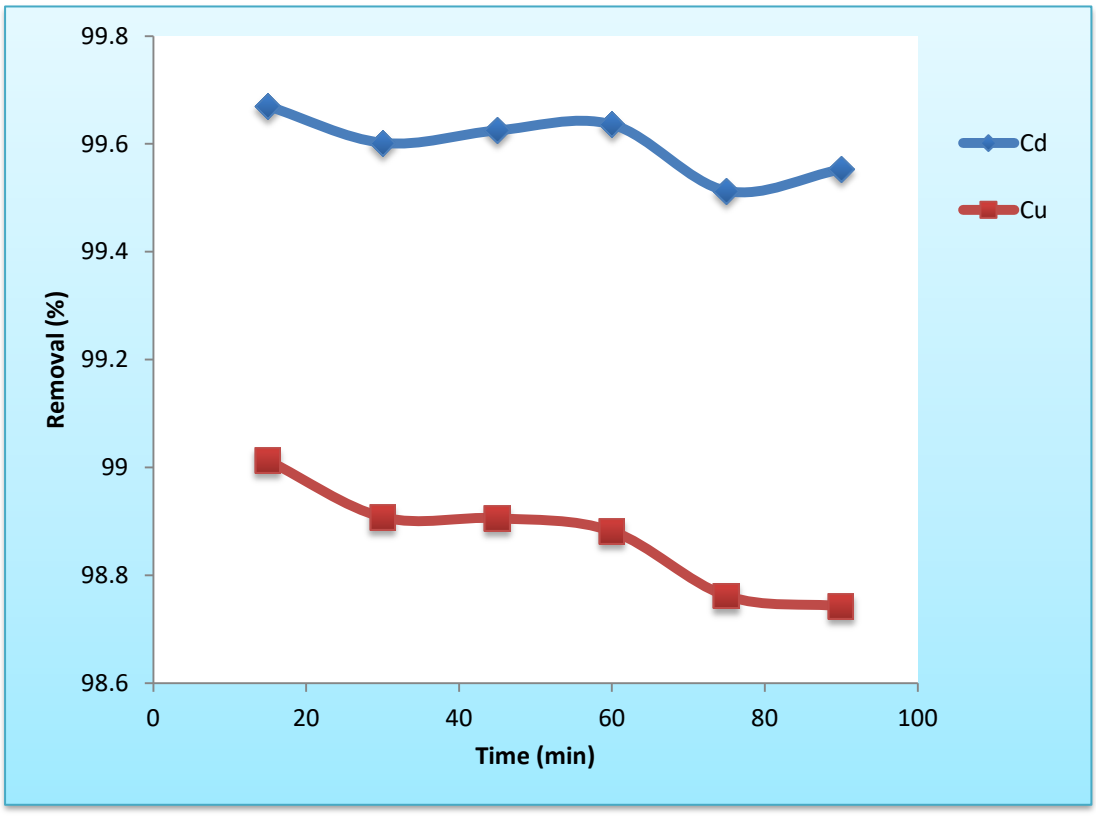

Figure (3.20): Effect of contact time on adsorption of Cd (II) and Cu (II) ions in binary system on the (CoMo/ γ.Al_2O_3) surfaces at 298 K.

3.2.2. Effect of adsorbent quantity on adsorption

The effect of adsorbent quantity was studied using (0.01, 0.05, 0.1, 0.15 and 0.2) g of CoMo/γ. Al_2O_3 on the removal of Cu^{+2} and Cd^{+2} ions in binary system using a fixed (25) ml of (100) mg/L Cu (II) solution and (25) ml of (100) mg/L of Cd (II) solutions, pH of (6), temperature of (298) K and stirring speed of (150) rpm. The contact time used was (15) min**.**

The influence of adsorbent quantity on the uptake of the binary metals Cd (II) and Cu (II) ions shown in Tables (3.13), and in Figure (3.21) with CoMo/ $\gamma.Al_2O_3$ increasing the quantity, the removal of the metal will increase, this means that the increase in the number of oxide nanoparticles increases the percentage removal for both metals. The increase in the percentage removal can be explained by the increasing surface area where the adsorption takes place it is shown that the optimum adsorbent quantity that can be used in cadmium (II) removal are (0.1)g, and copper (II) removal are (0.2)g the percentage removal will be increased slightly.

Table (3.13): Effect of adsorbent quantity on adsorption of Cd (II) and Cu (II) ions in binary system by (CoMo/ γ.Al_2O_3) surface at 298 K.

Adsorbent quantity (g)	Cd (II) ions		Cu (II) ions	
	Ce (mg/L)	R%	Ce (mg/L)	R%
0.01	3.232	96.768	0.534	99.466
0.05	2.396	97.604	0.412	99.588
0.10	0.286	99.714	0.229	99.771
0.15	0.233	99.766	0.200	99.799
0.20	0.89	99.11	0.146	99.854

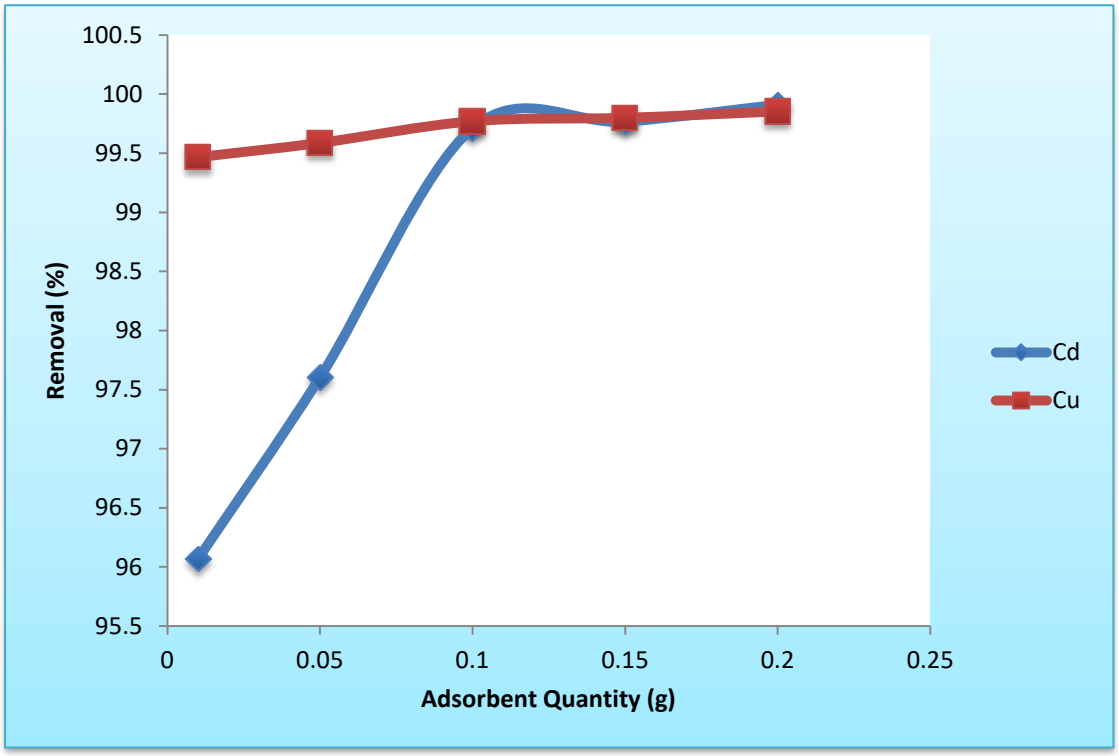

Figure (3.21): Effect of adsorbent quantity on adsorption of Cd (II) and Cu (II) ions in binary system on the (CoMo/ γ.Al_2O_3) surfaces at 298 K.

3.2.3. Effect of pH on adsorption

The effect of pH was investigated at pH (2,4,6 and 8). It was adjusted by drop wise addition of (0.1 M) NaOH or (0.1 M) HCl at following conditions, (0.1) g of adsorbent, (25) ml of Cu (II) and (25) mL of Cd (II) solutions in binary systems with initial concentration of (100) mg / L, temperature of 298 K and stirring speed (150) rpm. The contact time used was (15) min for cadmium and Copper, ions on adsorbent of CoMo/γ. Al_2O_3. Table (3.14) show results obtained for the effect of pH on Cd (II) and Cu (II) removal. It can be observed that the removal of Cd (II) and Cu (II) ions was maximum at pH of 6 using nano catalyst (CoMo/ γ.Al_2O_3) adsorbent.

The pH of the solution of the metal plays an important role in the whole adsorption process and particularly on the percentage adsorption, Figure (3.22) shown the percentage removal of binary metals ions by (CoMo/ γ.Al_2O_3). 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 Cu^{+2} ions at low pH is less than that at higher pH.

Besides, the higher concentration of H^+ in solution competes with Cd (II) and Cu (II) for the adsorption sites, resulting for the reduced in adsorptive of copper (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 Cu (II) and Cd (II) due to electrostatic attraction, at pH values higher than 6, cadmium (II) and Copper (II) ions precipitated out because of the high concentration of (OH-) ions in the aqueous solution.

Table (3.14): Effect of pH on the adsorption of Cd (II) and Cu (II) ions in binary system by (CoMo/ γ.Al_2O_3) surface at 298 K.

pH Amount	Cd (II) ions		Cu (II) ions	
	Ce (mg/L)	R%	Ce (mg/L)	R%
2	1.940	98.06	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

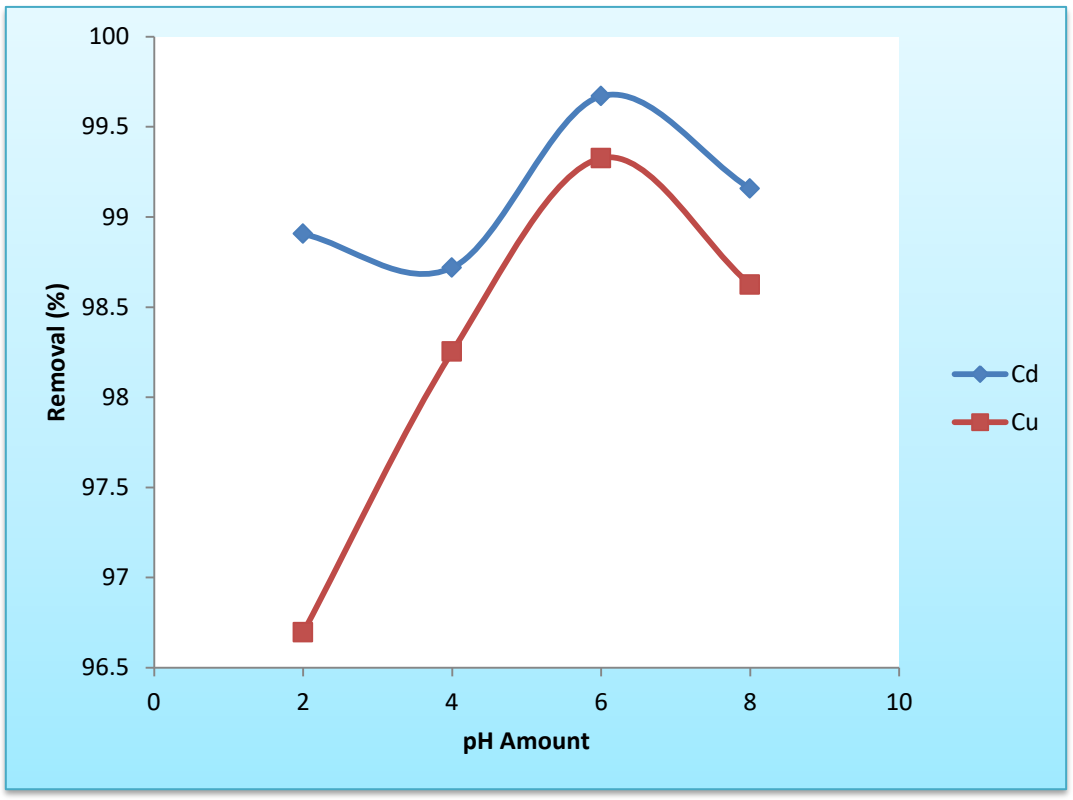

Figure (3.22): Effect of pH on adsorption of Cd (II) and Cu (II) ions in binary system on the (CoMo/ γ.Al_2O_3) surfaces at 298 K.

3.2.4. Effect of temperatures on adsorption

The effect of temperature was studied at (298,308,318, and 333) K with following conditions, (0.1) g of adsorbent, (25) ml of (100) mg/L Cu (II) solution and (25) ml Cd of (100) mg/L Cd (II) solution in binary system, pH of 6 and stirring speed of (150) rpm. The contact time for the binary heavy metal ion removal used was (15) min on the nano catalyst (CoMo/γ. Al_2O_3) adsorbent.

The experimental data and the general shapes of the cadmium (II) and copper (II) adsorption removal on the nano catalyst (CoMo/ γ.Al_2O_3) are given in tables (3.15), and figure (3.23). The data show that the percentage removal decrease with an increase in temperature. It is observed that the adsorption of binary metals (Cd^{+2} and Cu^{+2} ions) on the nano catalyst (CoMo/ γ.Al_2O_3) surfaces are exothermic in all cases, from the reduction in the rate of adsorption with an increase in the temperature, maybe backing weakening of interaction force between the active sites of the adsorption surface and the binary metals ions.

Table (3.15): Effect of temperature on the adsorption of Cd (II) and Cu (II) ions in binary system by (CoMo/ γ.Al_2O_3) surface.

Temperature (K)	Cd (II) ions		Cu (II) ions	
	Ce(mg/L)	R%	Ce(mg/L)	R%
298	0.265	99.735	1.547	98.453
308	0.738	99.262	1.569	98.431
318	0.764	99.236	3.961	96.039
333	0.980	99.023	4.531	95.469

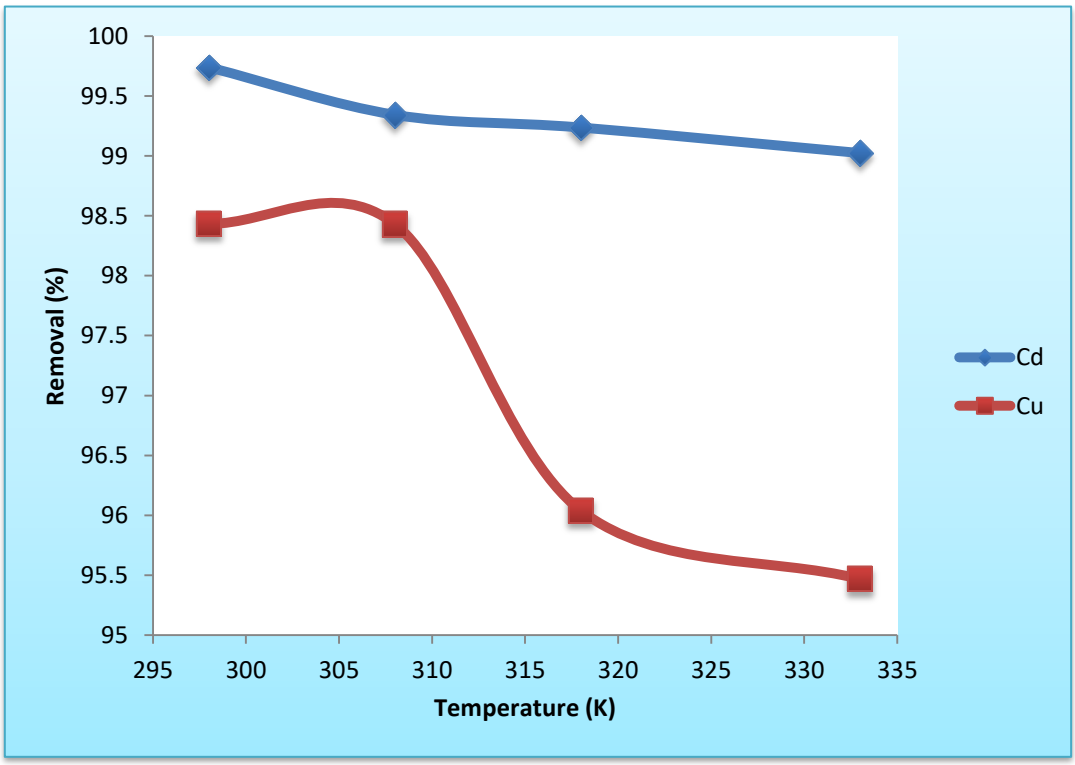

Figure (3.23): Effect of temperature on adsorption of Cd (II) and Cu (II) ions in binary system on the (CoMo/ γ.Al_2O_3) surfaces.

3.2.5. Effect of initial concentration

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

The results show in table (3.16), and figure (3.24), about the impact of the initial concentration indicate a little decrease in the removal when increasing initial concentration of Cd (II) and Cu (II) ions on the nano catalyst (CoMo/ $\gamma.Al_2O_3$). The small decrease in the percentage of the removal at higher concentration could be attributed to the limited number of active sites of the nano catalyst CoMo/ $\gamma.Al_2O_3$ adsorbents, which become more saturated with an increase in the concentration of metal ions (Cd^{+2} and Cu^{+2}), and the removal of cadmium (II) and Copper (II) on the nano catalyst (CoMo/ $\gamma.Al_2O_3$) then decreased.

Table (3.16): Effect of initial concentration on the adsorption of Cd (II) and Cu (II) ions in binary system by (CoMo/ γ.Al_2O_3) surface at 298 K.

Initial concentration (mg/L)	Cd (II) ions		Cu (II) ions	
	Ce(mg/L)	R%	Ce(mg/L)	R%
20	0.550	99.45	0.028	99.972
40	0.141	99.859	0.133	99.867
60	0.301	99.699	0.256	99.744
80	0.467	99.355	0.386	99.614
100	0.620	99.380	0.965	99.035

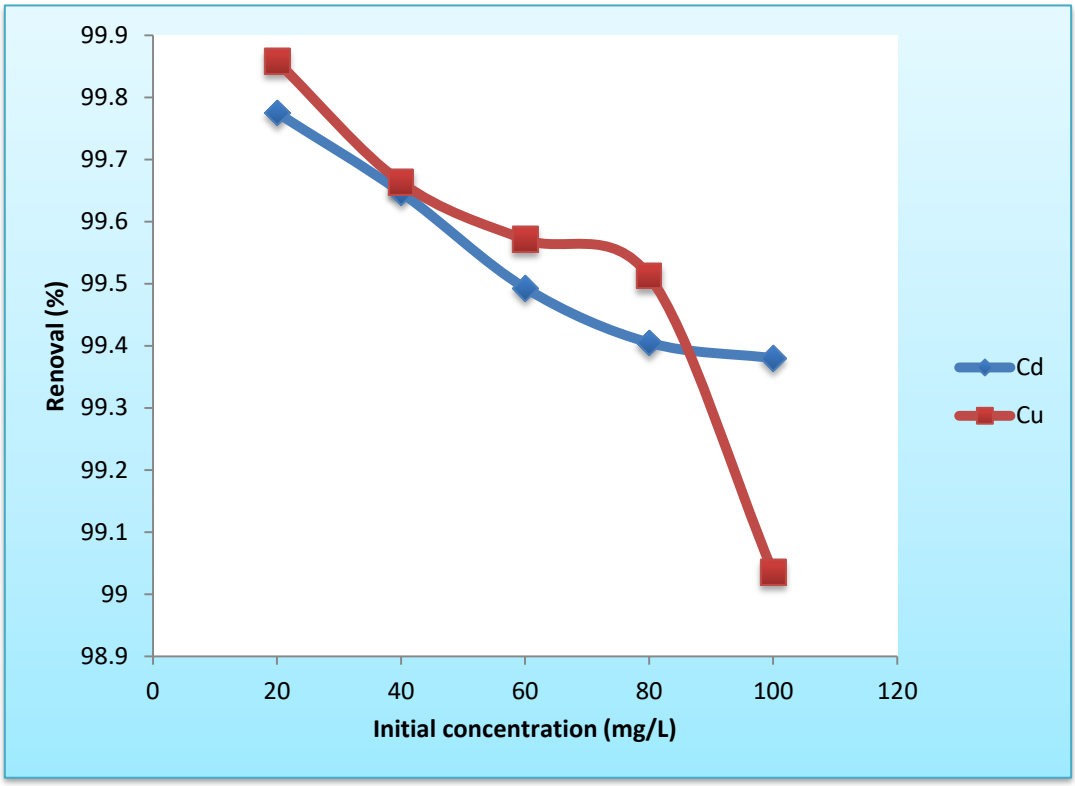

Figure (3.24): Effect of initial concentration on adsorption of Cd (II) and Cu (II) ions in binary system on (CoMo/ γ.Al_2O_3) surfaces at 298 K.

3.3. The adsorption isotherm

The adsorption of Cd (II) and Cu (II) ions from single and binary an aqueous solution on the nano catalyst (CoMo/ $\gamma.Al_2O_3$) was conducted at ideal condition, shown in Table (3.17):

Table (3.17): Ideal condition for adsorption.

No.	Conditions of adsorbent	Value	
		Cd (II) ion	Cu (II) ion
1	pH	6	6
2	Temperature	298 K	298 K
3	Volume of metals ions solution	Binary, 25mL Single,50mL	Binary,25mL Single,50mL
4	Contact time (CoMo/ γ.Al2O3)	15 (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 Cu (II) removal in single systems from an aqueous solution on (CoMo/ $\gamma.Al_2O_3$) surfaces at ideal condition data are listed in table (3.18). The results are represented by the initial concentration (C_o) of cadmium and copper ions, and the equilibrium concentration (C_e) measured at equilibrium state and the adsorption capacity (Q_e) values calculated from the experimental data. The adsorption capacity (Q_e) are plotted versus equilibrium concentration (C_e) to obtain general adsorption isotherm of Cd (II) ions removal which are described in figure (3.25) by using nano catalyst (CoMo/ $\gamma.Al_2O_3$) and also adsorption isotherm of Cu (II) ions removal which are explained in figures (3.26) by using nano catalyst (CoMo/ $\gamma.Al_2O_3$) surfaces.

Table (3.18): Adsorption parameters values Cd (II) and Cu (II) ions of the single solution by (CoMo/ γ.Al_2O_3) surfaces at ideal condition.

Metals	C_o (mg/L)	CoMo/ γ.Al_2O_3					
		C_e (mg/L)	Q_e (mg/g)	log Ce (mg/L)	log Q_e (mg/g)	In C_e (g/L)	C_e/Q_e (g/L)
Cd (II) ions	20	0.032	9.984	-1.494	0.999	-3.442	0.003
	40	0.136	19.932	-0.866	1.299	-1.995	0.006
	60	0.245	29.877	-0.610	1.475	-1.406	0.008
	80	0.332	39.834	-0.478	1.600	-1.102	0.008
	100	0.474	49.763	-0.324	1.696	-0.746	0.009
Cu (II) ions	20	0.050	9.975	-1.310	0.998	-2.995	0.005
	40	0.100	19.950	-1.000	1.299	-2.302	0.005
	60	0.199	29.900	-0.701	1.475	-1.614	0.005
	80	0.250	39.875	-0.602	1.600	-1.386	0.006
	100	0.300	49.850	-0.522	1.697	-1.203	0.006

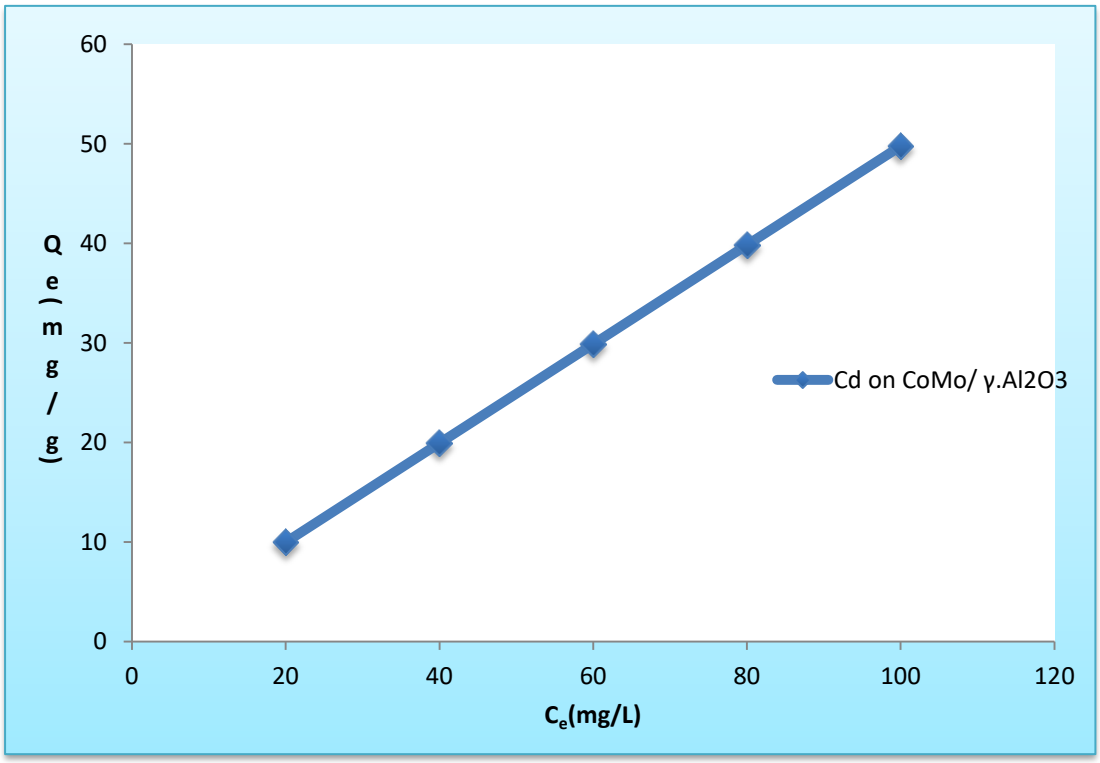

Figure (3.25): Adsorption isotherm of Cd (II) ions in single system by (CoMo/ γ.Al_2O_3) surface at various initial concentrations.

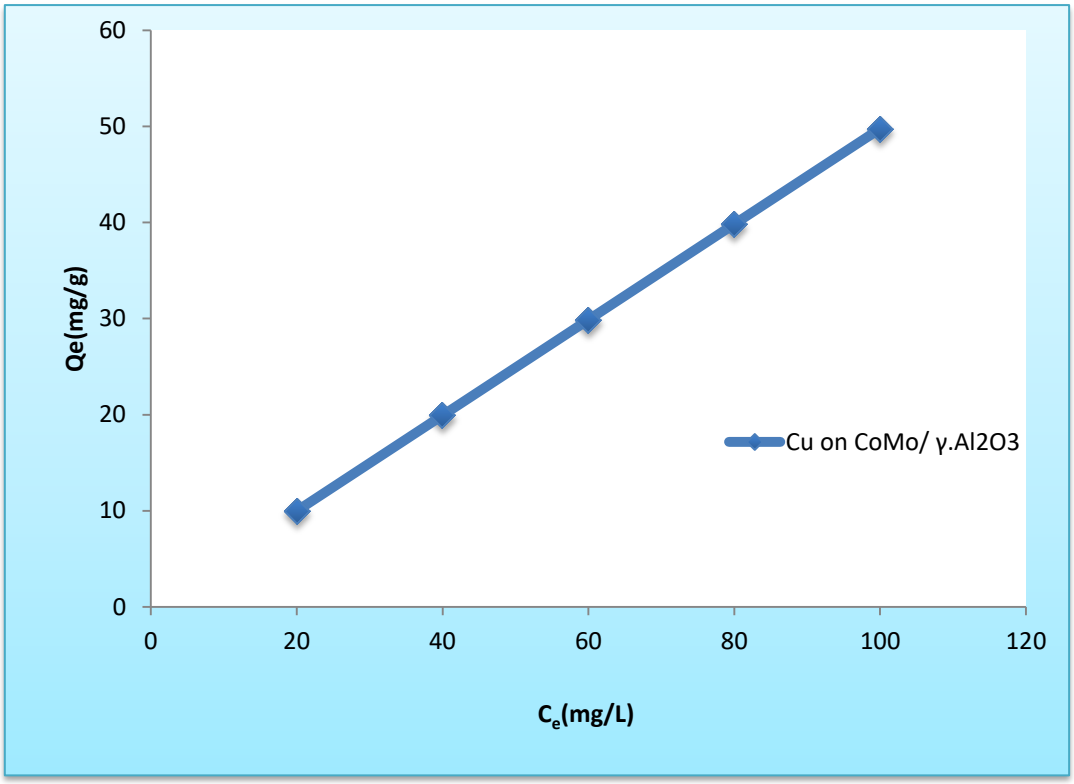

Figure (3.26): Adsorption isotherm of Cu (II) ions in single system by (CoMo/ γ.Al_2O_3) surface at various initial concentrations

The initial concentration provides the force to overcome the resistance to the mass transfer for Cd (II) and Cu (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 copper (II). The isotherm data of adsorption in single copper and Cd processes are shown in table (3.19) and in figures (3.7) and (3.28). The values of the isotherm constant are calculated by Langmuir constant (a) represents the adsorption capacity of the monolayer and (b) is a constant related to the adsorption energy from the slope and interceptions of the plots (C_e / Q_e) vs. (C_e) as shown in table (3.18).

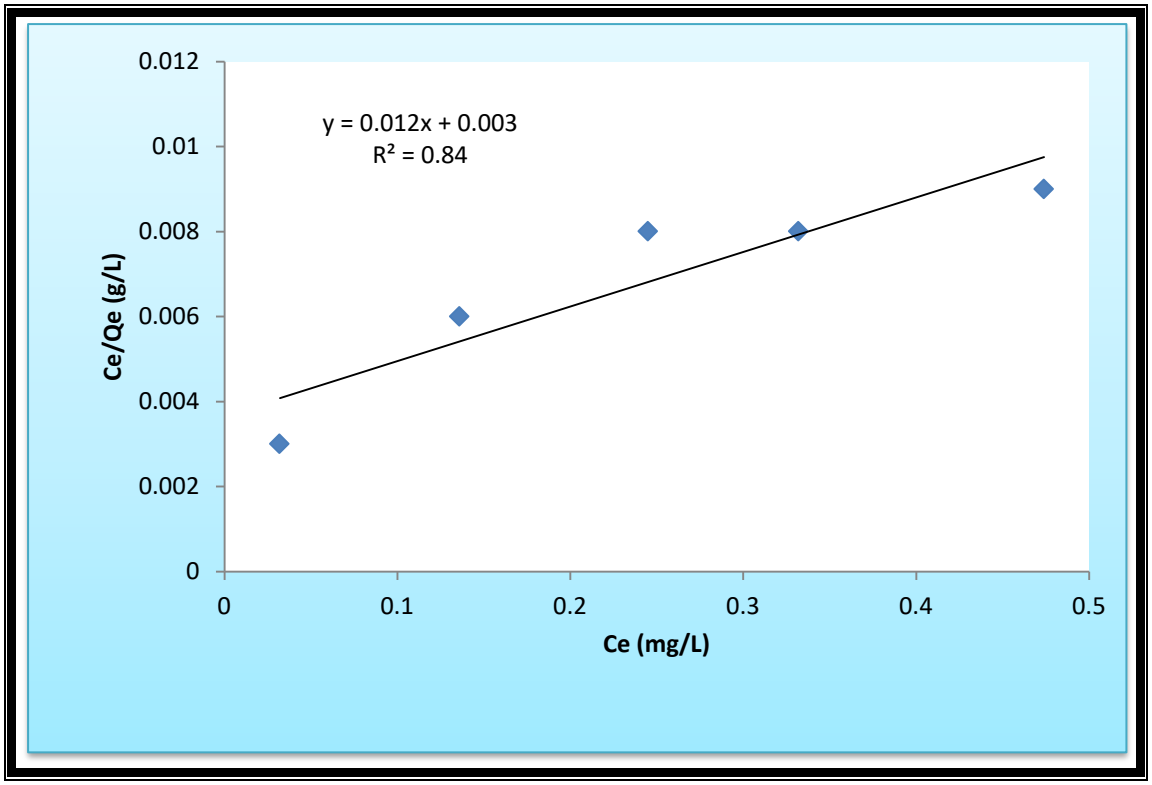

Figure (3.27): Linear Langmuir isotherm of Cd (II) ions removal in single system adsorption on (CoMo/ γ.Al_2O_3) surface at various initial concentrations

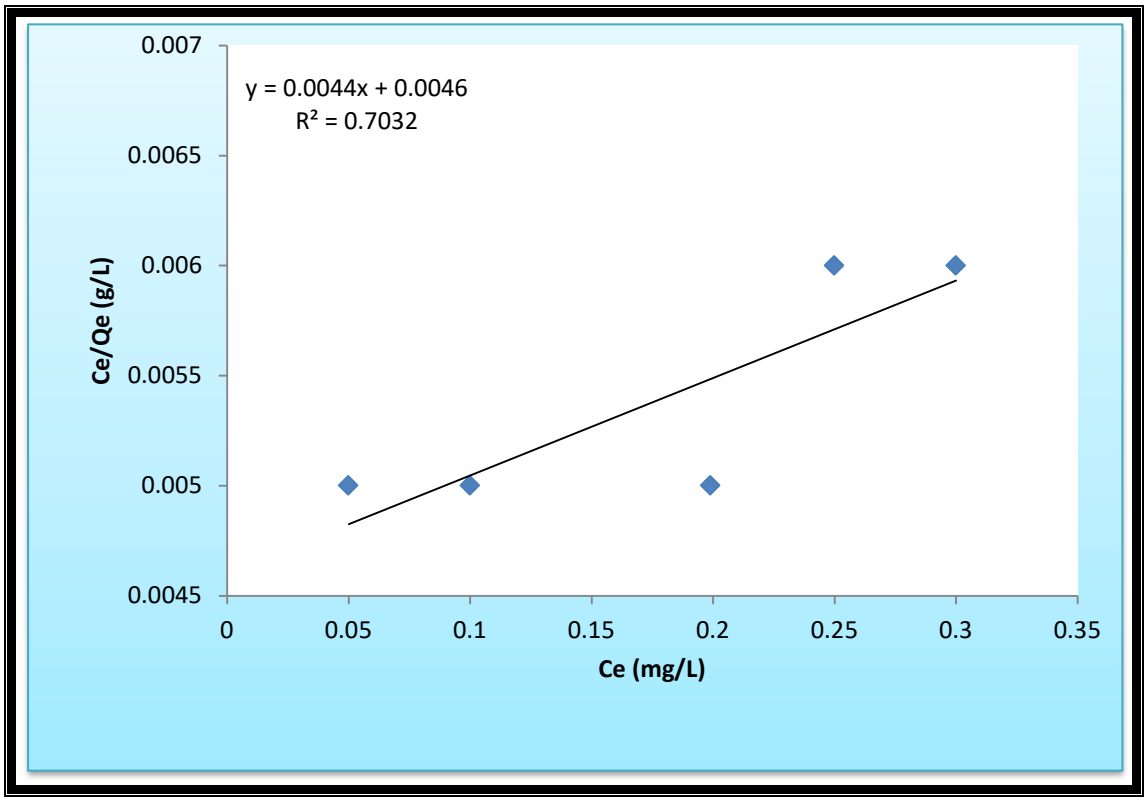

Figure (3.28): Linear Langmuir isotherm of Cu (II) ions removal in single system adsorption on (CoMo/ γ.Al_2O_3) surface at various initial concentrations.

3.3.1.2. Freundlich isotherm

The Freundlich (1.2) isotherm equation was applied to the adsorption of Cd^{+2} and Cu^{+2} ions systems. Isotherm data of adsorption of (Cd and Cu ions) were plotted and presented in tables (3.19) and figures (3.29) and (3.30). The Freundlich thermal constant: (Kf) is the adsorption capacity of adsorbents, and (n) is the intensity of adsorption that is calculated from the slope and intercept of the plot of (log Qe) versus (log C_e), and the results are shown in table (3.18).

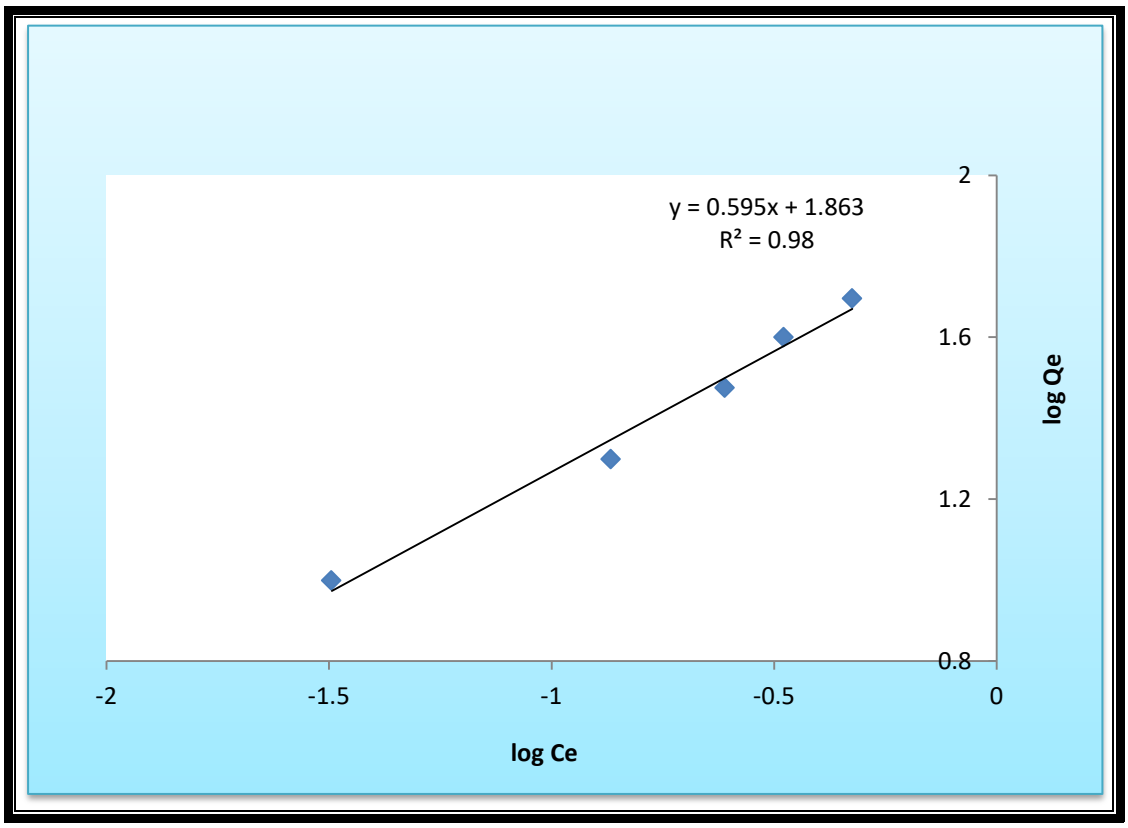

Figure (3.29): Linear Freundlich isotherm of Cd (II) ions in single system adsorption on (CoMo/ γ.Al_2O_3) surface at various initial concentrations.

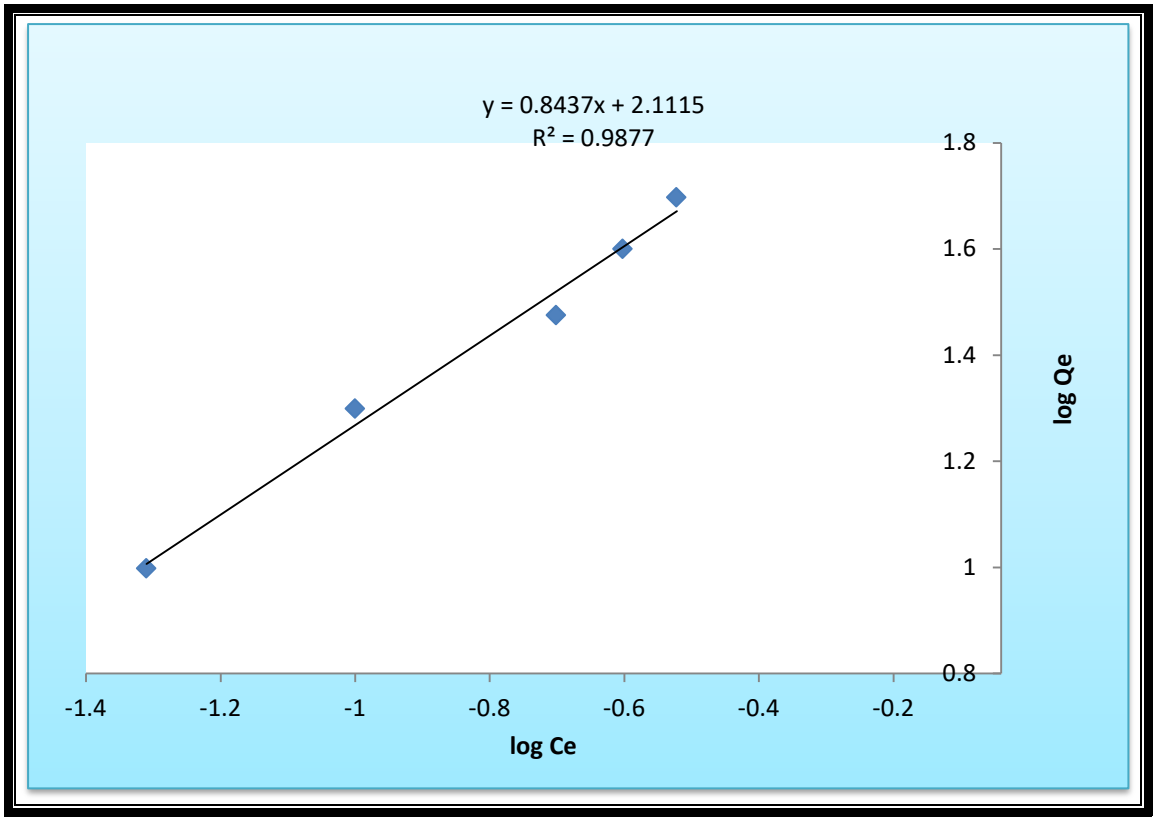

Figure (3.30): Linear Freundlich isotherm of Cu (II) ions in single system adsorption on (CoMo/ γ.Al_2O_3) surface at various initial concentrations.

3.3.1.3. Timken isotherm

The Temkin isotherm (1.3) equation was applied to the absorption of Cd (II) and Cu (II) ions in a single system of (CoMo/ γ.Al_2O_3). Isotherm data on adsorption of cadmium and copper ions were planned and presented and gaven in table (3.19) and figures (3.31) and (3.32).

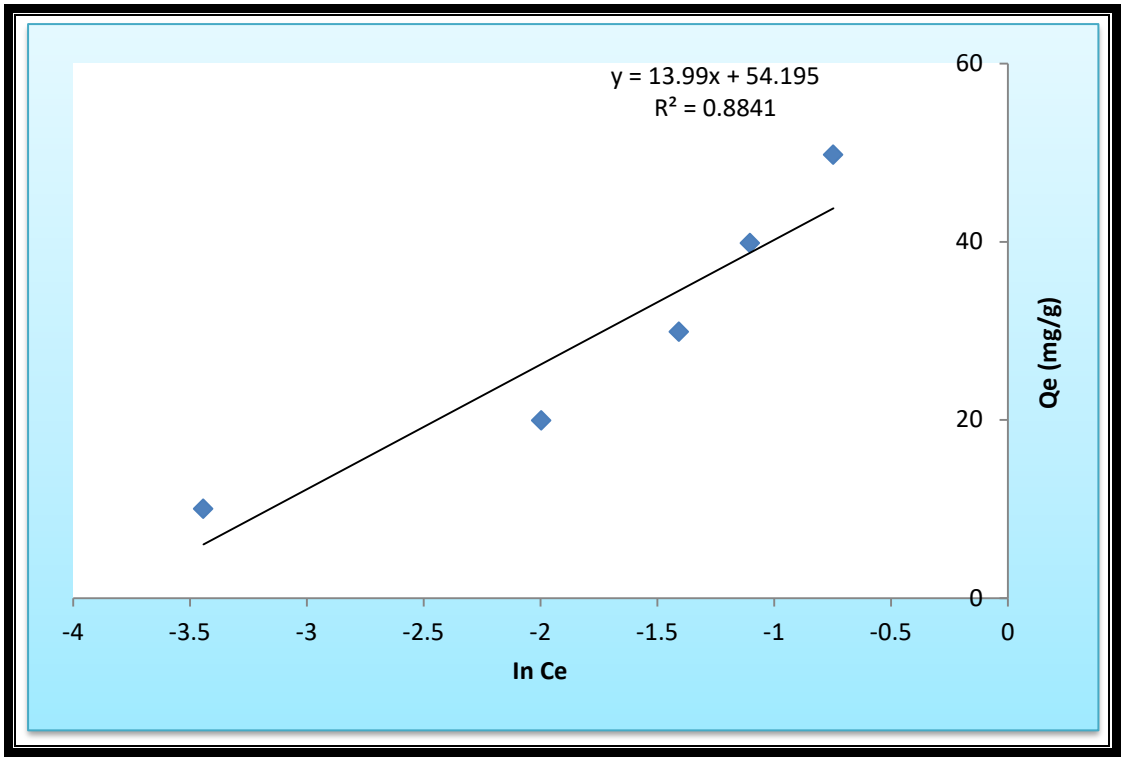

Figure (3.31): Temkin isotherm of Cd (II) ions removal in single system adsorption on (CoMo/ γ.Al_2O_3) surface at various initial concentrations.

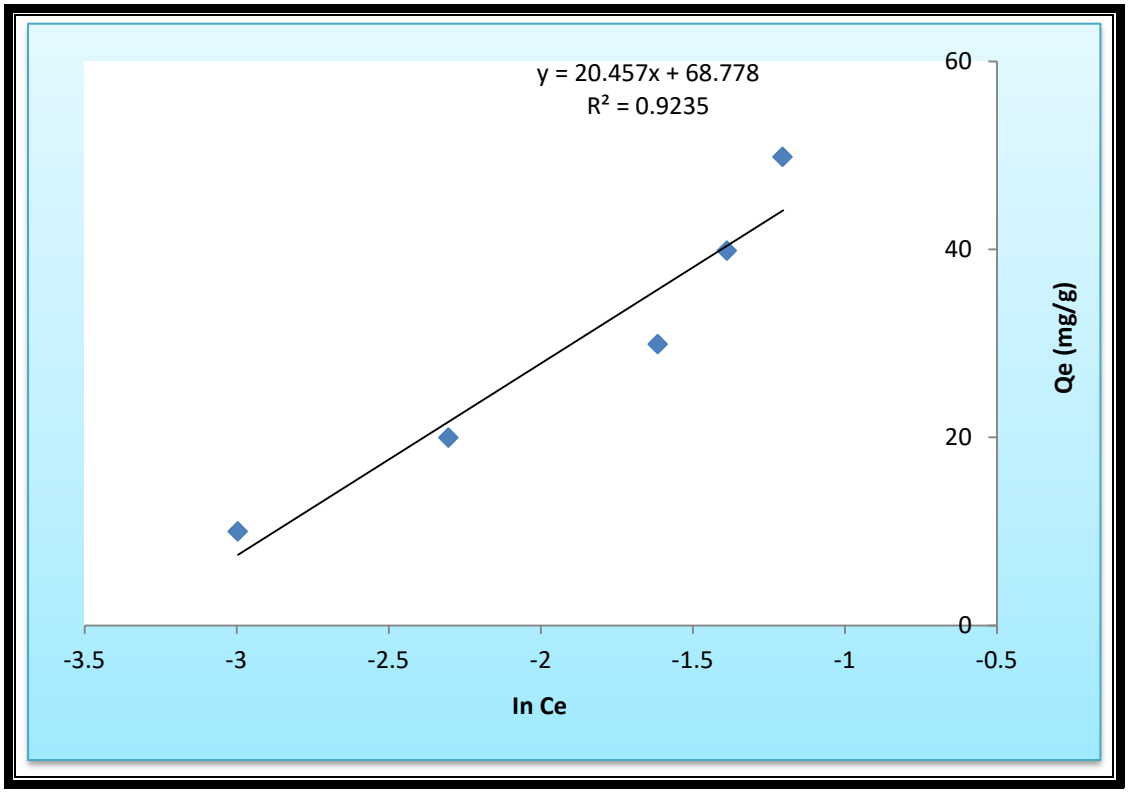

Figure (3.32): Temkin isotherm of Cu (II) ions removal in single system adsorption on (CoMo/ γ.Al_2O_3) surface at various initial concentrations.

Table (3.19): Langmuir, Freundlich and Temkin constants for the adsorption of Cd (II) and Cu (II) ions in single system with (CoMo/ γ.Al_2O_3).

Models & Metals	CoMo/γ.Al_2O_3		
Langmuir	a (mg/g)	b (L/g)	R^2
Cd (II)	77.519	3.225	0.830
Cu (II)	181.818	1.145	0.936
Freundlich	n	K_f (mg/g)	R^2
Cd (II)	1.68	73.097	0.98
Cu (II)	1.186	129.419	0.9877
Temkin	A_t (L/g)	B_t (J/mole)	R^2
Cd (II)	48.140	13.991	0.884
Cu (II)	28.847	20.459	0.923

Table (3.19) include adsorption data Cd (II) and Cu (II) on the nano catalyst (CoMo/ γ.Al_2O_3) of Langmuir and Freundlich and Temkin constants the removal of Cd (II) ions and Cu (II) ions on surface fit well with Freundlich isotherm and this is because the adsorption take place on hertrogeneous sites with different distribution of energy levels [19, 10].

3.3.2. The adsorption isotherm of binary metal ions systems

The adsorption isotherm studies of cadmium (II) and copper (II) (binary systems) from an aqueous solution on (CoMo/ γ.Al_2O_3) at ideal condition mentioned in the Tables (3.17).

The results are represented by initial concentration (C) of (Cd and Cu ions), and equilibrium concentration (C) measured at equilibrium state and values adsorption capacity (Q) are calculated from the experimental data by using equation (2.2). The adsorption capacity (Q) are plotted versus equilibrium concentration to obtain general adsorption isotherm for Cd (II) ions removal by using (CoMo/γ.Al_2O_3), with initial concentration varies (20, 40, 60, 80 and 100) mg/L at presence of Cu (II)

with a constant initial concentration in each experimental ranges (20, 40, 60, 80, and 100) mg/L, as shown in Tables (3.20) to (3.24) and Figures (3.33) and (3.34), and the general adsorption isotherm of Cu (II) ions removal by using ($CoMo/\gamma.Al_2O_3$), 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 (3.20) to (3.24) and Figures (3.33) and (3.34).

Table (3.20): Adsorption parameters values of Cd (II) ions removal in the presence (Cu) = 20 mg/L constant and values of Cu (II) ions in the presence (Cd) = 20 mg/L constant by ($CoMo/\gamma.Al_2O_3$) surfaces at ideal condition.

Metals	C_0 (mg/L)	$CoMo/\gamma.Al_2O_3$					
		C_e (mg/L)	Q_e (mg/g)	log Ce (mg/L)	log Q_e (mg/g)	In C_e (g/L)	C_e / Q_e (g/L)
Cd (II) ions	20	0.055	9.972	-1.259	0.998	-2.900	0. 005
	40	0.139	19.930	-0.856	1.299	-1.973	0.006
	60	0.247	29.876	-0.607	1.475	-1.398	0.008
	80	0.403	39.798	-0.394	1.599	-0.908	0.010
	100	0.532	49.734	-0.274	1.696	-0.631	0.010
Cu (II) ions	20	0.028	9.986	-1.552	0.999	-3.575	0.002
	40	0.123	19.938	-0.910	1.299	-2.095	0.006
	60	0.202	29.899	-0.694	1.475	-1.599	0.006
	80	0.294	39.853	-0.531	1.600	-1.224	0.007
	100	0.379	49.810	-0.421	1.697	0.970	0.007

Table (3.21): Adsorption parameters values of Cd (II) ions removal in the presence (Cu) = 40 mg/L constant and values of Cu (II) ions in the presence (Cd) = 40 mg/L constant by (CoMo/γ.Al_2O_3) surfaces at ideal condition.

Metals	C_0 (mg/L)	CoMo /γ.Al_2O_3					
		C_e (mg/L)	Q_e (mg/g)	log Ce (mg/L)	log Q_e (mg/g)	In C_e (g/L)	C_e / Q_e (g/L)
Cd (II) ions	20	0.065	9.967	-1.187	0.998	-2.733	0.006
	40	0.141	19.929	-0.85	1.299	-1.958	0.007
	60	0.258	29.871	-0.588	1.475	-1.354	0.008
	80	0.433	39.783	-0.363	1.599	-0.837	0.01
	100	0.545	49.727	-0.263	1.696	-0.606	0.01
Cu (II) ions	20	0.038	9.981	-1.420	0.999	-3.270	0.003
	40	0.133	19.933	-0.876	1.299	-2.017	0.006
	60	0.247	29.876	-0.607	1.475	-1.398	0.008
	80	0.334	39.833	-0.476	1.600	-1.096	0.008
	100	0.516	49.742	-0.287	1.696	-0.661	0.010

Table (3.22): Adsorption parameters values of Cd (II) ions removal in the presence (Cu) = 60 mg/L constant and values of Cu (II) ions in the presence (Cd) = 60 mg/L constant by (CoMo/γ.Al_2O_3) surfaces at ideal condition.

Metals	C_0 (mg/L)	CoMo /γ.Al_2O_3					
		C_e (mg/L)	Q_e (mg/g)	log Ce (mg/L)	log Q_e (mg/g)	In C_e (g/L)	C_e / Q_e (g/L)
Cd (II) ions	20	0.076	9.962	-1.119	0.998	-2.577	0.007
	40	0.141	19.933	-0.850	1.299	-1.958	0.007
	60	0.258	29.876	-0.588	1.475	-1.354	0.008
	80	0.433	39.833	-0.363	1.600	-0.837	0.010
	100	0.545	49.742	-0.263	1.696	-0.606	0.010
Cu (II) ions	20	0.076	9.962	-1.119	0.998	-2.577	0.007
	40	0.149	19.925	-0.826	1.299	-1.903	0.007
	60	0.256	29.872	-0.591	1.475	-1.362	0.008
	80	0.378	39.811	-0.422	1.600	-0.972	0.009
	100	0.807	49.596	-0.093	1.695	-0.214	0.016

Table (3.23): Adsorption parameters values of Cd (II) ions removal in the presence (Cu) = 80 mg/L constant and values of Cu (II) ions in the presence (Cd) = 80 mg/L constant by ($CoMo/\gamma.Al_2O_3$) surfaces at ideal condition.

Metals	C_0 (mg/L)	$CoMo/\gamma.Al_2O_3$					
		C_e (mg/L)	Q_e (mg/g)	log Ce (mg/L)	log Q_e (mg/g)	In C_e (g/L)	C_e / Q_e (g/L)
Cd (II) ions	20	0.093	9.953	-1.031	0.997	-2.375	0.009
	40	0.198	19.901	-1.703	1.298	-1.619	0.009
	60	0.301	29.849	-0.521	1.474	-1.200	0.010
	80	0.462	39.769	-0.335	1.599	-0.772	0.011
	100	0.556	49.722	-0.254	1.696	-0.586	0.011
Cu (II) ions	20	0.095	9.952	-1.022	0.997	-2.353	0.009
	40	0.191	19.905	-0.721	1.298	-1.660	0.009
	60	0.295	29.852	-0.530	1.474	-1.220	0.009
	80	0.386	39.807	-0.413	1.599	-0.951	0.009
	100	0.940	49.530	-0.026	1.694	-0.061	0.018

Table (2.24): Adsorption parameters values of Cd (II) ions removal in the presence (Cu) = 100 mg/L constant and values of Cu (II) ions in the presence (Cd) = 100 mg/L constant by ($CoMo/\gamma.Al_2O_3$) surfaces at ideal condition.

Metals	C_0 (mg/L)	$CoMo/\gamma.Al_2O_3$					
		C_e (mg/L)	Q_e (mg/g)	log Ce (mg/L)	log Q_e (mg/g)	In C_e (g/L)	C_e / Q_e (g/L)
Cd (II) ions	20	0.102	9.949	-0.991	0.997	-2.282	0.010
	40	0.214	19.893	-0.669	1.298	-1.541	0.010
	60	0.355	29.822	-0.449	1.474	-1.035	0.011
	80	0.486	39.757	-0.313	1.599	-0.721	0.012
	100	0.620	49.690	-0.207	1.696	-0.478	0.012
Cu (II) ions	20	0.105	9.947	-0.978	0.997	-2.253	0.010
	40	0.198	19.901	-0.703	1.298	-1.619	0.009
	60	0.298	29.851	-0.525	1.474	-1.210	0.009
	80	0.418	39.791	-0.378	1.599	-0.872	0.010
	100	0.965	49.517	-0.015	1.694	-0.035	0.019

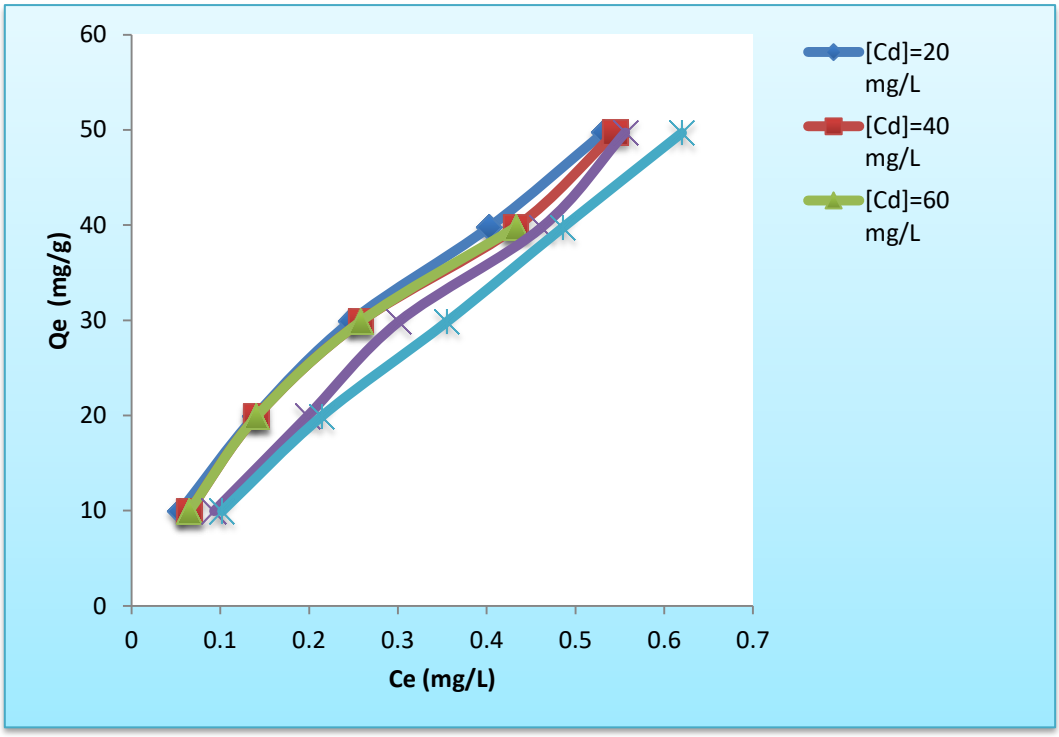

Figure (3.33): Adsorption isotherm of Cd (II) ions [C_o = 20 – 100] mg/L in the presence of increasing concentration of Cu (II) ions on (CoMo / γ.Al_2O_3) surface at ideal condition.

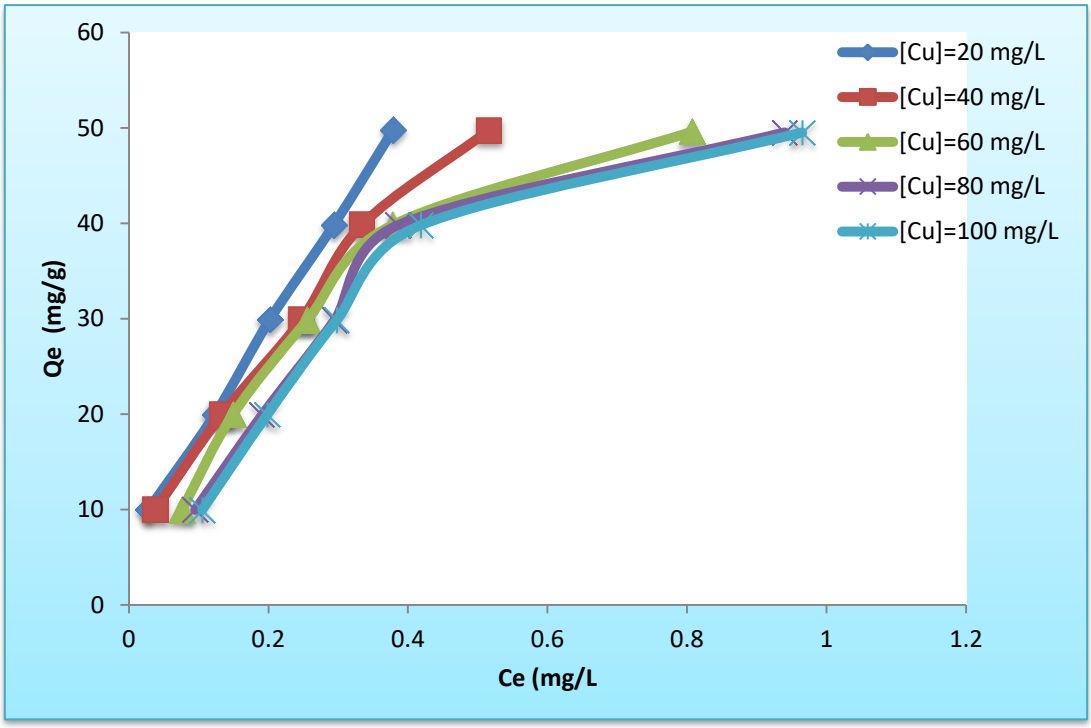

Figure (3.34): Adsorption isotherm of Cu (II) ions [C_o = 20 – 100] mg/L in the presence of increasing concentration of Cu (II) ions on (CoMo/ γ.Al_2O_3) surface at ideal condition.

The results showed an increase in adsorption capacities of the nano catalyst (CoMo/γ.Al_2O_3) with equilibrium concentration of the solution, the general shape of adsorption isotherm 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 Cu (II) ion concentration and also the observed equilibrium Cu (II) uptake increases with increasing initial Cu (II) concentration up to (100) mg/L at all Cd (II) ion concentration.

In general, the increase initial Cu (II) has non-effect on the individual adsorption yield of Cd (II) and the total adsorption yields for each experimental run and also the increase initial Cd (II) has non-effect on the individual adsorption yield of Cu (II) and the total adsorption for experiment.[91]

3.4. Thermodynamic study of binary metals ions systems

Effect of temperature on metal removal in the binary system nanoparticles were examined at different temperatures (298, 308, 318 and 333) K. This study will help to evaluate the basic thermodynamic function (free energy change ΔG (kJ/ mole), enthalpy ΔH (kJ/ mole), and entropy ΔS (J/ mole. K) for adsorption, equilibrium constant, K was explains thermodynamically by Van ’t Hoff equation given below:

$$\ln K = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \frac{\Delta S}{R} \quad \text{…….. } \mathbf{(3.1)}$$

The equilibrium constant, K were calculated at any temperature by equation[94]:

$$K = \frac{Qe\ m\ (g)}{Ce\ V\ (L)} \quad \text{…… } \mathbf{(3.2)}$$

Where:

Q_e: The adsorption capacity of metals ion, (mg/g).

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

C_e: The concentration equilibrium after removal of metals in binary system, (mg/L).

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

Table 3.22 illustrates (K) values for adsorption of Cd (II) and Cu (II) ions in binary system on (CoMo/ $\gamma.Al_2O_3$) at various temperatures.

Gibes free energy change can be calculated from relationship: [46, 20]

$$\Delta G° = -RT \ln k \ldots\ldots\ldots \textbf{(3.3)}$$

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 of the enthalpy change **(ΔH)** and entropy change **(ΔS)** can be calculated from the slope and intercept at drawing **(lnK)** versus **(1/T)** **[**9, 88], as shown figures (3.35), and explain in below equations:

$$\text{Slope} = -\Delta H/R \ldots\ldots\ldots \textbf{(3.4)}$$

$$\text{Intercept} = \Delta S/R \ldots\ldots \textbf{(3.5)}$$

A decrease in the amount of cadmium and copper ion absorption was observed with increasing temperature. Table (3.26) presents the thermodynamic value of Cd (II) and Cu (II) ion removal on (CoMo/ $\gamma.Al_2O_3$).

Table (3.25): Effect of temperature on thermodynamic equilibrium constant for the adsorption of Cd (II) and Cu (II) ions in binary system on (CoMo/ γ.Al_2O_3) surfaces.

Surface	Metals	Temperature (K)	1000/T, K^{-1}	Ce(mg/L)	Qe(mg/g)	K	ln K
CoMo/γ.Al_2O_3	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
	Cu (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

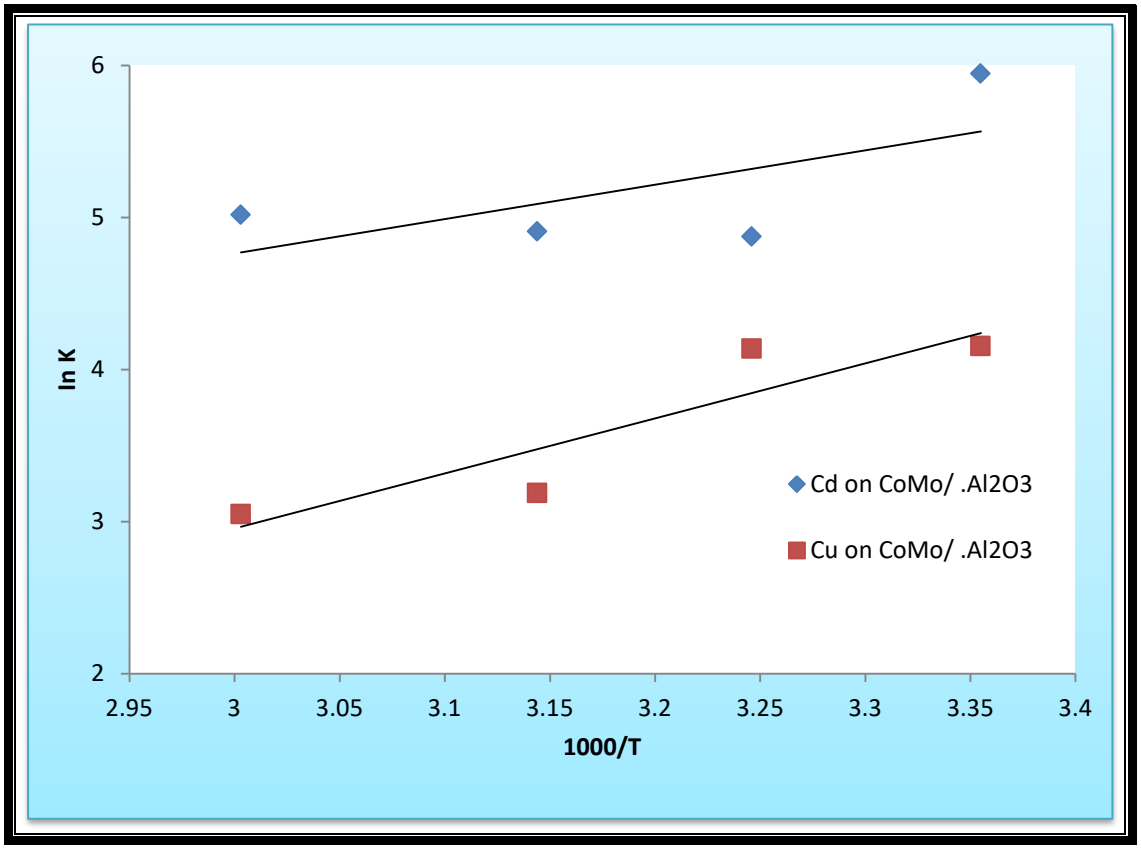

Figure (3.35): The Van ʾt Hoff Plot for adsorption of Cd (II) and Cu (II) ions in binary system on (CoMo/ γ.Al_2O_3) surface.

Table (3.26): Values of thermodynamic function for the adsorption of Cd (II) and Cu (II) ions in binary system on (CoMo/ γ.Al_2O_3) surfaces at different temperatures.

Surface	Metals	Temperature (K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol.K)
CoMo/γ.Al_2O_3	Cd (II) ions	295	- 14.730	-0.0281	- 47.397
		310	- 12.479		
		320	- 12.869		
		329	- 12.780		
	Cu (II) ions	295	- 10.290	- 0.0302	- 65.68
		310	- 10.591		
		320	- 8.430		
		339	- 8.440		

The negative ΔG value to remove the metal ion on the nano catalyst (CoMo /γ.Al_2O_3) indicated that the adsorption processes were spontaneous and that G values also can determine the rate of adsorption reaction as ΔG <0 indicated that the physisorption process is highly preferred. The rate increases with increasing ΔG. The value of ΔH was negative, suggesting that the adsorption process was exothermic, and negative ΔS indicates a decrease in randomness at the interface (solid solution) by absorbing the Cd (II) and Cu (II) ions on the nano catalyst (CoMo /γ.Al_2O_3).

3.5. Conclusions

1. Co-precipitation method is a very good method for synthesis of $\gamma.Al_2O_3$ with Nano size particle and the impregnation method is very wall to prepared $CoMo/\gamma.Al_2O_3$ Catalyst.
2. X-ray diffraction revealed that particle size obtained is at the nanometer range for both ($\gamma.Al_2O_3$) and nano catalyst ($CoMo/\gamma.Al_2O_3$) also, Atomic force Microscopy test found that the average diameter of particles of prepared nano catalyst $CoMo/\gamma.Al_2O_3$ in the same nanometer range.
3. The percentage removal of (Cd^{+2} and Cu^{+2}) in binary system reach equilibrium in contact time (15) min into nano catalyst $CoMo/\gamma.Al_2O_3$.
4. From the percentage removal (R%) of cd (II) and Cu (II) nano catalyst $CoMo/\gamma.Al_2O_3$ adsorbent at ideal condition is ($\approx$ 99%), it is also close to the percentage removal of two metals in the binary system.
5. In adsorption isotherm cd (II) on nano catalyst $CoMo/\gamma.Al_2O_3$ the Freundlich is more appropriate to describe adsorption. Removal Cu (II) on two adsorbents is best fit with Freundlich model which describe adsorption processes.
6. 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. Studying other adsorbent such as metal oxides, grapheme, Clays and Zeolites.
2. Experimenting adsorption of other heavy metals such as Zn, Mo, Hg …. etc.
3. Mathematical modeling of adsorption process and the factors and parameters effect it.
4. Using industrial waste water to study it is purifications instead of synthetically prepared aqueous solutions.
5. Preparation the $\gamma.Al_2O_3$ by other methods like Sol. gel electrochemical …. etc.
6. Studying of kinetics on Cadmium (II) and copper (II) ions in binary system into nano catalyst $CoMo/\gamma.Al_2O_3$ nanoparticles.
7. Calculation the removal percentage of Cadmium (II) and Copper (II) in binary system into nano catalyst $CoMo/\gamma.Al_2O_3$ Nano particles at temperature below 298K.

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وزارة التعليم العالي والبحث العلمي
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كليـــــــة العلوم
قسم الكيميـــــــاء

امتزاز أيونات Cd(II) و Cu(II) على المحفز النانوي $CoMo/\gamma.Al_2O_3$ في أنظمة أحادية وثنائية

رسالة مقدمة الى

مجلس كلية العلوم / جامعة ديالى

وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قبل الطالبة

إيثار ناشيء جواد

بكالوريوس في علوم الكيمياء

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المخلص

في هذا البحث تم تحضير الألومينا ($\gamma.Al_2O_3$) كحامل باستخدام طريقة (الترسيب) من سداسي هيدرات كلوريد الألمنيوم (كمصدر للألمنيوم) والكلسنة عند درجة حرارة 500°C بعدها تم تحضير Nano $CoMo/\gamma.Al_2O_3$ من نترات الكوبلت (كمصدر للكوبلت) ومولبيدات الأمونيوم (كمصدر للمولبيديوم) على الألومينا المحضرة.

استخدم طيف حيود الأشعة السينية (XRD) ومجهز القوة الذري لتشخيص هذه العوامل المساعدة، حيث أظهرت نتائج قياس (XRD) أن حجم الجسيمات كانت (4.33) نانومتر و(5.45) نانومتر لكل من السطحين ($CoMo/\gamma.Al_2O_3$). وتم تشخيص تركيب السطح باستخدام تقنية AFM و EDXA و FESEM.

إن تلوث المياه بالعديد من المعادن الثقيلة يشكل ضرراً كبيراً على البيئة، لذلك استخدم السطح $CoMo/\gamma.Al_2O_3$ المحضر لإزالة أيونات النحاس 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 والنحاس في النظام الثنائي والوصول إلى حالة الاتزان هو (15) دقيقة على السطح $CoMo/\gamma.Al_2O_3$.

ولقد تبين أن إزالة أيونات الكادميوم والنحاس 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 أن أفضل امتزاز لأيونات الفلزين الثقيلين على السطح المحضر كان عند الدالة الحامضية (6)، أما تأثير درجة الحرارة على امتزاز كل من الفلزين في النظام الثنائي فقد أشار أن نسبة الإزالة تقل بزيادة درجة الحرارة مما اتضح أن العملية باعثة للحرارة، وعند حساب قيم الثرموديناميكية لعملية الامتزاز (ΔG ، ΔH ، ΔS) تبين أن عملية الامتزاز هي تلقائية باعثة للحرارة، أقل عشوائية عند تداخل أيونات الفلزين الثنائية مع أكاسيد الفلزات النانوية المحضرة.