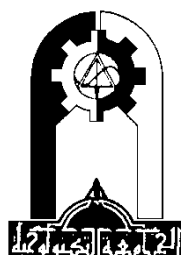


**Republic of Iraq
Ministry of Higher
Education
and Scientific Research**



**University of Technology
Department of Chemical
Engineering
Baghdad-Iraq**

Removal of Copper(II) From Wastewater Using Modified Carbon Nanotubes

**A Thesis
Submitted to the Department of Chemical Engineering
University of Technology
In a Partial Fulfillment of the
Requirements for the Degree of Master
Of Science in Chemical Engineering**

By

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**September
2012**

CERTIFICATION

This is to certify that I have read the thesis titled "***Removal of Some Heavy Metals From Water Using Modified Carbon Nanotubes***" and corrected any grammatical mistakes I found. This thesis is, therefore, qualified for debate.

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Acknowledgment

First of all, I thank God Who has given me patience, power and faith in a way that words cannot express.

*I would like to express my sincere thanks, gratitude and appreciation to my supervisors **Asst. Prof. Dr. Mohammed Ibrahim** and **Asst. Prof. Dr. Adnan A. AbdulRazak** for their kind supervision, advice, reading and criticizing the proofs of this study.*

*My respectful regards to the head of **Chemical Engineering Department** at the University of Technology **Prof. Dr. Thamer J. Mohammed** for his kind help in providing facilities.*

*My respectful regards are to all staff of **pilot plant** for their kind help in providing facilities.*

My deepest gratitude and sincere appreciation go to my beloved family for their patience and encouragement that gave me so much hopes and support that I feel short of expressing my gratitude's.

Ayad

Abstract

Carbon materials are a class of significant and widely used engineering adsorbent. As a new member of the carbon family, carbon nanotubes (CNTs) have exhibited great potentials in applications.

In the present work, carbon nanotubes were prepared by Chemical Vapor Deposition (CVD) method, Acetylene gas was used as a carbon source. In CVD system, a catalytic growth of CNTs is carried out by decomposition of Acetylene (C_2H_2) at a temperature of $750\text{ }^{\circ}C$ for one hour, Argon is used as an oxidation protection gas. The carbon nanotubes produced are purified to remove impurities such as metal catalyst and then functionalized by treating with HNO_3 .

Scanning Electron Microscopy (SEM), FT-IR spectra and BET for Surface Area measurement technique were used for characterization of CNTs. CNTs with about 30 nm in diameter and with length of several microns were obtained. The surface area of CNTs was $53\text{ m}^2/\text{gm}$. FTIR spectrum of CNTs exhibited stretching and bending vibration absorption peaks of carboxylic group at the range between 1500 to 1700 cm^{-1} while C-C bond corresponding to CNTs is clearly shown at 1554.63 cm^{-1} .

The effects of initial concentration of metal (ppm), pH, carbon nanotube (CNT) dosage (mg/L) and contact time (min) on the adsorption of Cu^{+2} ion were studied.

The results show that the pH of aqueous solution is one of the major parameters that control the adsorption of ion at the solid-water interfaces. Maximum removal percentage of Cu^{+2} species is achieved at pH 8, CNT dosage of 50 mg/L and initial concentration of 50 mg/L and it is 98.39%.

The constants of Langmuir and Freudlich models are obtained from fitting the adsorption equilibrium data. The correlation coefficients of Langmuir and Freudlich models are 0.75 and 1, respectively, indicating that the Freudlich model is more appropriate to describe the adsorption characteristics of Cu^{+2} onto CNTs.

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List of Symbols

C_0	Initial concentration	mg/ L
C_f	Final concentration	mg/ L
d_p	Outer diameter	nm
K	Langmuir constant	L/mg
K_F	Freundlich constant	$(\text{mg/g})(\text{mg/L})^{-1/n}$
M_s	Weight of adsorbent	gm
n	nano	10^{-9}m
q_t	Adsorption capacity	mg/g
q_m	Maximum adsorption capacity	mg/g
R_L	Separation factor or equilibrium constant	
R^2	Correlation coefficient	
t	Contact time	min

List of abbreviation/ nomenclature

AC	Activated Carbon
Ads	Adsorption
As	Arsenic
BET	Brunauer, Emmett and Teller
CNF	Carbon Nanofiber
CNTs	Carbon Nanotubes
CMK-3	Ordered Nanoporous Carbons
CVD	Chemical Vapor Deposition
DAF	Dissolved Air Flotation
EC	Electro Coagulation
FE-SEM	Field Emission Scanning Electron
FTIR	Fourier-Transformed Infrared Spectra
GAC	Granular Activated Carbon
Lead	Pb(II)
MWCNTs	Multi Wall Carbon Nanotubes
M-CNT	Modified Carbon Nanotube
OCMK-3	Modified Nanoporous Carbon
PAC	Particle Activated Carbon
PEG	Poly Ethylene Glycol
SEM	Scanning Electron Microscopy

List of abbreviation/ nomenclature

SWCNTs	Single Wall Carbon Nanotubes
TEM	Transmission Electron Microscope
US	Ultra-Sound

Chapter One

Introduction

1-1 General

The pollution of water resources due to the disposal of heavy metals has been causing worldwide concern. Nationally and internationally, the challenge to remedy hazardous metal-containing waste streams from present or former mining operations, industrial sites, and groundwater is immense^[1]. Metal ions such as Cu(II); Pb(II); and Cd(II), etc have been included in U.S. Environmental Protection Agency's list of priority pollutants^[2].

The main sources of these metals are mining, metallurgical and chemical manufacturing, tannery, battery manufacturing industries, fossil fuel the modern chemical industry based largely on catalysts, many of which are metals or metal compounds production of plastics, such as polyvinyl chloride, involving the use of metal compounds, particularly as heat stabilizers. The effects of heavy metals such as copper, lead, zinc, mercury, chromium and cadmium on human health have been investigated extensively and have negative effects on water resources, Cu⁺² is found as a contaminant in food , especially shell fish, liver, muslrooms and nuts^[3].The maximum contaminant level goals for copper are 1.3 mg/ L^[4] .

Several methods have been applied over the years for the elimination of metal ions in industrial waste waters. The traditional methods commonly used for the removal of heavy metal ions from aqueous solutions include ion-exchange, solvent extraction, chemical precipitation, phytoextraction, ultrafiltration, reverse osmosis, electrodialysis and adsorption^[5].

Carbon nanotubes (CNTs) have come under intense multidisciplinary study because of their unique physical and chemical properties. They have been used as an adsorbent for hydrogen and other gases due to their highly porous and hollow structure, large specific surface area, light mass density and strong interaction between carbon and hydrogen molecules. Carbon nanotubes (CNTs) modified with chemical treatment are relatively new adsorbents that have proven very efficient for treating many kinds of trace pollutants such as copper and cadmium^[6].

1-2 Objective

The main purpose of the present study is to prepare CNTs by CVD technique, functionalization of CNTs and use the CNTs to remove the Cu^{+2} ions from wastewater as raw. It also provides the adsorption conditions in term of various system parameters such as initial concentration, pH, contact time and CNTs dosage. The study also aims to evaluate the adsorption isotherm of the experimental data.

Chapter Two

Theoretical and Literature Survey

2-1 Introduction

Since Ijima's original report, carbon nanotubes have been recognized as fascinating materials with nanometer dimensions promising exciting new areas of carbon chemistry and physics^[7].

The past decade witnessed significant progress in carbon nanotube synthesis, as well as the investigations in to their electrical, mechanical, optical, and chemical properties.

Carbon nanotubes (CNTs), including single walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) distinguished by their number of layers, have been the research focus due to their unique 1-dimensional structures, exceptional mechanical properties, excellent electronic properties and potential applications. Besides the possibility of making advanced composites^[8].

2-2 Structure of Carbon Nanotube

Many exotic structures of fullerenes exist: regular spheres, cones, tubes and also more complicated and strange shapes. Single Walled Nanotubes (SWNT) Fig.(2.1), can be considered as long wrapped graphene sheets. nanotubes generally have a length to diameter ratio of about 1000 so they can be considered as nearly one-dimensional structures.

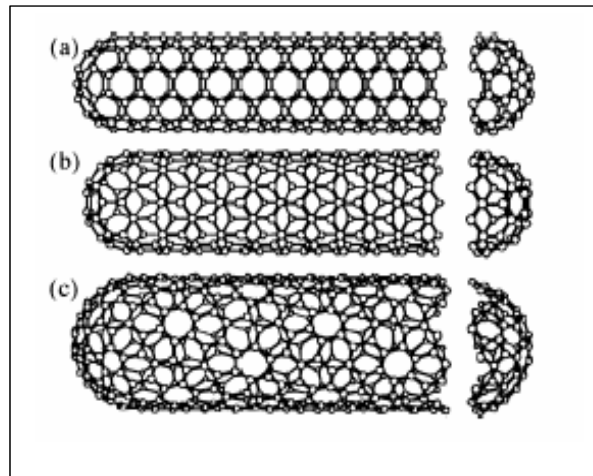


Figure (2.1): Some SWNTs with different chiralities. The difference in structure is easily shown at the open end of the tubes. a) armchair structure b) zigzag structure c) chiral structure^[9].

Multi walled nanotubes (MWNT) can be considered as a collection of concentric SWNTs with different diameters. The length and diameter of these structures differ a lot from those of SWNTs and, of course, their properties are also very different, Fig.(2.2).

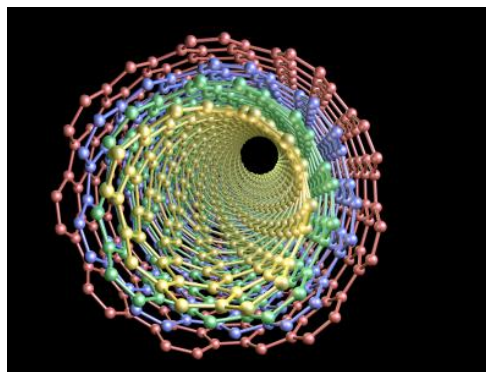


Figure (2.2): Structures of MWNTs^[9].

Carbon nanotubes may be viewed as a cylindrical structure formed from graphene sheets and closed by Fullerenoid end-caps. There are single wall carbon nanotubes and multiwall carbon nanotubes, consisting of several nested co-axial single wall tubules. Typical dimensions of multiwall nanotubes are: outer diameter, 2-20 nm, inner diameter, 1-3 nm, lengths $\sim 1 \mu\text{m}$ ^[10].

2-3 Growth Mechanism

The way in which nanotubes are formed is not exactly known. The growth mechanism is still a subject of controversy, and more than one mechanism might be operative during the formation of CNTs. One of the mechanisms consists of these steps:-

1. First a precursor to the formation of nanotubes and fullerenes, is formed on the surface of the metal catalyst particle, from this met stable carbide particle, a rod like carbon is formed rapidly.
2. Secondly there is a slow graphitization of its wall. This mechanism is based on TEM(Transmission Electron Microscope) observations.

The actual growth of the nanotube seems to be the same for all techniques mentioned Fig.(2.3). There are several theories on the exact growth mechanism for nanotubes. One theory postulates that metal catalyst particles are floating or are supported on graphite or another substrate. It presumes that the catalyst particles are spherical or pear-shaped.

The carbon diffuses along the concentration gradient and precipitates on the opposite half, around and below the bisecting diameter^[11].

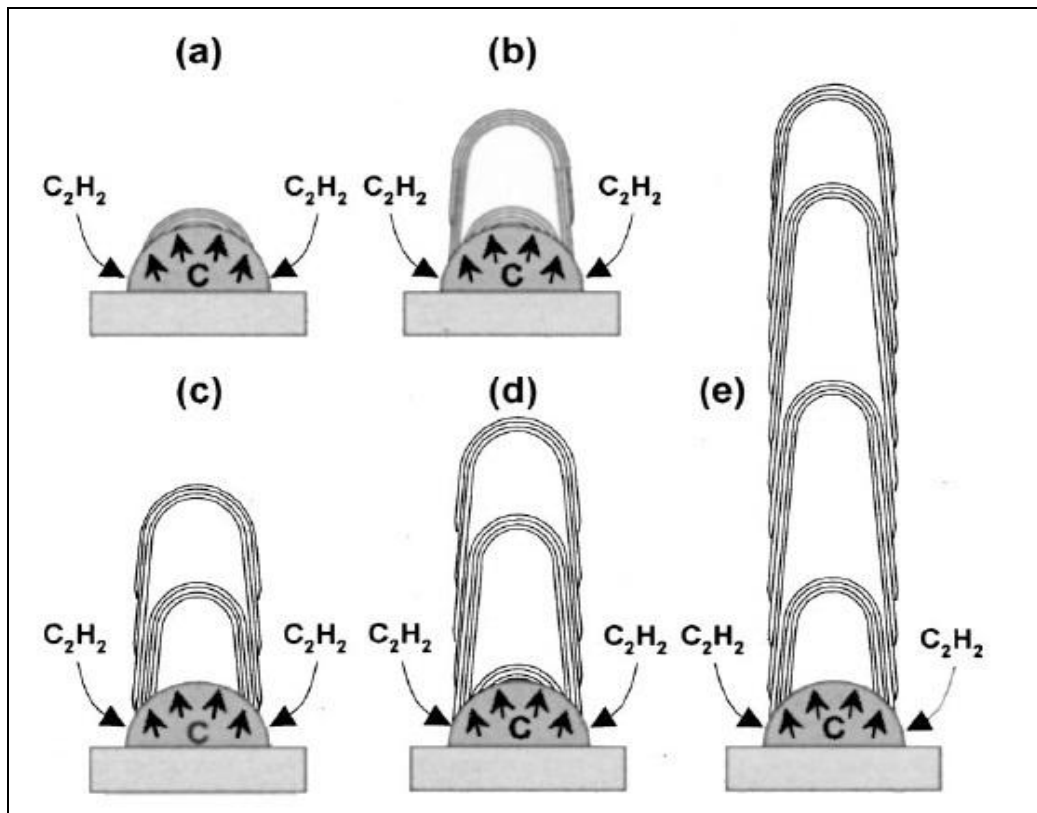


Figure (2.3): Explaining of a possible carbon nanotube growth mechanism^[11].

2-4 Carbon Nanotube Preparation

There are several basic methods by which carbon nanotubes are made. Scientists can make modifications to each technique to suit their specific research purpose.

2-4-1 Arc Discharge

The arc discharge CNT synthesis method relies upon the vaporization of carbon in the presence of catalyst (iron, nickel, cobalt, molybdenum) while under a vacuum of inert gas such as Argon or Helium. The vital components inside of an electric arc chamber are the two graphite rods that provide the arc necessary for synthesis. After creating an arc between these two rods, plasma is formed consisting of a mixture of carbon vapor, catalyst vapor and the inert gas.

The two millimeter diameter rods are spaced a few millimeters apart as shown in Fig.(2.4) and typical arc power settings are an arc current of 80 amps and a generating voltage of 60 kilovolts. The discharge vaporizes one of the carbon rods and forms a small rod shaped deposit on the other rod. Producing nanotubes in high yield depends on the uniformity of the plasma arc and the temperature of the deposit form on the carbon electrode.

Depending on the exact technique, it is possible to selectively grow SWNTs or MWNTs. Two distinct methods of synthesis can be performed with the arc discharge apparatus^[12].

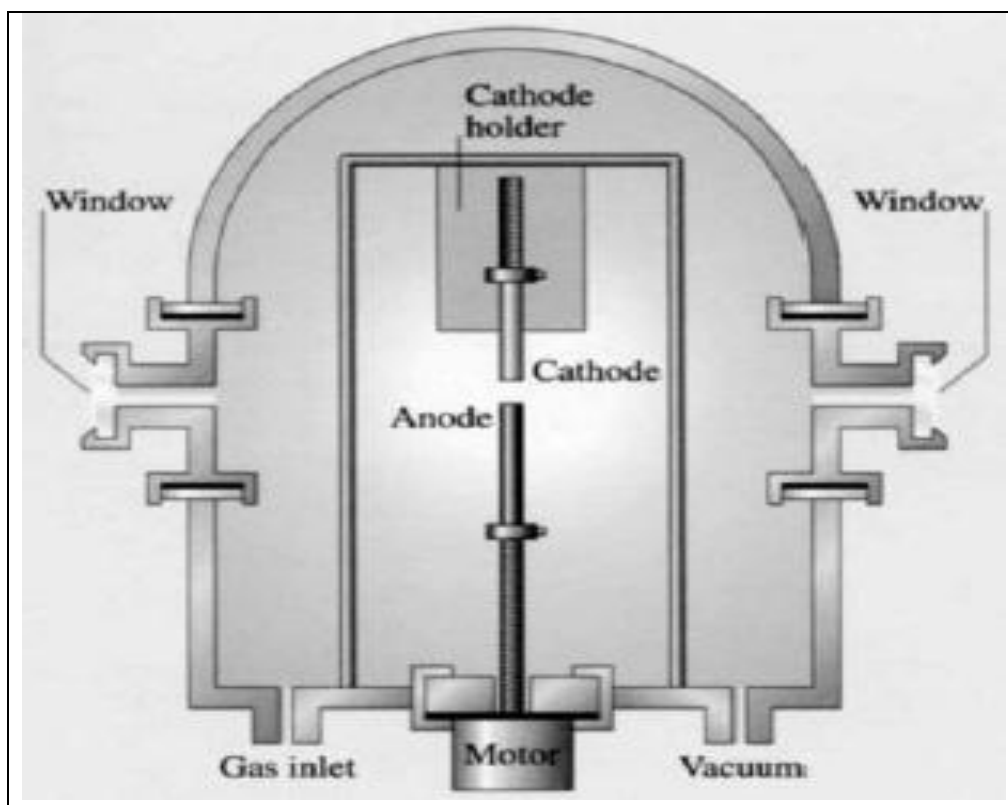
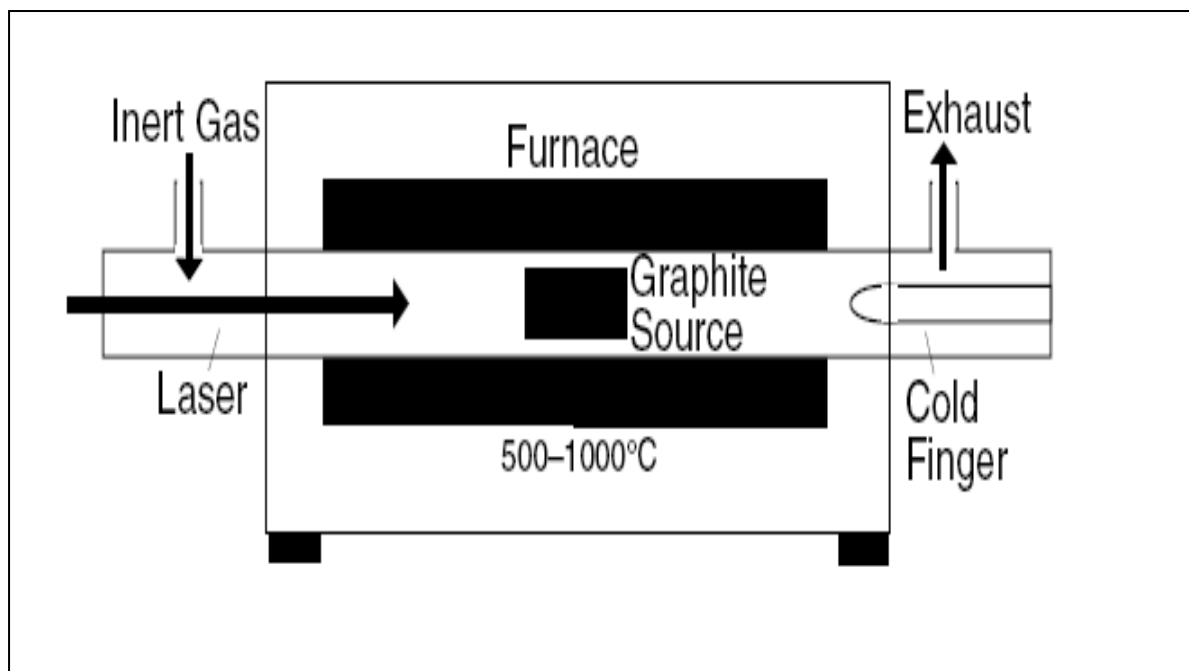


Figure (2.4): Arc discharge synthesis chamber^[12].

2-4-2 Laser Ablation

The laser ablation technique uses a 1.2 % of cobalt/nickel with 98.8% of graphite composite target that is placed in a 1200°C quartz tube furnace with an inert atmosphere of ~500 Torr of Ar or He and vaporized with a laser pulse. A pulsed- or continuous-wave laser can be used. Nanometer-size metal catalyst particles are formed in the plume of vaporized graphite. The metal particles catalyze the growth of SWCNTs in the plasma plume, but many by-products are formed at the same time. In principle, arc discharge and laser ablation are similar methods, as both use a metal-impregnated graphite target (or anode) to produce SWCNTs, and both produce MWCNT when pure graphite is used instead. The diameter distribution of CNTs made by this method is roughly between 1.0 and 1.6 nm^[13], shown in Fig.(2.5)



Figure(2.5): Schematic of a laser ablation furnace^[13].

2-4-3 Chemical Vapor Deposition

Chemical Vapor Deposition (CVD) technique is shown in Fig.(2.6), chemical reactions occur, which involve transforming gaseous molecules, called precursor, into a solid material on the surface of a substrate such as Al_2O_3 . CVD is a very versatile crystal growth process. The products by CVD can be in different forms: coatings, powders and fibers. With this method, it is possible to produce almost any metallic or non-metallic elements, including carbon and silicon, as well as compounds such as carbides, nitrides, borides, oxides and many others^[14].

Chemical Vapor Deposition (CVD) is a method of choice to produce thin and high quality films with precise chemical composition and structural uniformity. The optimization of the CVD process conditions (eg. pressure, temperature, precursors and reactor configuration) for better control of the film growth rate, uniformity and composition can be achieved using reactor scale models. Such models in turn require detailed understanding of the deposition chemistry, which can be achieved experimentally^[15].

CVD carbon nanotube synthesis is essentially a two-step process consisting of a catalyst preparation step followed by the actual synthesis of the nanotube. The catalyst is generally prepared by sputtering a transition metal onto a substrate and then using thermal annealing to induce catalyst particle nucleation. Thermal annealing results in cluster formation on the substrate, from which the nanotubes will grow. The temperatures for the synthesis of nanotubes by CVD are generally within the 650–900 °C range. Typical yields for CVD are approximately 30%.

Recently a new form of carbon nanocoil has been achieved by Mohamed Ibrahim^[16]. using modified CVD technique, the yield CNTs is increased by a factor of two when a cylindrical grid is introduced through the reactor.

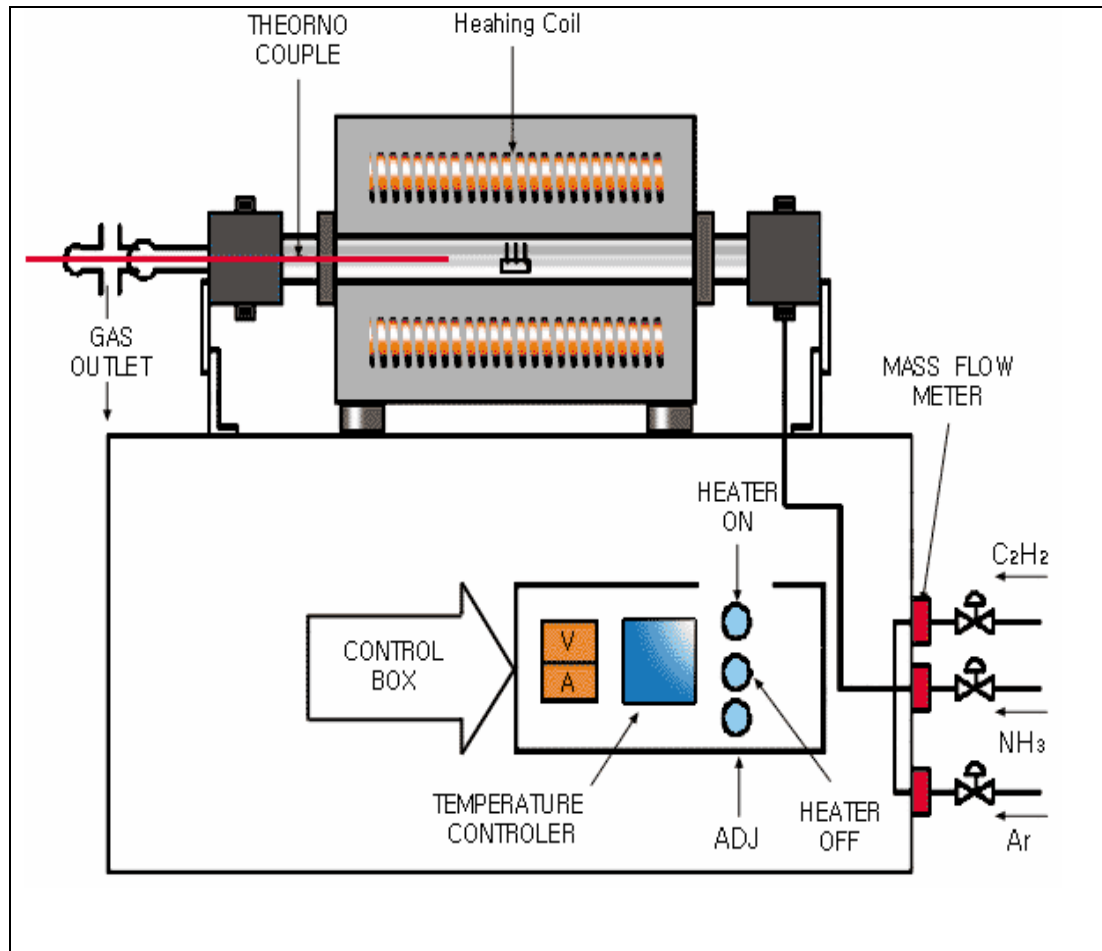


Figure (2.6): Schematic drawing of a chemical vapor deposition^[17].

In recent years, different techniques for the carbon nanotubes synthesis with CVD have been developed, thermal chemical CVD, alcohol catalytic CVD, vapor phase growth, and laser assisted CVD^[17].

2-5 Carbon Nanotube Purification

For the physico-chemical measurements and practical utilization in some cases the purification of nanotubes is necessary. In particular case, purification means the separation of filaments from the substrate-silica support. The carbon-containing catalyst was treated by ultra-sound (US) in acetone under different conditions. The power of US treatment, and the time and regime (constant or pulsed), were varied. Even the weakest treatments made it possible to extract the nanotubes from the catalyst. With the increase in the time the power of treatment increased the amount extracted.

The quantity of carbon species separated from the substrate was no more than 10% from all deposited carbon after the most powerful treatment. Moreover, the increase power led to the partial destruction of silica grains, which were then extracted with the tubules. As a result, even in the optimal conditions the final product was never completely free of silica^[17].

For better purification, the tubule-containing catalyst was treated with HF (40%) for 72 hours. The resulting extract was purer than that obtained after US treatment. The addition of nitric acid also makes it possible to free the tubules of metal particles on the external surface. The conditions of the acid treatment and tubule extraction have yet to be optimized^[18].

2-6 Carbon Nanotube Functionalization

Functionalization of nanotubes with other chemical groups on the sidewall may help modify the properties required for the application in hand. For example, chemical modification of the sidewalls may improve the adhesion characteristics of nanotubes in a host polymer matrix to make functional composites. Functionalization of the nanotube ends can lead to useful chemical sensors and biosensors^[19].

The purification and functionalization of prepared multiwall carbon nanotubes were treated with boiling concentrated HNO_3 under a reflux condenser for about 50 hour at $120 \pm ^\circ\text{C}$ in order to purify and oxidize the raw material. The oxidized multiwall carbon nanotubes were rinsed with deionized water until stabilization of the filtrate $\text{pH}^{[20]}$, as shown Fig.(2.7).

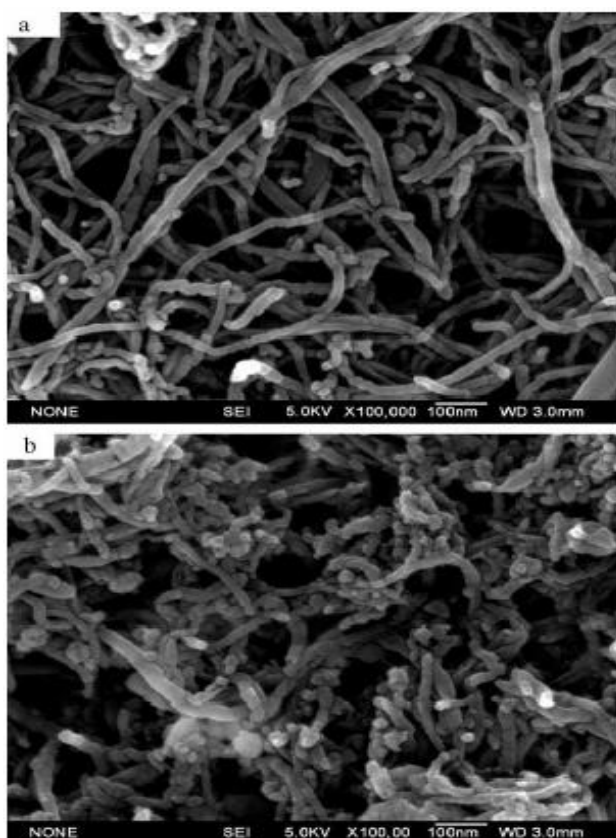


Figure (2.7): SEM images of (a) normal CNTs and (b) activated CNTs^[20]

2-6-1 CNT Oxidation and Carboxyl-Based Couplings

The oxidative introduce carboxyl groups represent useful sites further modifications, as they enable the covalent coupling of molecules through the creation of amide and ester bonds, Fig.(2.8)^[21].

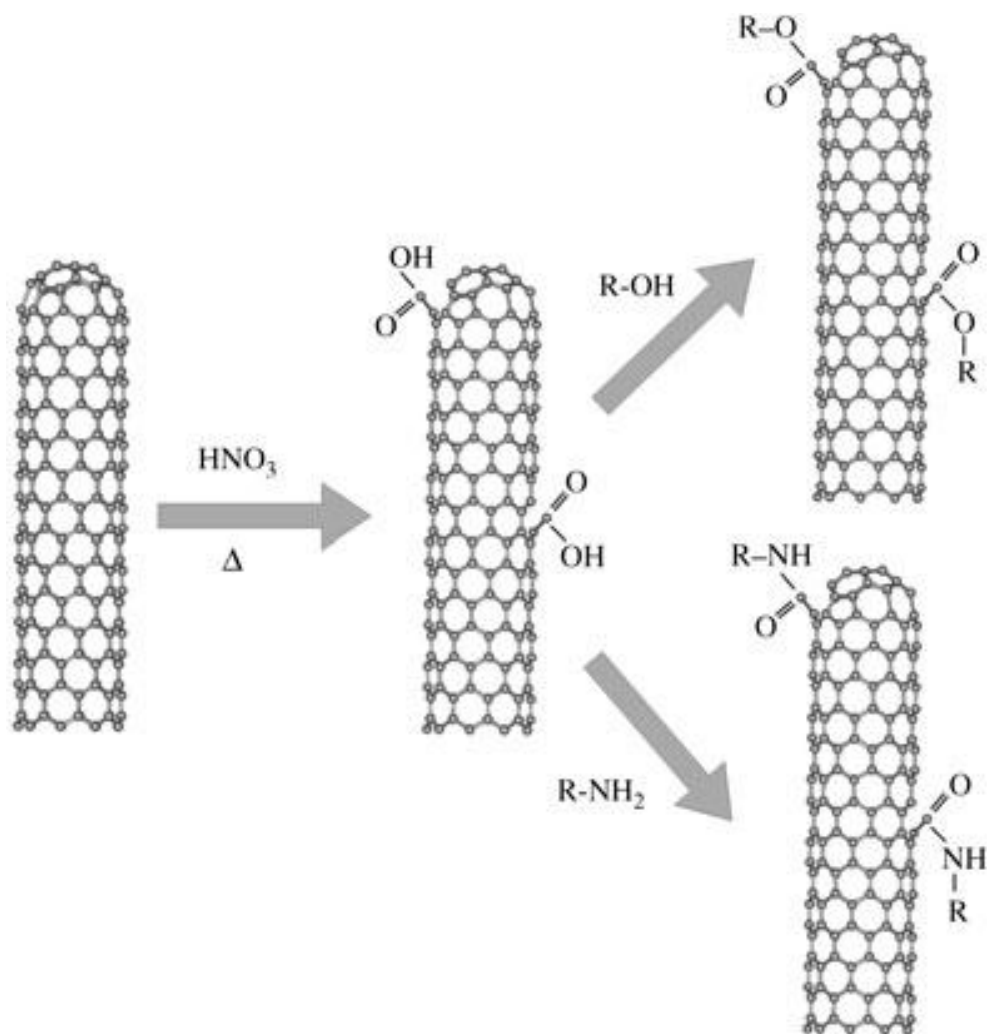


Figure (2.8). Chemical modification of nanotubes through thermal oxidation, followed by subsequent carboxyl groups^[21].

The presence of (modified) carboxyl groups leads to a reduction in Van der Waals interactions between the CNTs, which strongly facilitates the separation of nanotube bundles into individual tubes. Additionally, the attachment of suitable groups renders the tubes soluble in aqueous or organic solvents, opening the possibility for further modifications through subsequent solution-based chemistry.

A high water solubility of a few tenths of a gram per milliliter has recently been achieved on the basis of the carboxyl-based coupling of hydrophilic polymers such as poly ethylene glycol (PEG). SWCNTs with a good solubility in organic solvents which can be obtained by covalent^[22].

2-6-2 Addition Reactions at the Sidewall

While the two-step functionalization of nanotubes through the oxidative introduction of carboxyl groups followed by the formation of amide or ester linkages does allow for a stable chemical modification, it has only a relatively weak influence on the electrical and mechanical properties of the nanotubes. By comparison, addition reactions enable the direct coupling of functional groups onto the conjugated carbon framework of the tubes.

The required reactive species (atoms, radicals, carbenes, or nitrenes) are in general made available through thermally activated reactions, and small-diameter tubes are preferred as they show higher chemical reactivity^[20].

A series of addition reactions have been well documented, the most important of which are listed in Fig.(2.9).

While in the initial experiments, it was found that at addition reactions at the sidewall only one to three functional groups were found per 100 carbon atoms, the procedures developed more recently have reached functionalization degrees of at least 10%^[23].

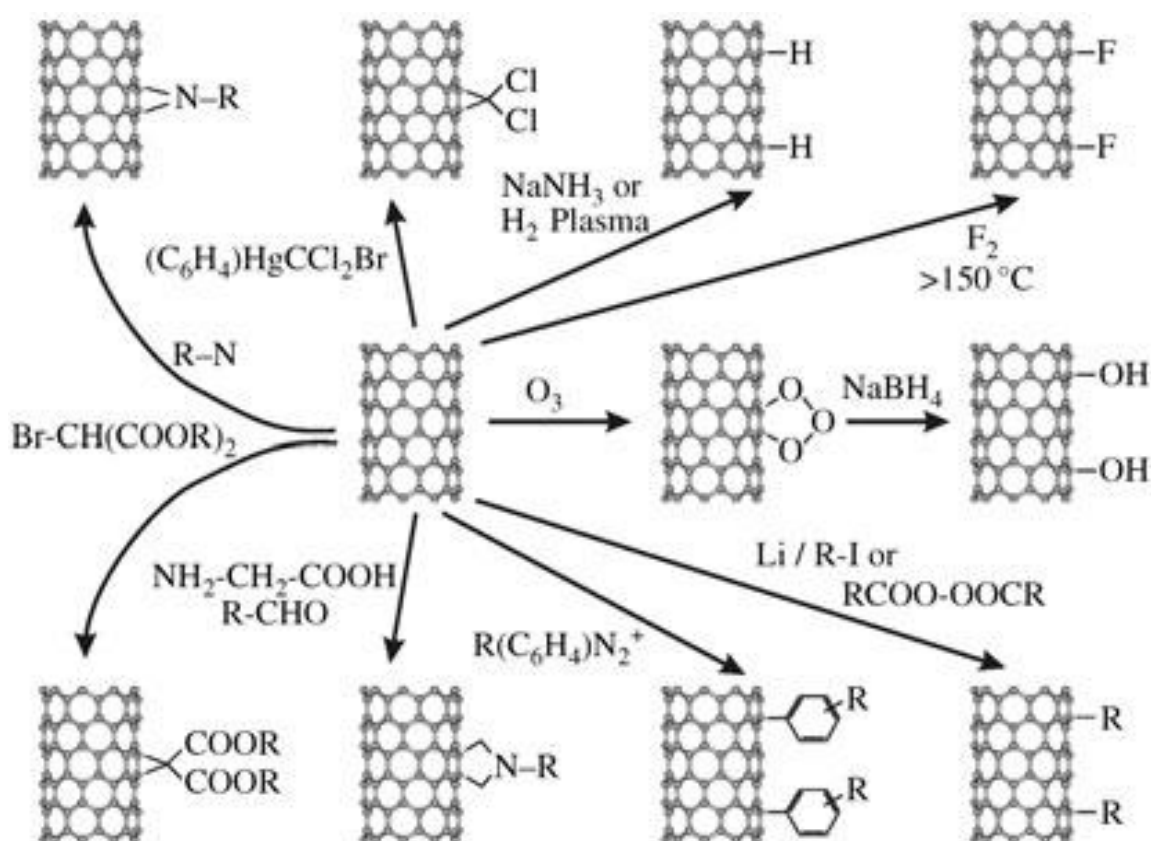


Figure (2.9). Overview of possible addition reactions for the functionalization of the nanotube sidewall^[23].

In principle, the addition reaction could be initiated exclusively on the intact sidewall, or in parallel at defect sites from where the reaction could proceed further.

Analogous to nanotube functionalization with carboxyl groups, the direct covalent attachment of functional moieties to the sidewalls strongly enhances the solubility of the nanotubes. The good solubility of nanotubes modified with organic groups has been exploited for their effective purification. In this procedure, small particles are first separated from the solution through chromatography or filtration, and then the covalently attached groups are removed through thermal annealing ($T > 250\text{ }^{\circ}\text{C}$)^[24].

2-6-3 Substitution Reactions on Fluorinated Nanotubes

The fluorine atoms in fluorinated carbon nanotubes can be replaced through substitution reactions for providing the sidewalls with various types of functional groups, as illustrated in Fig.(2.10). Which have resulted in up to 15% of the carbon atoms of the sidewall bearing a functional group. The nanotubes can be covalently cross-linked with each other^[25].

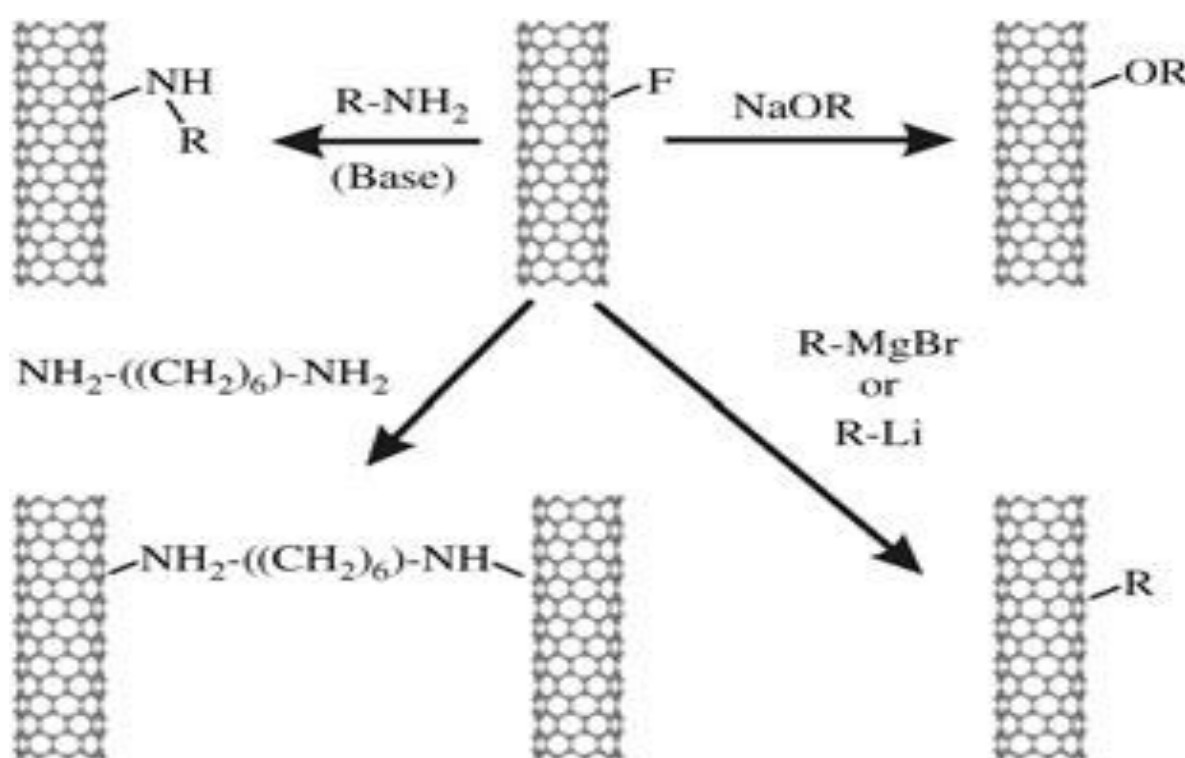


Figure (2.10). Functionalization of the sidewall substitution reactions in fluorinated nanotubes^[26].

2-7 Application of Carbon Nanotubes

The remarkable properties of carbon nanotubes have attracted the attention of researchers. Their low density, high strength, electrical and thermal conductive properties bring up the possibility of a novel structure with CNTs which possess extraordinary properties.

The following are some of the most significant applications of carbon nanotubes:

- 1- High performance nanocomposites
- 2- Nano- filters
- 3- Nanotube based field emit
- 4- Nanocables for nanoelectronics
- 5- Fuel cell applications
- 6- Probes for Atomic Force Microscope and sensors
- 7- Nanotube based transistors
- 8- Vessel for drug delivery
- 9- Superconductors
- 10- Nanotube based coating materials for corrosion protection
- 11- Nanostructure films for X-ray sources and gas discharge tubes.

Recent improvements in the synthesis and processing of nanotubes have made the practical application of nanotubes a reality. Structural and electrical application have generated the most interest^[27].

2-8 Wastewater Treatment Plant Operations

Wastewater treatment plants can be divided into two major types: chemical, biological and physical types. Biological plants are more commonly used to treat domestic or combined domestic and industrial wastewater from a municipality. They use basically the same processes that would occur naturally in the receiving water, but give them a place to happen under controlled conditions, so that the cleansing reactions are completed before the water is discharged into the environment^[28].

Treatment of wastewater produced by an industry takes place in a plant purposely built in the area of production, or after transport in the sewage system by purpose-built structures within the urban waste treatment plant. Moreover, treatment carried out within the area of production can confer those characteristics on the industrial waste that allow it to be deposited directly into the formal receiver, or even used again, either completely or partially, in the productive cycle, hence giving the wastewater the necessary qualities for its discharge into the public sewage system.

The treatment of industrial wastewater involves the same processes as those used in the treatment of domestic water. However, because of specific compositions, the systems tend to vary. The chemo-physical type processes are especially important for the removal of inorganic matter. The basic processes used are:

- Neutralization
- The reduction and oxidation of inorganic compounds (such as chromic salt, chromates) and also of organics.
- The precipitation of cations and anions in the form of insoluble compounds, such as the precipitation of metals, as hydroxides, and chromates^[29].

The dissolved and suspended solids in wastewater contain organic and inorganic material. Organic matter may include carbohydrates, fats, oils, grease, surfactants, proteins, pesticides and other agricultural chemicals, volatile organic compounds, and other toxic chemicals. Inorganic may include heavy metals, nutrients (nitrogen and phosphorus), pH, alkalinity, chlorides, sulfur, and other inorganic pollutants. Gases such as carbon dioxide, nitrogen, oxygen, hydrogen sulfide, and methane may be present in a wastewater. Several methods have been developed for decontamination of municipal and industrial waters and wastewaters. Among different heavy metal removal methods^[30].

2-9 Wastewater Treatment Systems

2-9-1 Preliminary Treatment Systems

Preliminary systems are designed to physically remove or cut up the larger suspended and floating materials, and to remove the heavy inorganic solids and excessive amounts of oil and grease. The purpose of preliminary treatment is to protect pumping equipment and the subsequent treatment units. Preliminary systems consist of flow measurement devices and regulators (flow equalization), racks, and screens, comminuting devices(grinders, cutters and (possibly) chlorination. The quality of wastewater is not substantially improved by preliminary treatment^[31],as shown in Fig.(2.11).

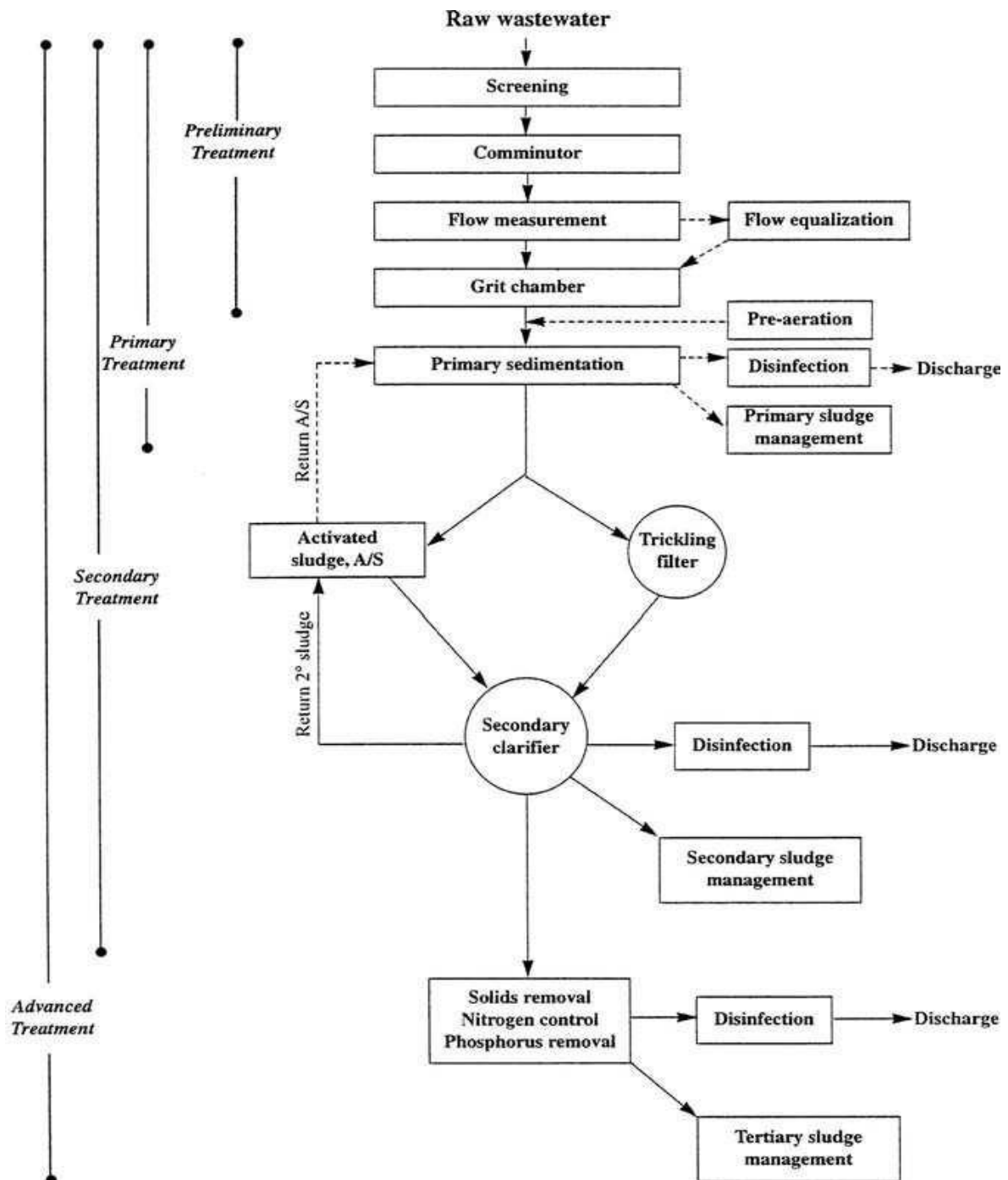


Figure (2.11): Flowchart for wastewater treatment processes^[31].

2-9-2 Primary Treatment Systems

The objective of primary treatment is to reduce the flow velocity of the wastewater sufficiently to permit suspended solids to settle, i.e. to remove settleable materials. Floating materials are also removed by skimming. Thus, a primary treatment device may be called a settling tank (or basin). Due to variations in design and operation, settling tanks can be divided into four groups: plain sedimentation with mechanical sludge removal, two story tanks (Inhofe tank, and several patented units), up flow clarifiers with mechanical sludge removal, and septic tanks. When chemicals are applied, other auxiliary units are needed. Auxiliary units such as chemical feeders, mixing devices, and flocculators and sludge (biosolids) management (treatment and dispose of) are required if there is no further treatment.

Primary clarification is achieved commonly in large sedimentation basins under relatively quiescent conditions. The settled solids are then collected by mechanical scrapers into a hopper and pumped to a sludge treatment unit. Fats, oils, greases and other floating matter are skimmed off from the basin surface. The sedimentation basin effluent is discharged over weirs into a collection conduit for further treatment, or to a discharging outfall. The effect of varying organic loading rates on the treatment performance of the complex biomass within most filter systems used for primary treatment is unknown^[32].

A water treatment facility differs in this regard because the primary objective is to produce high quality water by removing or destroying as much of the contaminants as possible. We cannot produce high quality water without generating the wasteful by-product, sludge, very often in large quantities. Water treatment plants are simply pollution control technologies, whether they are applied to industrial applications or municipal^[33].

2-9-3 Secondary Treatment Systems

After primary treatment the wastewater still contains organic matter in suspended, colloidal, and dissolved states. This matter should be removed before discharging to receiving waters, to avoid interfering with subsequent downstream users.

Secondary treatment is used to remove the soluble and colloidal organic matter which remains after primary treatment. Although the removal of those materials can be effected by physic-chemical means providing further removal of suspended solids, secondary treatment is commonly referred to as the biological process. Several industrial wastewater streams may contain heavy metals including the waste liquids generated by metal finishing or the mineral processing industries. The toxic metals, probably existing in high concentrations (even up to 500 mg.L^{-1}), must be effectively treated/removed from the wastewaters. If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, whilst the direct discharge into the sewerage system may affect negatively the subsequent modern wastewater treatment.

The term advanced treatment may be applied to any system that follows the secondary, or that modifies or replaces a step in the conventional process. The term tertiary treatment is often used as a synonym; however. A tertiary system is the third treatment step that is used after primary and secondary treatment processes^[34].

2-10 Heavy Metal Wastewater Treatment Techniques

2-10-1 Chemical Precipitation

Chemical precipitation is effective and by far the most widely used process in industry because it is relatively simple and inexpensive to operate. In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. The forming precipitates can be separated from the water by sedimentation or filtration. And the treated water is then decanted and appropriately discharged or reused. Metal precipitation is primarily dependent upon two factors: the concentration of the metal, and the pH of the water. Heavy metals are usually present in wastewaters in dilute quantities (1 - 100 mg/L) and at neutral or acidic pH values (< 7.0). Both of these factors are disadvantageous with regard to metals removal. The conventional chemical precipitation processes include^[35]:

2-10-1-1 Hydroxide Precipitation

The most widely used chemical precipitation technique is hydroxide precipitation due to its relative simplicity, low cost and ease of pH control. The solubility of the various metal hydroxides are minimized in the pH range of 8.0-11.0. The metal hydroxides can be removed by flocculation and sedimentation. A variety of hydroxides has been used to precipitate metals from wastewater, based on the low cost and ease of handling, lime is the preferred choice of base used in hydroxide precipitation at industrial settings^[36].

Although widely used, hydroxide precipitation also has some limitations.

- Firstly, hydroxide precipitation generates large volumes of relatively low density sludge, which can present dewatering and disposal problems.

- Secondly, some metal hydroxides have the problem that the mixed metals create a problem in using hydroxide precipitation since the ideal pH for one metal may put another metal back into solution.
- Thirdly, when complex components are in the wastewater, they will inhibit metal hydroxide precipitation^[37].

2-10-1-2 Sulfide Precipitation

Sulfide precipitation is also an effective process for the treatment of toxic heavy metals ions. One of the primary advantages of using sulfides is that of solubility of the metal sulfide precipitates is dramatically lower than that of hydroxide precipitates and sulfide precipitates are not amphoteric. And hence, the sulfide precipitation process can achieve a high degree of metal removal over a broad pH range compared with hydroxide precipitation. Metal sulfide sludge also exhibits better thickening and dewatering characteristics than the corresponding metal hydroxide sludge^[38].

2-10-1-3 Chemical Precipitation Combined with other Methods

Chemical precipitation has shown to be successful in combination with other methods reported like sulfide precipitation to reuse and recover heavy metal ions and employ nano filtration as a second step. Results indicated sulfide precipitation is successful in reducing the metal content and nano filtration yield solutions capable of being directly reused in the plant^[39].

2-10-1-4 Heavy Metal Chelating Precipitation

Conventional chemical precipitation processes have many limitations and it is difficult to meet the increasingly stringent environmental regulations by application of conventional precipitation processes to treat the heavy metal

wastewaters especially containing coordinated agents. As an alternative, many companies use chelating precipitants to precipitate heavy metals from aqueous systems.

Trimercaptotriazine, potassium / sodium thiocarbonate and sodium dimethyl dithiocarbamate are three widely used commercial effectiveness of heavy metal precipitants. Since commercial heavy metal precipitants today either lack the necessary binding sites or pose too many environmental risks to be safely utilized, there is a definite need for new and more effective precipitant to be synthesized to meet the discharged requirements^[40].

2-10-2 Ion Exchange

Ion exchange processes have been widely used to remove heavy metals from wastewater due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics. Ion-exchange resin, either synthetic or natural solids in, has the specific ability to exchange its cations with the metals in the wastewater.

Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution. Besides synthetic resins, natural zeolites, naturally occurring silicate minerals, have been widely used to remove heavy metal from aqueous solutions due to their low cost and high abundance. Many researchers have demonstrated that zeolites exhibit good cation-exchange capacities for heavy metal ions under different experimental conditions^[41].

2-10-3 Adsorption

Adsorption is now recognized as an effective and economic method for heavy metal wastewater treatment. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process.

2-10-3-1 Activated Carbon Adsorbents

Carbonaceous materials have long been known to provide adsorptive properties. The earliest applications may date back centuries with the discovery that charred materials could be used to remove tastes, colours and odours from water. Now activated carbons are used widely in industrial applications which include decolorizing sugar solutions^[42].

Activated carbon (AC) adsorbents are widely used in the removal of heavy metal contaminants. Its usefulness derives mainly from its large micropore and mesopore volumes and the resulting high surface area. A large number of researchers are studying the use of AC for removing heavy metals. Nowadays, the depleted source of commercial coal-based AC results in the increase in price. To make progress in heavy metals adsorption to AC without the expense of decline in the pollutants adsorption, additives and AC composite could be an option. Additives of tannic acid, magnesium, surfactants and AC composite could be effective adsorbents for heavy metals. And searching for alternative AC from abundant and inexpensive sources is of concern. Converting carbonaceous materials into AC for heavy metals remediation has been reported^[43].

2-10-3-2 Carbon Nanotubes Adsorbents

Carbon nanotubes (CNTs), a fascinating new member in the carbon family, including single walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) distinguished by their number of layers, have been the research focus due to their unique one dimensional structures, exceptional mechanical properties, excellent electronic properties and potential applications. Besides the possibility of making advanced composites and nano scale electrode devices, their high thermal and chemical stabilities of CNTs have also stimulated the applications as catalyst carriers. Structurally, their large specific surface areas, hollow and layered structures make them an ideal adsorption material^[44].

2-10-3-3 Low-Cost Adsorbents

Adsorption processes are effective techniques and they have long been used in the water and wastewater industries to remove inorganic and organic pollution for their easy handling, minimal sludge production and their regeneration capability. Granular or powdered activated carbon is the most widely used adsorbent but its use is usually limited due to its high cost. Such a possibility offers a method that uses sorbents of biological origin. But more recently, the search for new effective sorbents involving removal of metal from wastewater has directed attention and natural sorbents are searched for among many vegetable and waste materials from food and agricultural industry^[45].

2-10-3-4 Bioadsorbents

Biosorption of heavy metals from aqueous solutions is a relatively new process that has been confirmed a very promising process in the removal of heavy metal contaminants. The major advantages of biosorption are its high effectiveness in reducing the heavy metal ions and the use of inexpensive biosorbents. Bio-sorption processes are particularly suitable to treat dilute heavy metal wastewater. Typical biosorbents can be derived from three sources as follows:

- Non-living biomass such as bark, lignin, shrimp, squid, crab shell, etc..
- Alga biomass.
- Microbial biomass, e.g. bacteria, fungi and yeast. Different forms are so fine, non living plant material such as potato peels^[46].

2-10-4 Membrane Filtration

In recent years, the polymer- enhanced technique has been shown to be a promising technique for removal of heavy metals in solution. The process involves removal of toxic heavy metals such as Cu(II), Ni(II), and Cr(III) from synthetic wastewater solutions. Membrane filtration has received considerable attention for the treatment of inorganic effluent, since it is capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultra filtration, nano filtration and reverse osmosis can be employed for heavy metal removal from wastewater^[47].

2-10-5 Coagulation and Flocculation

Coagulation and flocculation followed by sedimentation and filtration are also employed to remove heavy metal from wastewaters. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Many coagulants are widely used in the conventional wastewater treatment processes such as alum, ferrous sulfate and ferric chloride, resulting in the effective removal of wastewater particulate and impurities by charge neutralization of particles and by enmeshment of the impurities on the formed amorphous metal hydroxide precipitates. Coagulation is one of the most important methods for wastewater treatment, but the main objects of coagulation are only the hydrophobic colloids and suspended particles^[48].

2-10-6 Flotation

Flotation has nowadays found extensive use in wastewater treatment. Flotation has been employed to separate heavy metal from a liquid phase using bubble attachment, originated in mineral processing. Dissolved air flotation (DAF), ion flotation and precipitation flotation are the main flotation processes for the removal of metal ions from solution. DAF was widely studied to remove heavy metal in 1990s. Ion flotation has shown a promising method for the removal of heavy metal ions from wastewaters. The process of ion flotation is based on imparting the ionic metal species in wastewaters hydrophobic by use of surfactants and subsequent removal of these hydrophobic species by air bubbles^[49].

2-10-7 Electrochemical Treatment

Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state. Electrochemical wastewater technologies involve relatively large capital investment and the expensive electricity supply, so they haven't been widely applied. However, with the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades. The established technologies, electro coagulation, electro flotation, and electro deposition were examined. Electro coagulation (EC) involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions from aluminum or iron electrodes^[50].

2-11 Carbon nanotubes in Wastewater Treatment

Wastewater discharge from domestic, industrial or agricultural sources encompasses a wide range of contaminants and has drawn major concern worldwide since they adversely affect the quality of water. The contaminants found in wastewater, such as heavy metal ions are non-degradable, highly toxic and inorganic and can result in accumulative poisoning, cancer and nervous system damage.

Removal of these contaminants relies on the sorption behavior of a sorbent. CNTs with their high surface active site to volume ratio and controlled pore size distribution, have an exceptional sorption capability and high sorption efficiency compared to conventional granular and powder activated carbon, which has intrinsic limitations like surface active sites and the activation energy of sorption^[51].

CNTs are very hydrophobic and tend to aggregate in aqueous solution because of high Van der Waals interaction forces along the tube outside. As a result, they are not readily dispersible in water. However, their dispersibility in aqueous solutions can be increased by functionalization such as surface oxidation or by addition of surfactant.

Extensively studies found that the adsorption capacity of CNTs depends on both the surface functional groups and the nature of the sorbate. For instance, the amounts of surface acidity (carboxylic, lactonic and phenolic groups) favor the adsorption of polar compounds. On the other hand, the unfunctionalized CNTs surface is proved to have higher adsorption capacity towards non-polar compounds such as polycyclic aromatic hydrocarbons.

The sorption behaviors of CNTs mainly involve chemical interaction for polar compounds and physical interaction for non-polar compounds. The sorption of both polar and non-polar compounds is normally fitted with Langmuir or Freundlich isotherms^[52].

Sorption capacity of CNTs is effective over a broad pH range. Particularly, optimum performance was reported in the pH range of 7 to 10.

Other than this pH range, ionization and competition between ionic species could occur.

Although CNTs are more expensive compared to conventional activated carbon, their sorption and desorption cycles are more efficient than conventional activated carbon. Sorption/desorption studies have shown the availability and performance of CNTs under a numbers of sorption and desorption cycles. A regeneration study showed that the adsorption and desorption of Ni^{2+} in CNTs slightly decrease, but those of granular activated carbon (GAC) sharply decrease after a number of cycles. This phenomenon could be explained by the fact that the porous structure of GAC makes desorption of Ni^{2+} more difficult as the ions have to move from the inner surface to the external surface of the pores.

In addition to serving as sorbent for organic and inorganic contaminants, CNTs have been used by current technology as nanofilters to reduce particle concentrations in wastewater .

Application of CNTs in wastewater treatment is not limited to filtration and sorbent; several researchers have observed strong antimicrobial properties of CNTs. Such behavior allows CNTs to replace chemical disinfectants as a new effective way to control microbial pathogens^[25].

2-12 Fundamentals of Pure Component Adsorption Equilibrium

Adsorption equilibrium information is the most important piece of information in understanding an adsorption process. No matter how many components is present in the system, the adsorption equilibrium of pure components are the essential ingredient for the understanding of how much those components can be accommodated by a solid adsorbent. This information can be used in the study of adsorption kinetics of a single component, adsorption equilibrium of multicomponent systems, and then adsorption kinetics of multicomponent systems.

Langmuir (1918) was the first to propose a coherent theory of adsorption onto a flat surface based on a kinetic viewpoint, that is there is a continual process of bombardment of molecules onto the surface and a corresponding evaporation (desorption) of molecules from the surface to maintain zero rate of accumulation at the surface at equilibrium Fig.(2.12).

The assumptions of the Langmuir model are:

- Surface is homogeneous, that is adsorption energy is constant over all sites.
- Adsorption on surface is localized, that is adsorbed atoms or molecules are adsorbed at definite.

- Each site can accommodate only one molecule or atom. The Langmuir theory is based on a kinetic principle, that is the rate of adsorption is equal to the rate of desorption from the surface^[53].

The Langmuir model is based on the assumption of homogeneous monolayer coverage with all sorption sites to be identical and energetically equivalent. The Freundlich model assumes physicochemical adsorption on heterogeneous surfaces.

The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption and it is often expressed as:

$$q = \frac{q_m KC}{(1 + K_L C)} \quad \text{-----}(2-2)$$

where;

q = the adsorption density at the equilibrium solute concentration C_e (mg of adsorbate per gm of adsorbent)

C = the concentration of adsorbate in solution (mg/L)

q_m = the maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per gm of adsorbent)

K_L = the Langmuir constant related to energy of adsorption (L of adsorbent per mg of adsorbate)

The above equation can be rearranged to the following linear form:

$$\frac{C}{q} = \frac{1}{q_m K_L} + \frac{C}{q_m} \quad \text{-----}(2-3)$$

The linear form can be used for linearization of experimental data by plotting C/q against C . The Langmuir constants q_m and K_L can be evaluated from the slope and intercept of linear equation.

In addition, we can describe adsorption with Langmuir if there is a good linear fit. If not, then maybe some other model will work. Therefore, we can use Freundlich Isotherm.

$$q = K_F C^{1/n} \quad \text{-----} (2-4)$$

where;

q = the adsorption density (mg of adsorbate per gm of adsorbent)

C = the concentration of adsorbate in solution (mg/L)

K_f and n = the empirical constants dependent on several environmental factors and n is greater than one.

This equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\log q = \log K_f + 1/n \log C \quad \text{-----} (2-5)$$

A plot of $\log(C)$ against $\log(q)$ yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants can be determined from the slope and the intercept^[54].

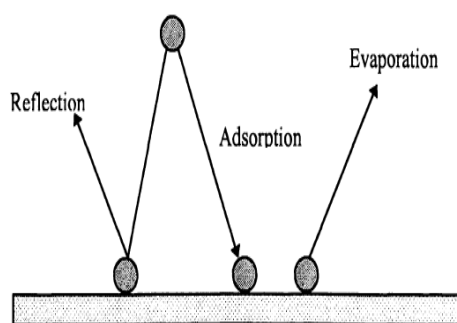


Figure (2.12): Schematic diagram of Langmuir adsorption mechanism on a flat surface^[54].

2-13 Literature Survey

Muataz Ali Atieh^[55] study was carried out to evaluate the environmental application of modified and non-modified carbon nanofiber through the experiment removal of zinc from water. Results of the study showed that raw (non-modified) CNFs have very poor efficiency in removing zinc from water by conventional adsorption mechanism. However, when CNFs were modified with carboxylic group, a significant improvement in the zinc removal efficiency was observed. Five independent variables including pH, CNFs dosage, contact time, agitation speed and initial concentration were studied to determine the influence of these parameters on the adsorption capacity of the zinc from water. For results analysis, adsorption isotherms have been used in order to study the kinetics of the adsorption behavior and to determine the adsorption capacity of the adsorbents.

Omid Moradi^[28] investigated the interaction between some heavy metal ions such as of Pb(II), Cd(II) and Cu(II) ions from aqueous solution adsorbed by single walled carbon nanotube (SWCNTs) and carboxylate group functionalized single walled carbon nanotube (SWCNT-COOH) surfaces. The effect of contact time, pH, initial concentration of ion, ionic strength and temperature on the adsorption of ion were investigated. The results indicated that Langmuir model fits adsorption isotherm data better than the Freundlich model. The results also demonstrated that SWCNT-COOH surfaces can more effectively adsorb mentioned ions than a SWCNTs surface.

Also thermodynamic parameters values showed that the adsorption of ions on SWCNT-COOH and SWCNTs at 283-313 °K is spontaneous and endothermic.

Muataz Ali Atieh^[54], evaluate the environmental application of modified and non-modified carbon nanotubes through the experimental removal of chromium trivalent (III) from water. The aim was to find out the optimal condition of the chromium (III) removal from water under different treatment conditions of pH, adsorbent dosage, contact time and agitation speed. Multi wall carbon nanotubes (MW-CNTs) were characterized by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). Adsorption isotherms were used to model the adsorption behavior and to calculate the adsorption capacity of the adsorbents. The removal of Cr (III) is attributed mainly to the affinity of chromium (III) to the physical and chemical properties of the CNTs. The adsorption isotherms plots were well fitted with experimental data.

Chungsyng Lu^[56] studied commercial single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) purified by sodium hypochlorite solutions and employed as adsorbents to study the adsorption of zinc from water. The properties of CNTs such as purity, structure and nature of the surface were greatly improved after purification which made CNTs more suitable for adsorption of Zn^{+2} . The adsorption capacity of Zn^{+2} onto CNTs increased with the increase of pH range of 1–8, fluctuated very little and reached maximum range of 8–11 and decreased at a pH of 12. A comparative study on the adsorption of Zn^{+2} between CNTs and commercial powdered activated carbon (PAC) was also conducted.

The maximum adsorption capacities of Zn^{+2} calculated by the Langmuir model are 43.66, 32.68, and 13.04 mg.gm^{-1} with SWCNTs, MWCNTs and PAC, respectively, at an initial Zn^{+2} concentration range of 10–80 mg l^{-1} .

The short contact time needed to reach equilibrium as well as the high adsorption capacity suggests that SWCNTs and MWCNTs possess highly potential applications for the removal of Zn^{+2} from water.

Gerrard Eddy^[57], The study adsorption characteristics of the composite for arsenic As(V) removal were carried out as function of pH, adsorbent dose, As(V) concentration and contact time. Although pure CNT did not show any significant adsorption, CNT-Ferrihydrite proved to be a good adsorbent for arsenic. The adsorption followed the Langmuir isotherm model and from the data its monolayer adsorption capacity was estimated to be 44.1 mg/g. The adsorption data were best described by the pseudo-second order kinetic model.

Ghasem Zolfaghari^[58], The aim of this study is surface modification of ordered nanoporous carbons CMK-3 using nitric acid as oxidizing agent. Furthermore, the modified nanoporous carbon, OCMK-3, was used as a nano adsorbent for removal of Pb(II) from water. The effect of various operating parameters such as initial concentration, contact time and adsorbent dose on the adsorption capacity of Pb(II), batch sorption experiments were conducted. The results indicate that the time required for equilibrium is 2 h and order of adsorption in terms of the removal percentage is: OCMK > CMK-3, as shown in table (1.1)

Table (1.1): Summary literature survey.

	Name	Raw	Material	Results	year
1-	Muataz Ali Atieh ^[55]	Zn	CNF	97% Zn removed at pH=7, 150 rpm and 2 hr	2011
2-	Omid Moradi ^[28]	Pb(II), Cd(II) and Cu(II)	SWCNT	37% Pb(II), 20% Cd(II) and 26% Cu(II) removed at pH=5, CNT=50 mg/l, time=120 min and T=293 K for C ₀ = 20 mg/l	2011
3-	Muataz Ali Atieh ^[54]	Chromium (III)	Modified and Nonmodified Carbon Nanotubes	18% chromium (III) removal by modified carbon nanotubes (M-CNTs) at pH=7, 150 rpm, and 2 hours for a dosage of 150 mg of CNTs.	2011
4-	Chungsyng Lu ^[56]	Zn(II)	SWCNT MWCNT	36 mg/g adsorption capacity at C ₀ =60mg/l by SWCNT, 30 mg/g adsorption capacity at C ₀ =60mg/L by MWCNT and time 360 min	2005
5-	Gerrard Eddy ^[57]	As(V)	CNT and CNT-ferrihydrite composites	At (PH=4.2, ads% for CNT=.5) and for composites (pH=2, ads.% = .55), adsorbent dose= 1g/L, contact time= 2.5 hr, C ₀ =50 mg/L	2010
6-	Ghasem Zolfaghari ^[58]	Pb(II)	OCMK and CMK-3	Maximum removal of Pb is 65 % for initial concentration of 10 mg/l for OCMK-3 after 360 min. This value is 40 % for CMK-3 (adsorbent dose: 0.5g/l, pH= 6 and temperature=25 °C).	2011

Chapter Three

Experimental Work

3-1 Introduction

Experimental work consists of preparation , purification, functionalization, characterization using carbon nanotubes (CNTs) and removal process for metal (Cu^{+2}) .

3-2 Raw Material

No.	The Material	Purity	The Supplier
1	NaOH	99%	BDH England
2	HCl	37%	Riedel-deHaen
3	HNO_3	95%	Biosolove
4	Acetylene	99%	Furat Company
5	Argon	99.99%	Furat Company
6	Al_2O_3	Catalyst	HAZARDOUS/South Australia
7	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	99%	Biosolove

3-3 The Apparatuses

No.	The Apparatus
1	Chemical Vapor Deposition (CVD) Experimental apparatus
2	Ultra Sonic Bath
3	Scanning Electron Microscopy (TESCAN)
4	Fourier-transformed infrared spectra (Bruker- Tensor 27)
5	Q-surf 9600
6	U.V spectrophotometer

3-4 Preparation of Catalyst Material

In order to grow the CNTs, the mixture of gases is allowed to flow through the heating zone of quartz tube in which the temperature is raised up to 750 °C for one hour. The precipitated carbon produced then collected for further purification, functionalization and characterization.

3-5 Preparation of CNTs

The carbon nanotubes CNTs are produced by the pyrolysis of Acetylene gas as shown in Picture(3.1) on particles of catalyst (Al_2O_3) in a Chemical Vapor Deposition(CVD) with Argon as inert gas(10 L/ min) mixed with the Acetylene (1 L/min) [(1:10) Acetylene to Argon ratio].

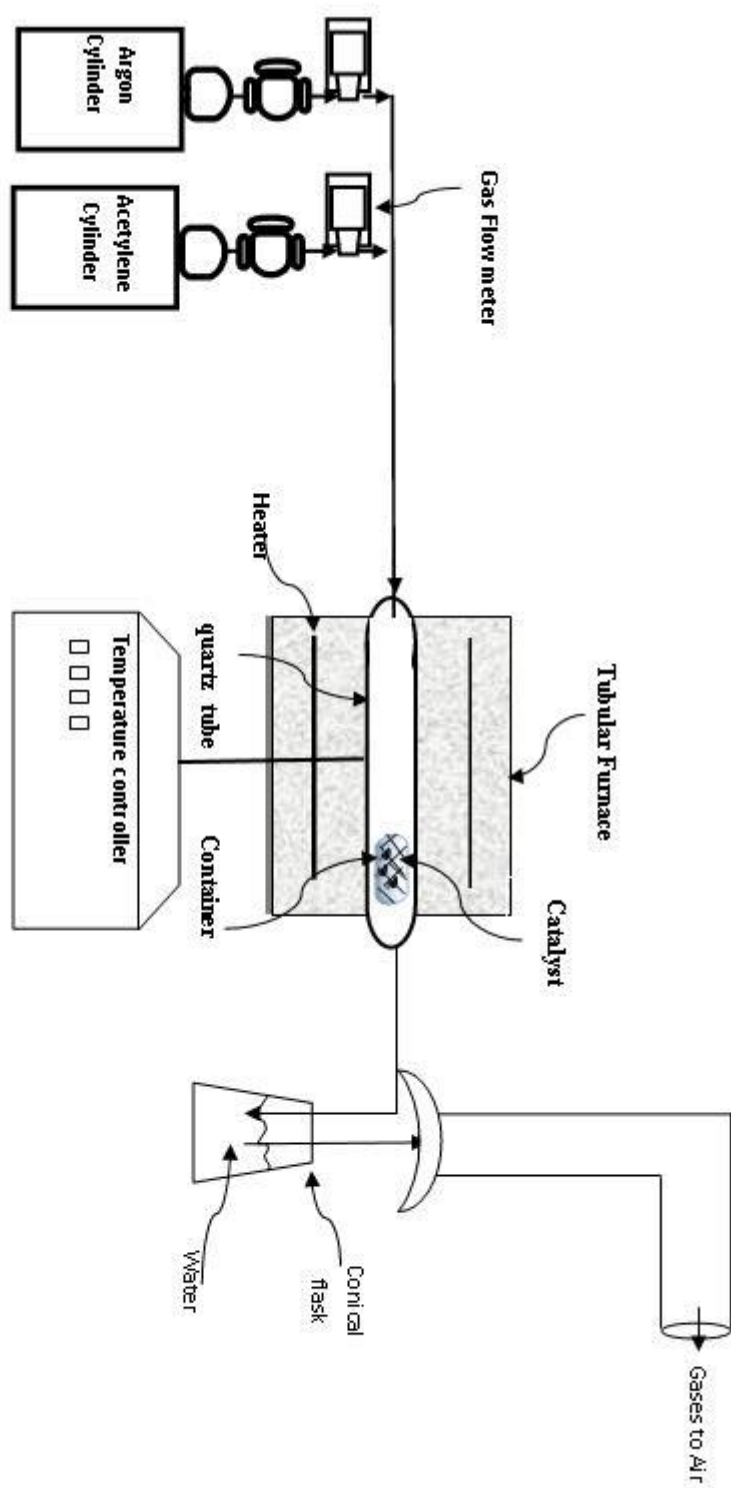
The experimental setup for preparation of CNTs is shown schematically in Fig.(3.1). The system is based on CVD technique ,in which the CNTs is produced by pyrolysis of Acetylene gas under influence of high temperature 750 °C. The inside diameter of the furnace is 300 mm with volume (70x24x43) cm³. The left end of the quartz tube 2.5cm diameter and 150 cm length is used to introduce the Acetylene and Argon gas mixture, while the other end is connected to a water trap and then to outer end of gases discharge. A microprocessor controller is used to control the furnace temperature . The catalyst material is placed in ceramic boat located at distance of 150 mm from the right end of quartz tube.

Under the proper growth conditions, carbon nanotubes will be formed following the mechanism described before. CVD carbon nanotube synthesis is essentially two-step process. The first step is preparation of catalyst critical to the nanotube synthesis. The next step is heating up the substrate in a carbon rich gaseous environment. Normally, we put the substrates into a quartz tube heated

by a furnace for one hour and the temperature of 750 C^0 in a quartz tube to produce the nanocarbon with flowing mixed gases of Acetylene and Argon.



Picture (3.1): Chemical Vapour Deposition(CVD) experimental apparatus.



Fig(3.1):Schematic diagram of Chemical Vapor Deposition (CVD)

3-6 Purification of CNTs

One gram of CNTs produced was heated at 350 °C for 30 min to remove amorphous carbon. After thermal treatment, half gram of CNTs was dispersed into a flask containing 20 ml of 70% sodium hypochlorite solution. The solution was then shaken in an ultrasonic cleaning bath(model CD-2600,china), Picture(3.2). for 20 min and was heated at 85 °C in a water bath for 3 hours to remove metal catalysts. After cooling, the CNTs were washed with deionised water until the pH of the solution reached 7. Finally, the solution was filtered by centrifugal filtration and dried at 200 °C and purified CNTs were obtained.



Picture (3.2) :The Ultra sonic process.

3-7 Functionalization of CNTs

For functionalization, nanocarbon tubes were oxidized by nitric acid under optimal oxidation temperature. 0.1 g of dried CNTs powder was treated with 15 ml of HNO_3 solution (2 M) for 1 hour in the 80°C under refluxing as shown in Fig.(3.2). After oxidation, samples were recovered and washed thoroughly with distilled water until the pH was close to 7. Finally, carbon supports were filtered, washed with distilled water and dried at 108°C for 12 hour.

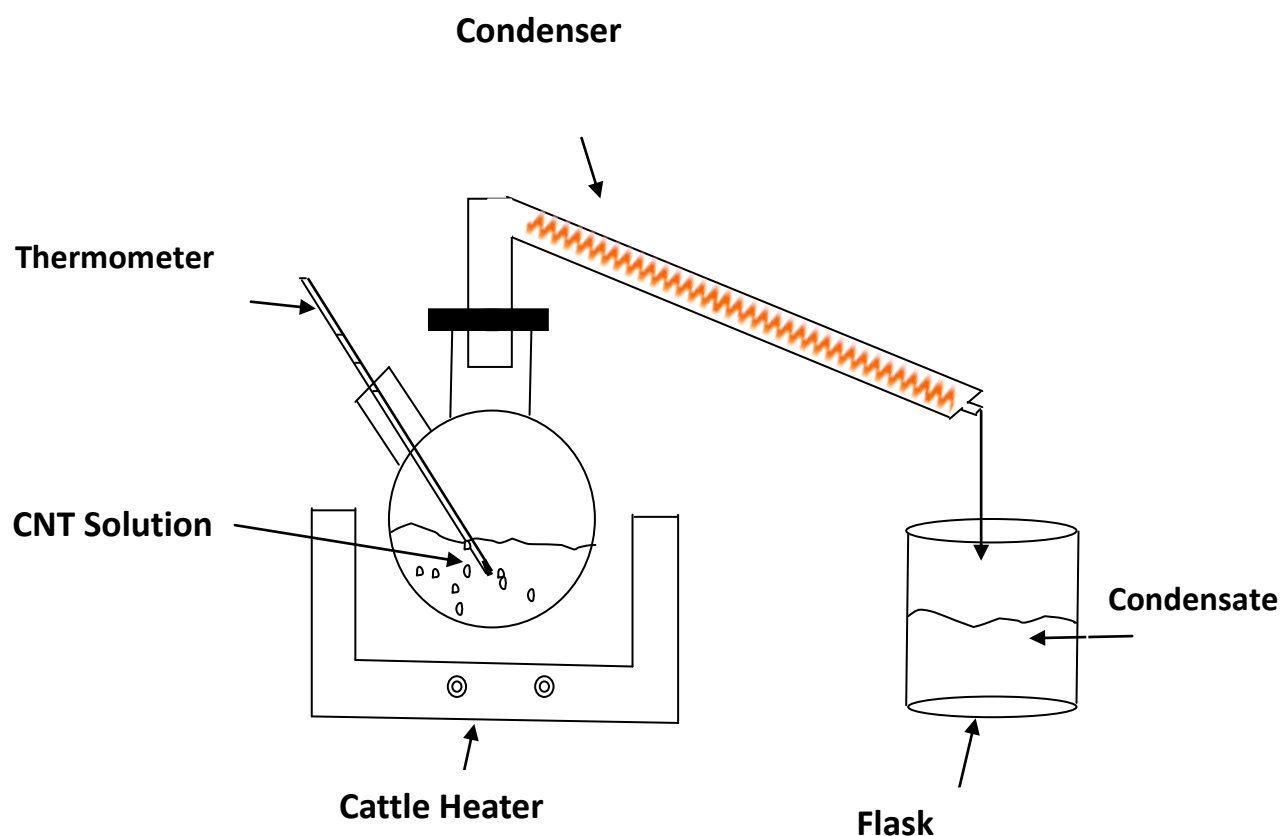
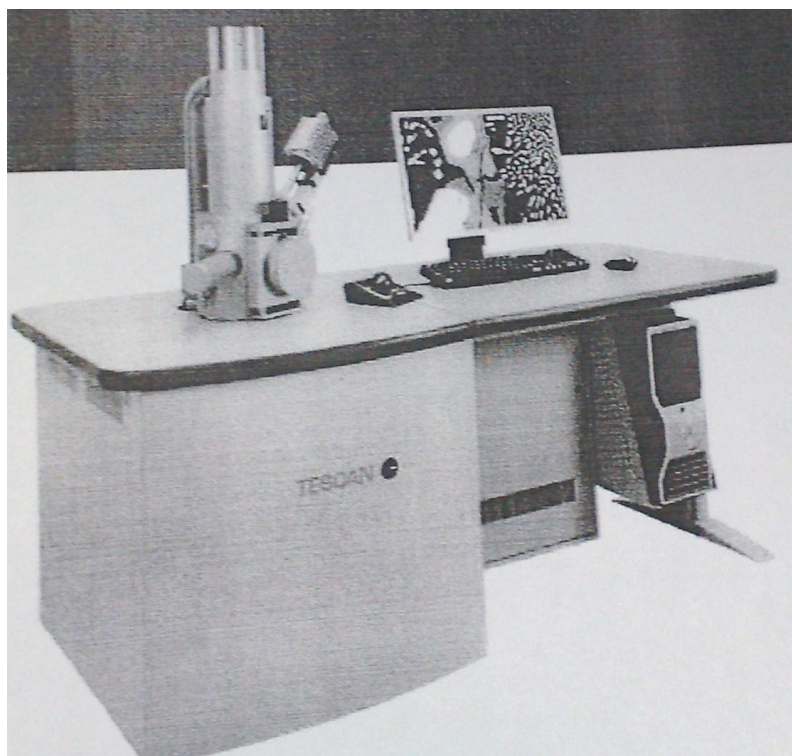


Figure (3.2): The functionalization process for CNTs.

3-8 Characterization of CNT

3-8-1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) (Type TESCAN) in University of Technology /Center of nano Technology and Advanced Materials as shown in Picture(3.3) was used to observe the carbon nanotubes CNTs produced by CVD method after purification.



Picture (3.3): The Scanning Electron Microscope type TESCAN.

3-8-2 Fourier-Transformed Infrared Spectra

The FT-IR instrument Picture(3.4) ,type (Bruker –Tensor 27/ Germany) in University of Technology / Chemical Engineering Department, is used to analyze the chemical bonds and the functional groups grafted on to the nanotubes. Such technique can provide direct means in observing the interactions between the surface of CNTs and adsorbed species.

The FT-IR spectra of CNT Bands at $1000\text{--}1300\text{ cm}^{-1}$ denoted the absorption of stretching vibration of C=O bonds. The other peak at $\sim 1700\text{ cm}^{-1}$ can be assigned to the stretching and bending vibration modes of -COOH on the surface of carbon materials. indicating that more C=O and -COOH functional groups were introduced when the oxidation was done. Thus, the efficiency of the modification with nitric acid is demonstrated by a significant increase in the C–O and -COOH functional groups.



Picture(3.4):FTIR explaining the presende of carboxylic group in these prepared CNTs.

3-8-3 The Surface Area of CNTs

The specific surface area of CNTs was measured using instrument model Q-surf 9600 (USA), based on Brunauer, Emmett and Teller (BET). The instrument in Petroleum Research and Development Centre in Baghdad is shown in Picture (3.5).



Picture (3.5):The Surface area measuring.

3-9 Batch Mode Adsorption Experiment

The standard solutions of fixed concentration of (10,30,50) mg/L were prepared by dissolving the required amount of Cu^{+2} stock solutions with distilled water. The desired weight of adsorbent, in this case, the CNTs (10,30 and 50 mg/L) was added to 100 mL of the solution. Flasks are then agitated with the speed of (200 rpm) at room temperature using a mechanical shaker. The pH of each solution was adjusted using 0.1 M HCl or 0.1 M NaOH. Table (3.2) shows the parameter values of batch mode adsorption process.

Table(3.2): The parameter values of batch mode adsorption process.

Time (min)	CNT Dosage (mg/L)	pH	Initial concentration of Cu^{+2} C_0 (mg/ L)
0-60	10	3,5,8,12	10
	30		30
	50		50

After the equilibrate time of (10, 20, 30, 40,50 and 60 min) passed, CNTs were separated from the samples by filtering and the filtrates were analyzed using a U.V-1100 spectrophotometer (Chrom Tech-Chine) available in University of Technology / Chemical Engineering Department . The photograph of instrument is shown in Picture (3.6).



Picture (3.6): U.V spectrophotometer

In order to determine the effect of each parameter, the other parameters were fixed on the extent of adsorption Cu(II) ion were studied in a batch mode of operation. Each of the Cu(II) ion solutions was prepared by dissolving $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in water and used as stock solutions. Then they were diluted to the required concentration. Calibration curves between 10 and 50mg/L were prepared. For adjusting each adsorption isotherm, different initial concentrations of Cu(II) ion were agitated with different adsorbent dosage (CNTs) for several times. The adsorbents (CNTs) were separated by filtering. The adsorption percentage of each metal ion is calculated as follows:

$$\text{Adsorption(\%)} = \frac{C_0 - C_f}{C_0} \quad \text{----- (3-1)}$$

where, C_0 and C_f are the initial and final metal ion concentrations (after contact to adsorbents), respectively.

The metal sorption capacity (q_t) is calculated by the following equation^[61]:

$$\text{Adsorption Capacity (mg/g)} = \frac{C_0 - C_f}{M_s} \times V \quad \text{----- (3-2)}$$

where:

V = volume of the solution (L)

M_s = weight of adsorbent (gm)

The calibration curve is drawn between absorpancy and a standard solutions of Cu^{+2} in water as shown in Fig.(3.3). Langmuir and Freundlich models are used to calculate the adsorption% [Eq. (3-1)]and adsorption capacity [Eq.(3-2)].

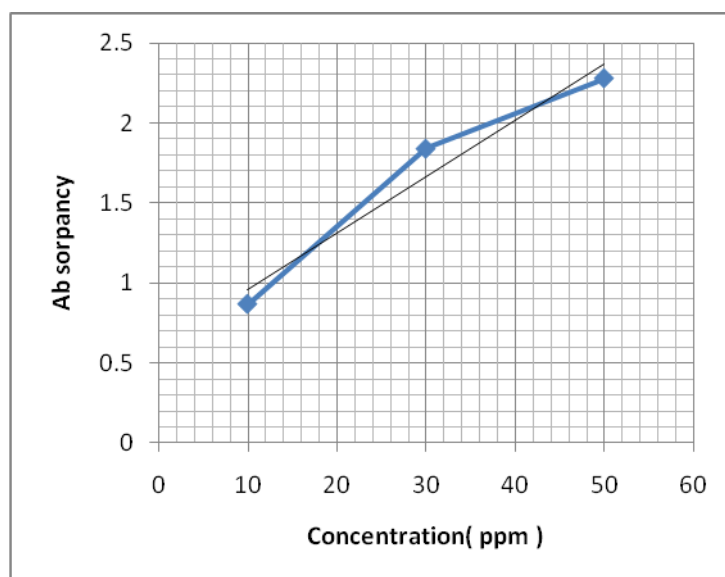


Figure (3.3): Calibration curve for copper(II) metal solution at pH=5.

Chapter Four

Results and Discussion

4-1 Characterization of CNTs

From the SEM image shown in Fig.(4.1), Carbon nanotubes (CNTs) with an average diameter of 30 nm and several micron in length can be identified. The mass of the sample used for analysis was approximately 50 mg.

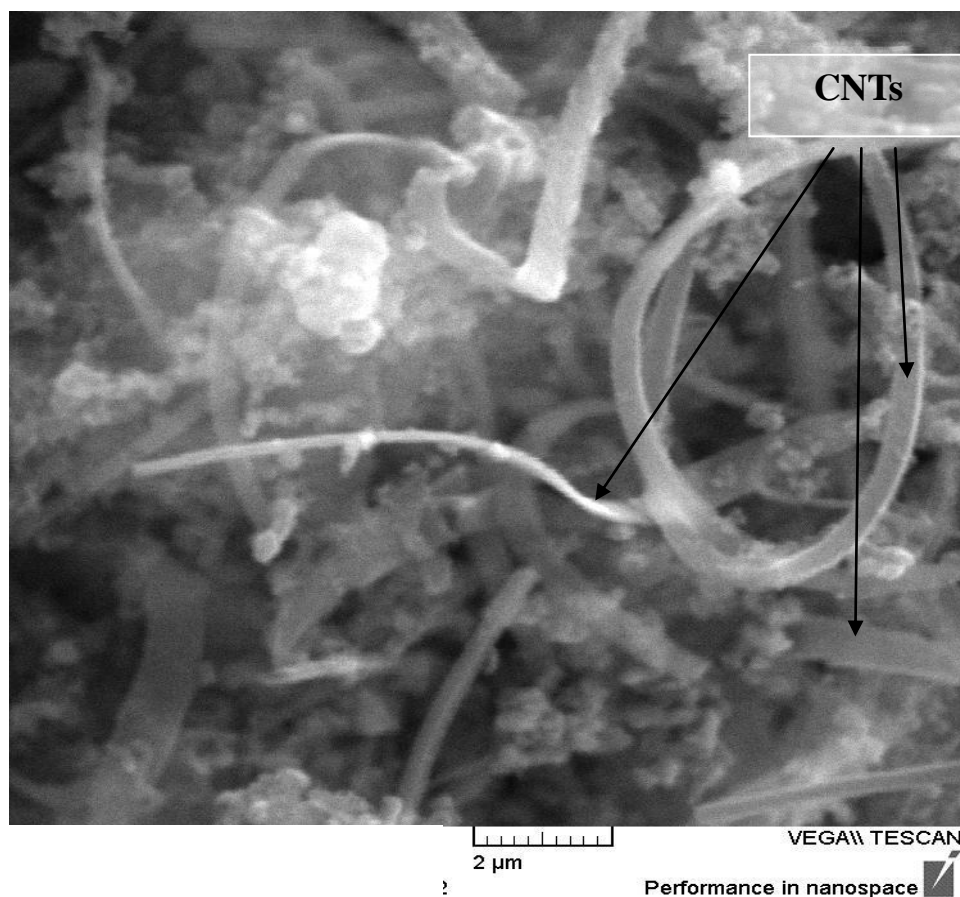


Figure (4.1):Scanning electron images of CNTs.

The observed CNTs are usually curve and have cylindrical shapes. Due to inter-molecular force, the CNTs have different sizes and directions and form an aggregated structural solid.

FTIR spectra of functionalized CNTs are shown in Fig.(4.2), the peaks which are identified at 1701.22 cm^{-1} , characterize C=O which can be attributed to acidic group, like carboxyl.

The peaks appearing at 2945.3 cm^{-1} and 3305.99 cm^{-1} are due to the carbon hydrogen bond stretch and hydroxyl group, respectively. The hydroxyl group can be attributed to the acid treatment of the CNTs after production to remove the metal catalyst for purification purpose. The results of FTIR confirm the growth of carbon structure due to the observation of stretching C-C bond at 1554.63 cm^{-1} .

These results are in good agreement with the results obtained by Chungsyng Lu^[56].

The surface area of CNTs, as determined by the BET method was found to be $53\text{ (m}^2\text{/g)}$.

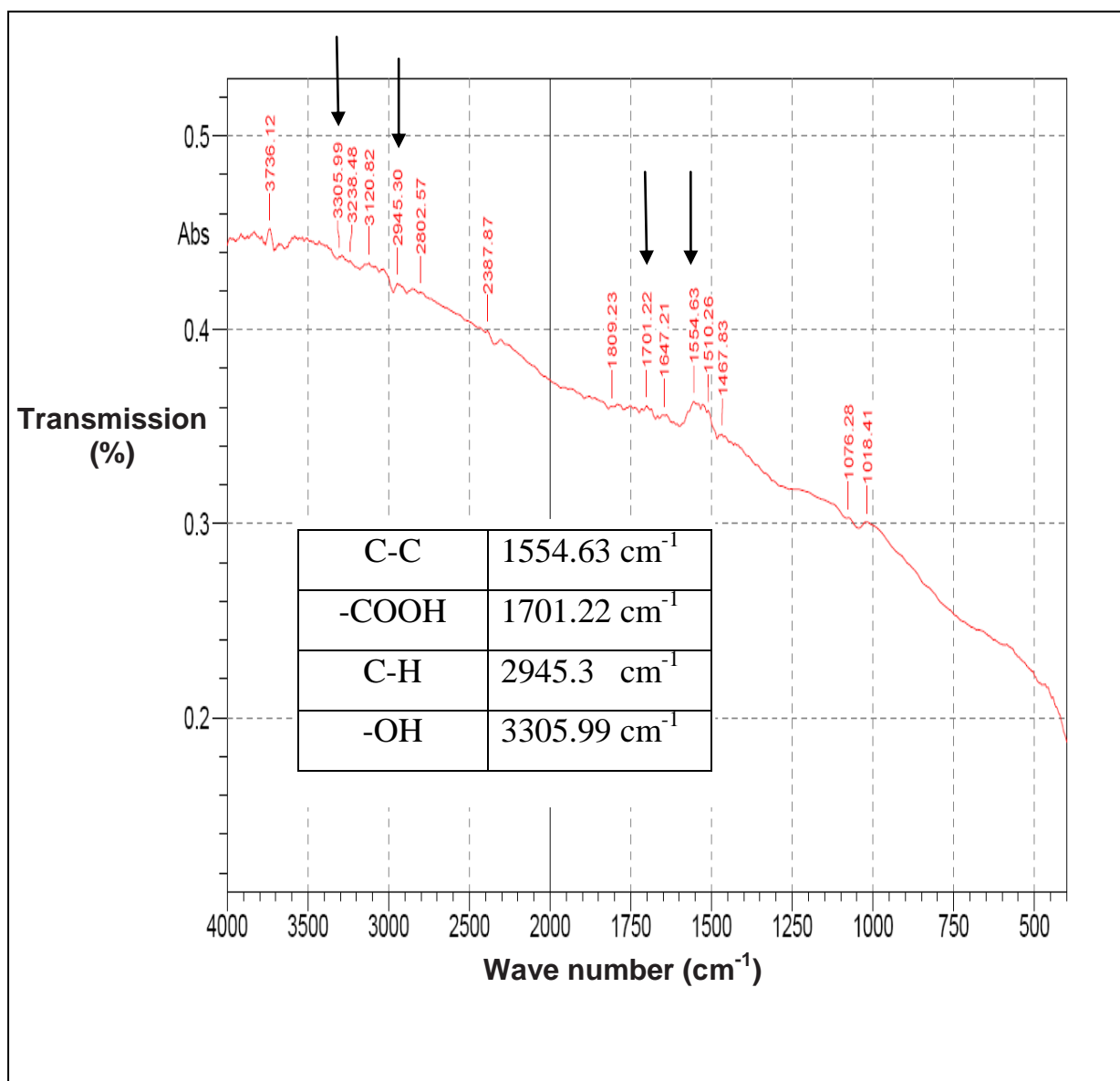


Figure (4.2): The presence of carboxylic group in the prepared CNTs.

4-2 Effect of Different Parameters on Adsorption of Heavy Metal by Modified CNTs

4-2-1 Effect of Contact Time:

The results shown in Fig.(4.4) to Fig.(4.15) show the percentage of adsorbed ion Cu^{+2} on to CNTs surfaces as a function of contact time. It is noted that the adsorption of Cu^{+2} increases rapidly with time and then reaches equilibrium. The contact time to reach equilibrium at $T=298\pm 1^0\text{K}$. Progresses steadily through the adsorber until it reaches the end of the process at time =(20, 28 and 32) min as shown in Fig.(4.4) for the concentration (10, 30 and 50) ppm respectively.

- Time to reach equilibrium =20 min for $C_0=10$ ppm
- Time to reach equilibrium = 28 min for $C_0= 30$ ppm
- Time to reach equilibrium = 32 min for $C_0= 50$ ppm

Two region can be observed on the curve of contact time .Region one in which the adsorption of Cu^{+2} takes place rapidly within a short time and the region of equilibrium. At equilibrium time there is no active site on the CNTs.

In general, a two-stage kinetic behavior is observed Figs.(4.4) to (4.15) rapid initial adsorption in a contact time of 20 min at $C_0= 10$ (Take Fig.(4.4) as an example for same behavior as in Fig.(4.15)) , followed by a second stage at a much lower adsorption rate. This is obvious from the fact that a large number of vacant surface sites are available for the adsorption during the initial stage.

Fig.(4.4) to Fig.(4.15) indicate that the time required for equilibrium is one hour.

In Fig.(4.12), the perfect results were obtained for Cu^{+2} ion: when the initial concentration was 50 mg/L at pH=8, equilibrium time was 3min and $T=298^{\circ}\text{K}$. In fact with time increase the percentage of ion adsorption increased.

This is due to the existence of free function group (- COOH) on the adsorbent. This functional group causes a rise in the negative charge on the carbon surface.

These results are in good agreement with the results obtained by Ghasem Zolfaghari^[57], who found that the adsorption percentage increases with increasing the contact time.

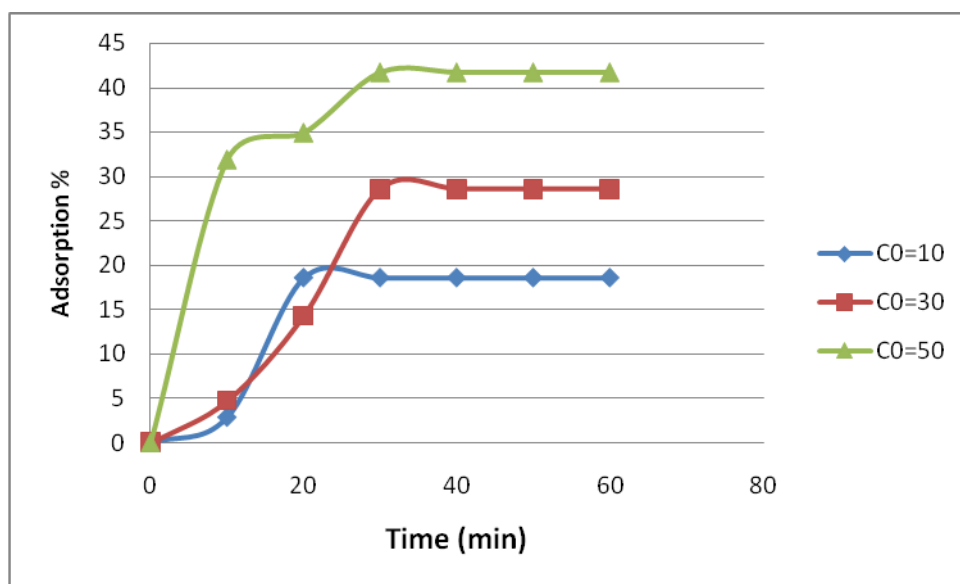


Figure (4.4) :The effect of contact time on percentage removal of Cu^{+2} at $\text{pH}=3$ and $\text{CNT}=10(\text{mg}/\text{L})$.

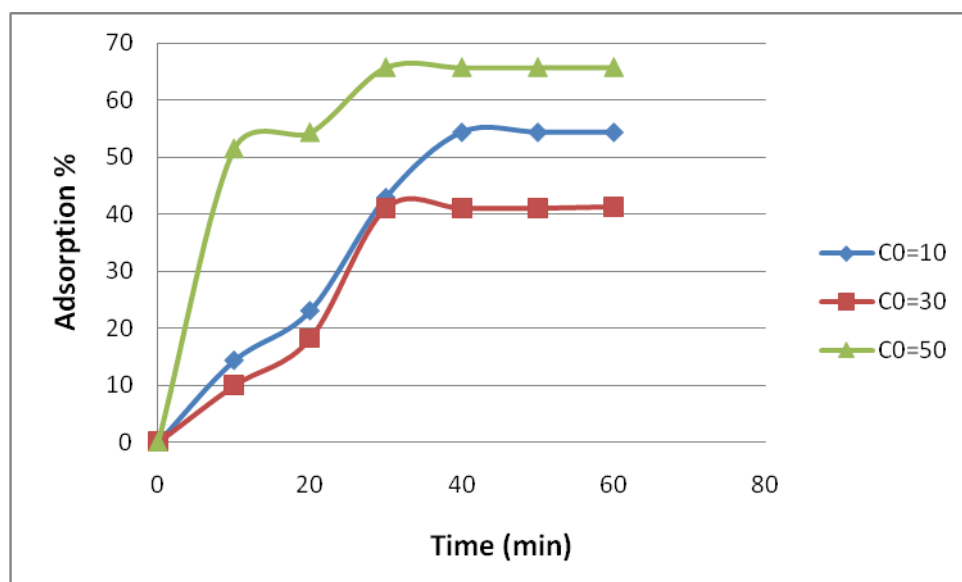


Figure (4.5) :The effect of contact time on percentage removal of Cu^{+2} at $\text{pH}=3$ and $\text{CNT}=30(\text{mg}/\text{L})$.

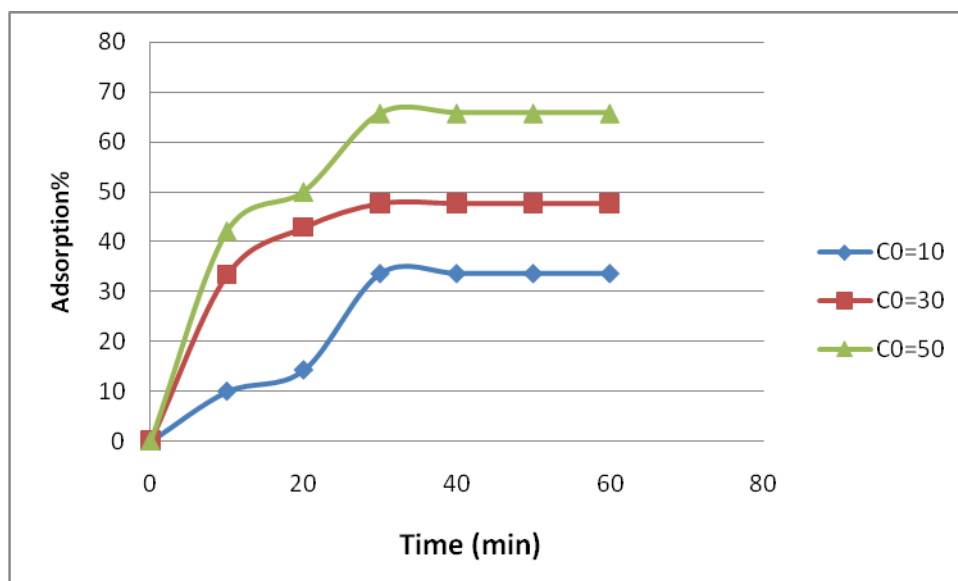


Figure (4.6) :The effect of contact time on percentage removal of Cu^{+2} at $\text{pH}=3$ and $\text{CNT}=50(\text{mg}/\text{L})$.

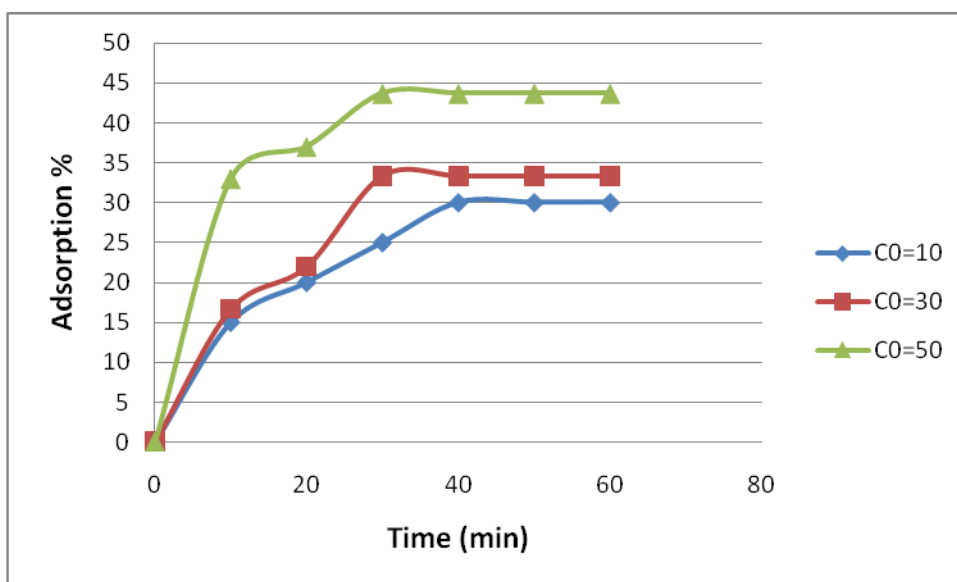


Figure (4.7) :The effect of contact time on percentage removal of Cu^{+2} at $\text{pH}=5$ and $\text{CNT}=10(\text{mg}/\text{L})$.

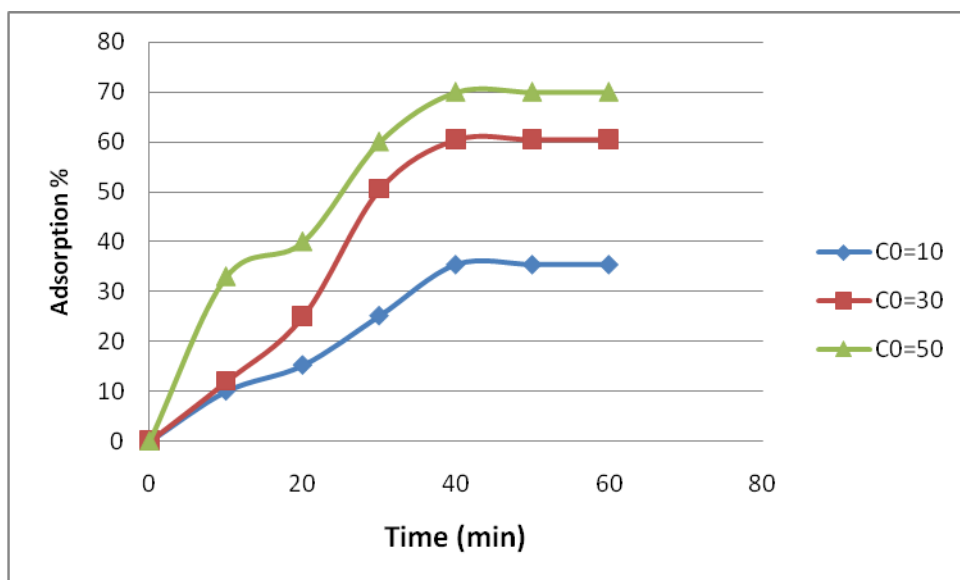


Figure (4.8) :The effect of contact time on percentage removal of Cu^{+2} at $\text{pH}=5$ and $\text{CNT}=30(\text{mg/L})$.

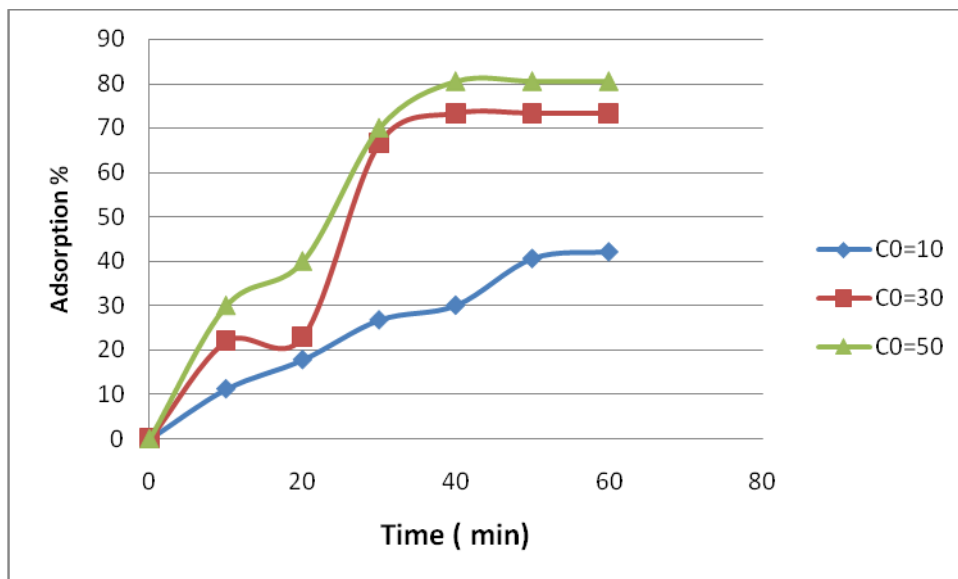


Figure (4.9) :The effect of contact time on percentage removal of Cu^{+2} at $\text{pH}=5$ and $\text{CNT}=50(\text{mg/L})$.

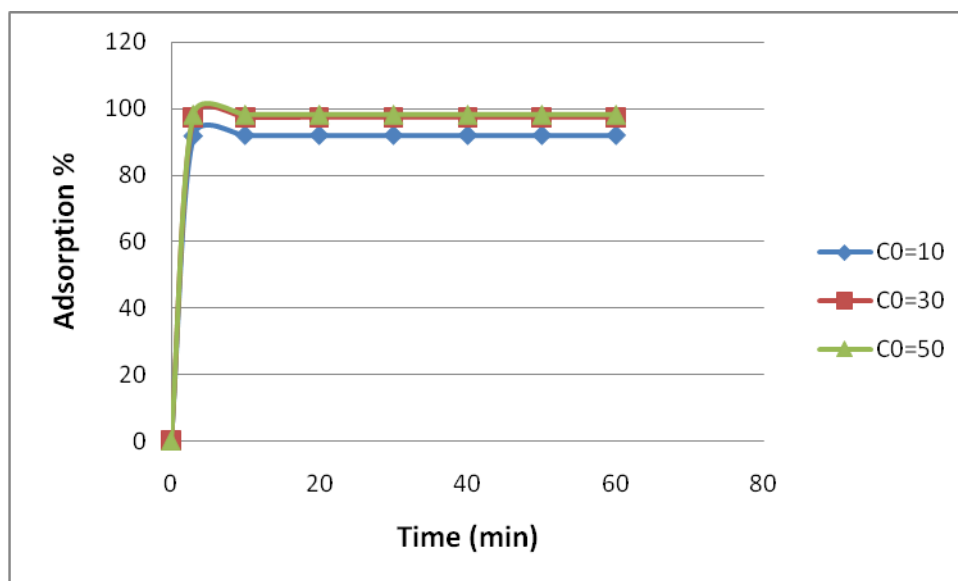


Figure (4.10) :The effect of contact time on percentage removal of Cu^{+2} at $\text{pH}=8$ and $\text{CNT}=10(\text{mg/L})$.

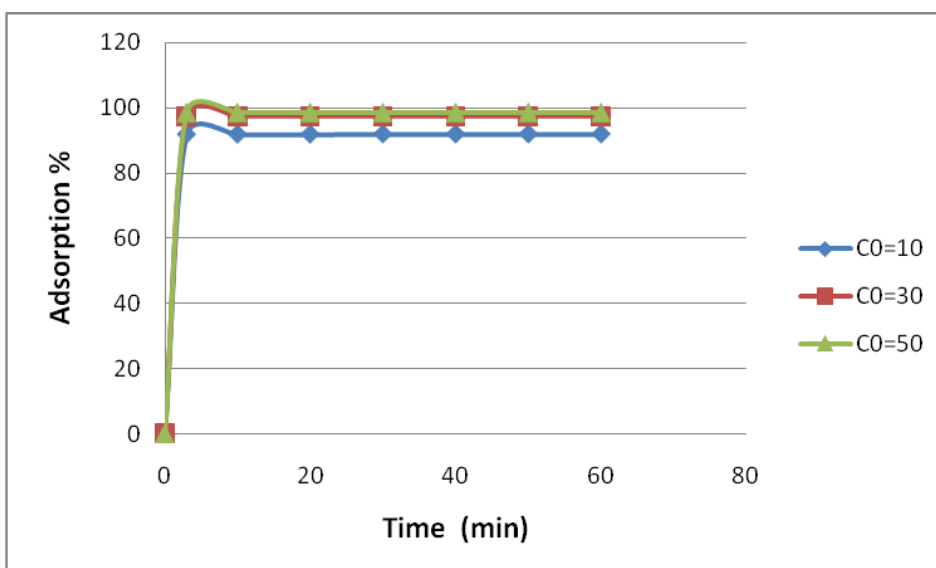
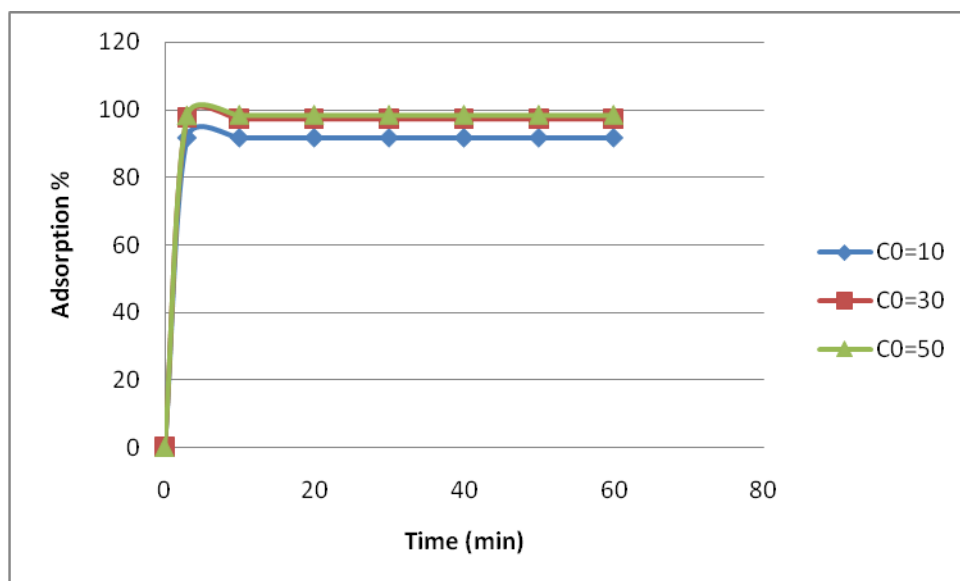
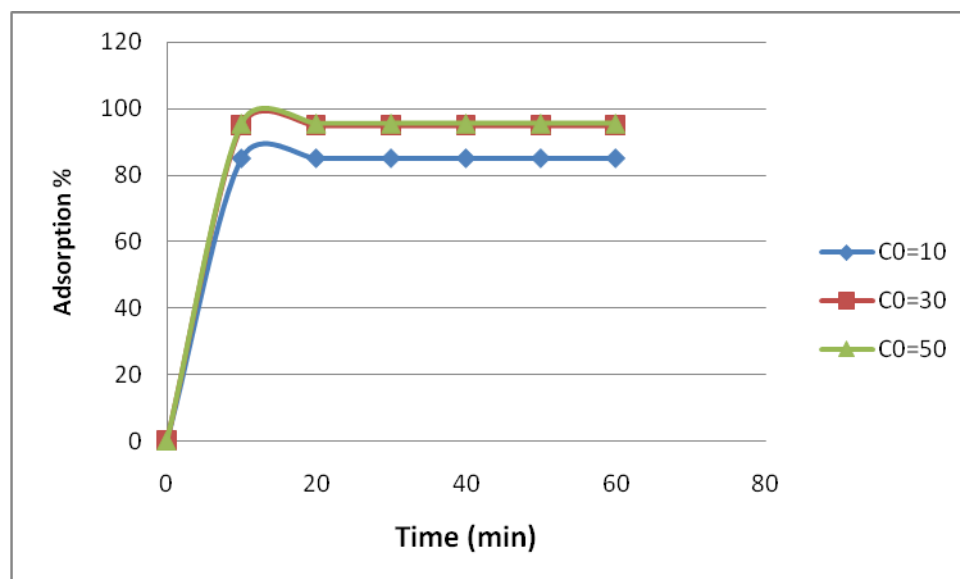


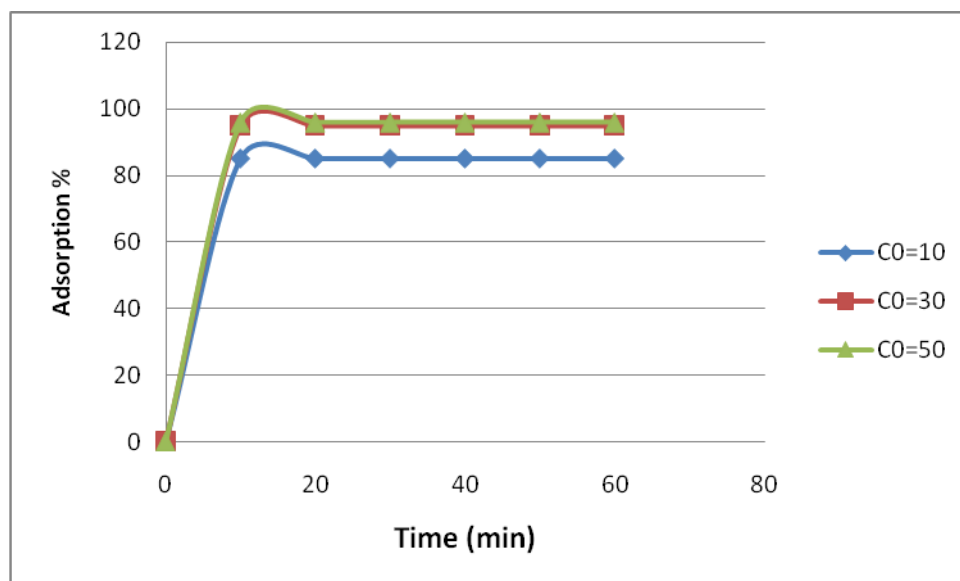
Figure (4.11) :The effect of contact time on percentage removal of Cu^{+2} at $\text{pH}=8$ and $\text{CNT}=30(\text{mg/L})$.



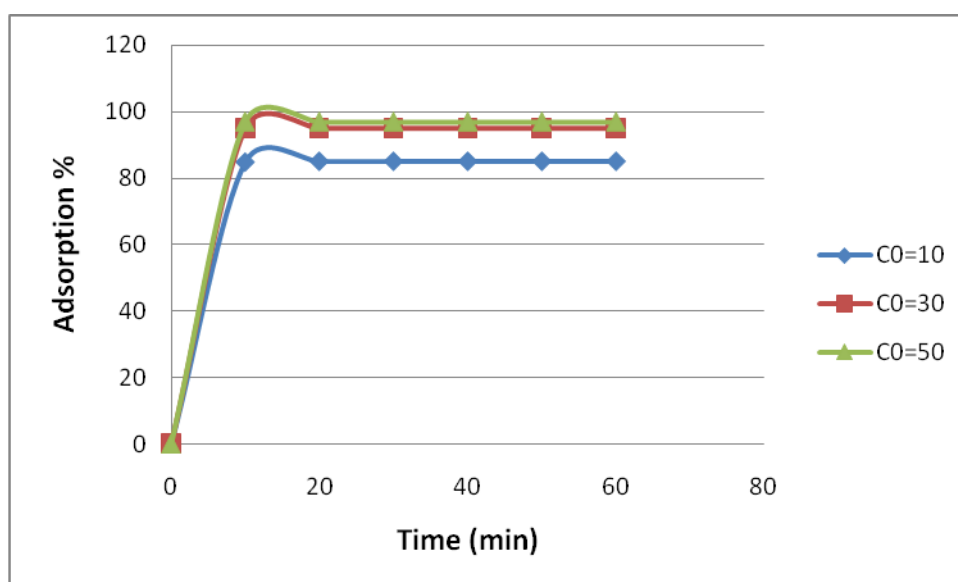
Figure(4.12) :The effect of contact time on percentage removal of Cu^{+2} at $\text{pH}=8$ and $\text{CNT} = 50(\text{mg/L})$.



Figure(4.13) :The effect of contact time on percentage removal of Cu^{+2} at $\text{pH}=12$ and $\text{CNT} = 10(\text{mg/L})$.



Figure(4.14): The effect of contact time on percentage removal of Cu^{+2} at $\text{pH}=12$ and $\text{CNT}=30$ (mg/L).



Figure(4.15) :The effect of contact time on percentage removal of Cu^{+2} at $\text{pH}=12$ and $\text{CNT}=50$ (mg/L).

4-2-2 Effect of pH on Ion Adsorption

Figs. (4.16) to (4.24) show the effect of pH on the adsorption of Cu^{+2} onto CNTs. As can be seen, the pH of the solution plays an important role in affecting the adsorption characteristics of Cu^{+2} onto CNTs. With the C_0 of 10 mg/L, the adsorption of Cu^{+2} onto CNTs increases with the increase in pH range of 3–8, fluctuates very little and reaches a maximum in the pH range of 8 and decreased at a pH of 12.

The ionic adsorption capability is known to be mainly determined by the functional groups which are usually introduced by chemical treatments such as oxidation. Appropriate treatments can introduce functional groups such as hydroxyl (-OH), carboxyl (-COOH) and carbonyl ($>\text{C}=\text{O}$), on the surface of CNTs. Introduction of functional groups on CNT enhances its ionic adsorption properties^[57].

The initial concentration of each ion was (10,30 and 50) mg.L^{-1} and $T = 298^\circ\text{K}$. The uptake of Cu^{+2} ion by the adsorbents in aqueous solution increased as the pH increased from 3 to 8. Although a maximum uptake was noted at pH 8, the metal ions started to precipitate when the pH increased over 8. Therefore, there was no increasing adsorption at pH beyond 8.

The increase in adsorption capacity at $\text{pH} = 8$ could be due to the adsorption of ions onto the surface of adsorbents and precipitation. It is considered that CNTs-COOH has a maximum adsorption capacity at $\text{pH} = 5$, if the precipitated amount is not considered. The optimum pH was found to be 8 for Cu^{+2} ion in the adsorption^[59].

These results are in good agreement with the results obtained by Omid Moradi et al^[28].

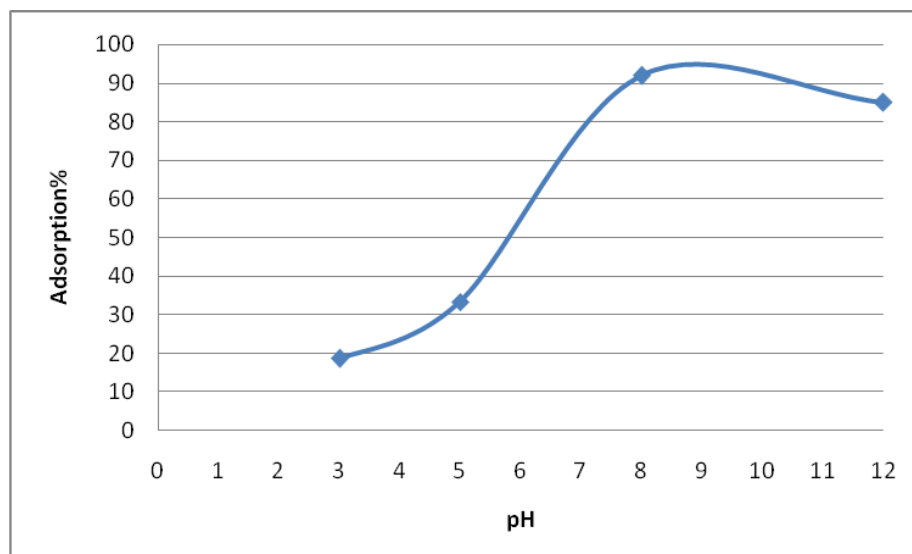


Figure (4.16) :The effect of pH on the percentage of adsorption of Cu^{+2} , Initial concentration of metal ion is 10 mg/L, CNTs dosage 10 mg/L and contact time 60 min .

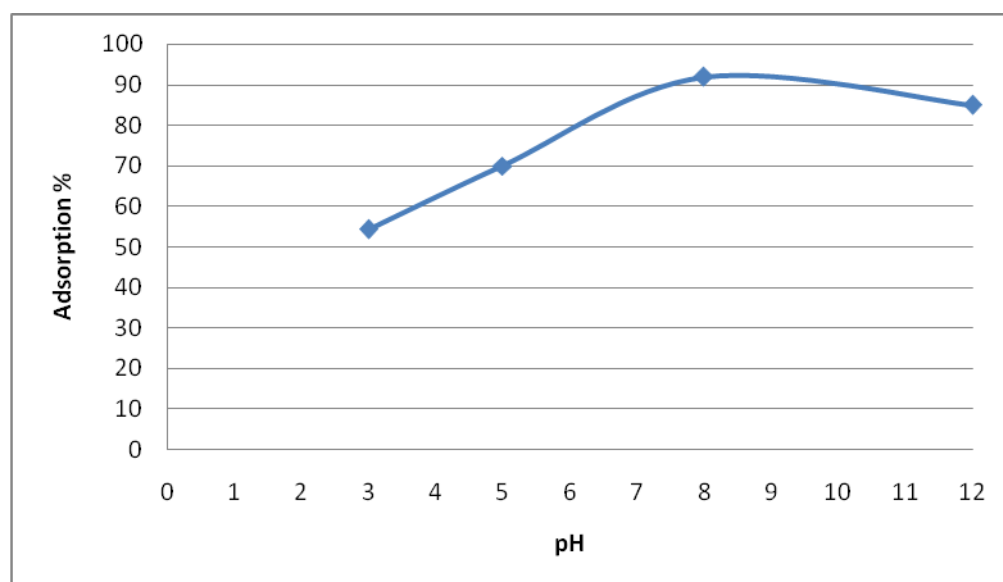


Figure (4.17) :The effect of pH on the percentage of adsorption of Cu^{+2} , Initial concentration of metal ion is 10 mg/L, CNTs dosage 30 mg/L and contact time 60 min .

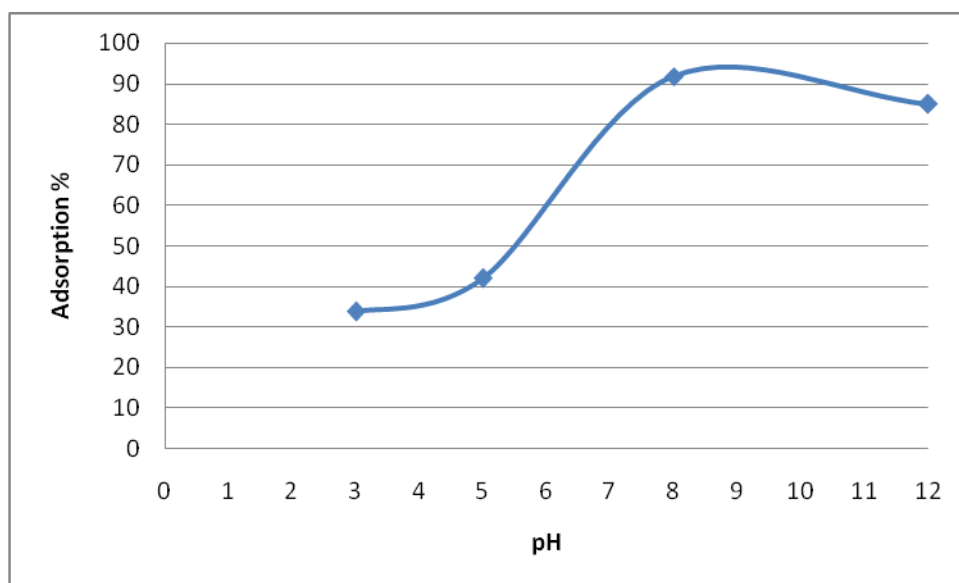


Figure (4.18) :The effect of pH on the percentage of adsorption of Cu^{+2} , Initial concentration of metal ion is 10 mg/L, CNTs dosage 50 mg/L and contact time 60 min .

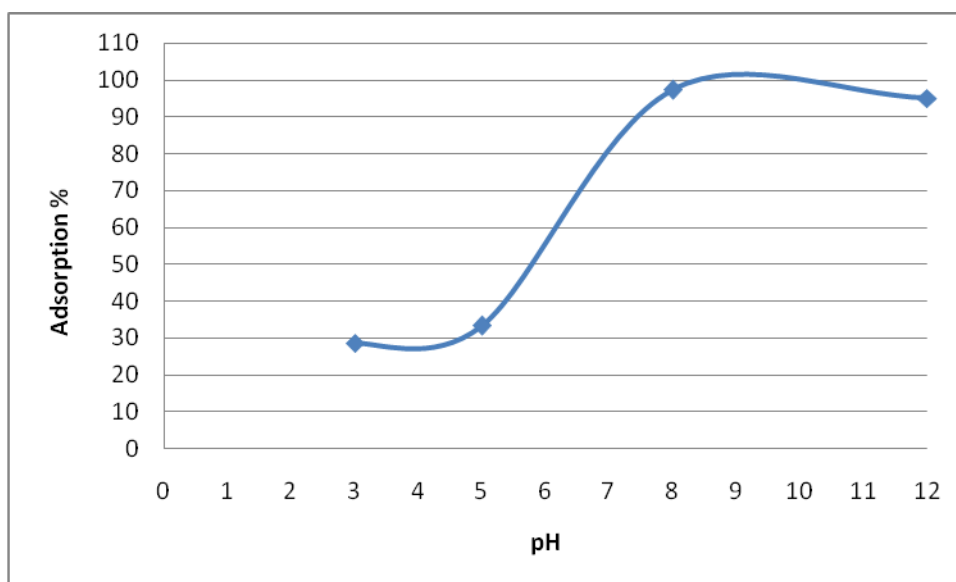


Figure (4.19) :The effect of pH on the percentage of adsorption of Cu^{+2} , Initial concentration of metal ion is 30 mg/L, CNTs dosage 10mg/L and contact time 60 min .

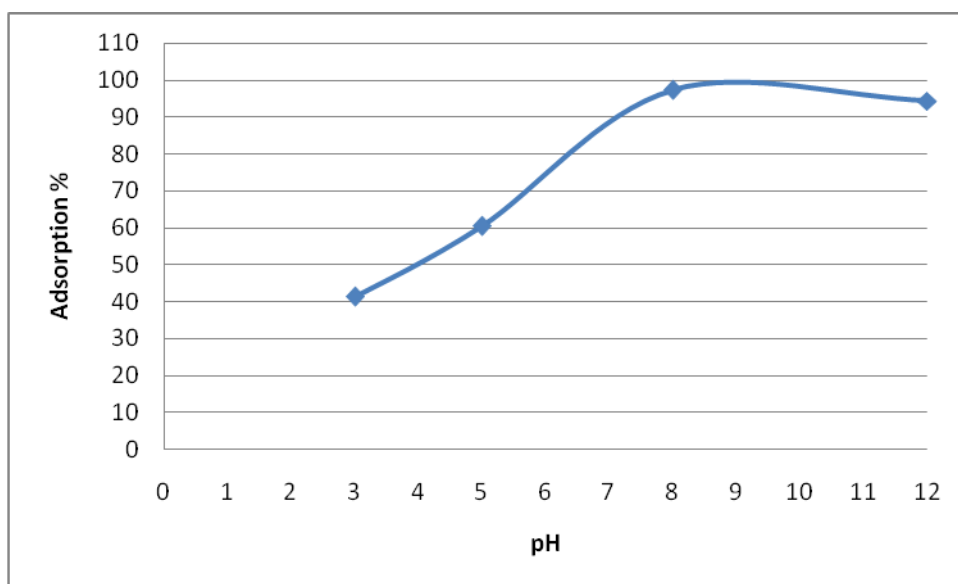


Figure (4.20) :The effect of pH on the percentage of adsorption of Cu^{+2} , Initial concentration of metal ion is 30 mg/L, CNTs dosage 30mg/L and contact time 60 min .

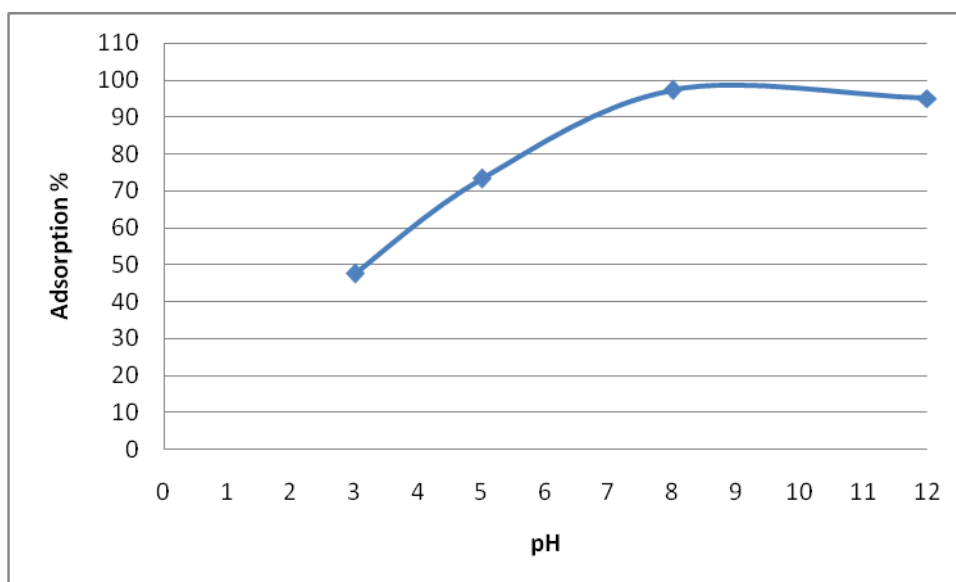


Figure (4.21) :The effect of pH on the percentage of adsorption of Cu^{+2} , Initial concentration of metal ion is 30 mg/L, CNTs dosage 50mg/L and contact time 60 min .

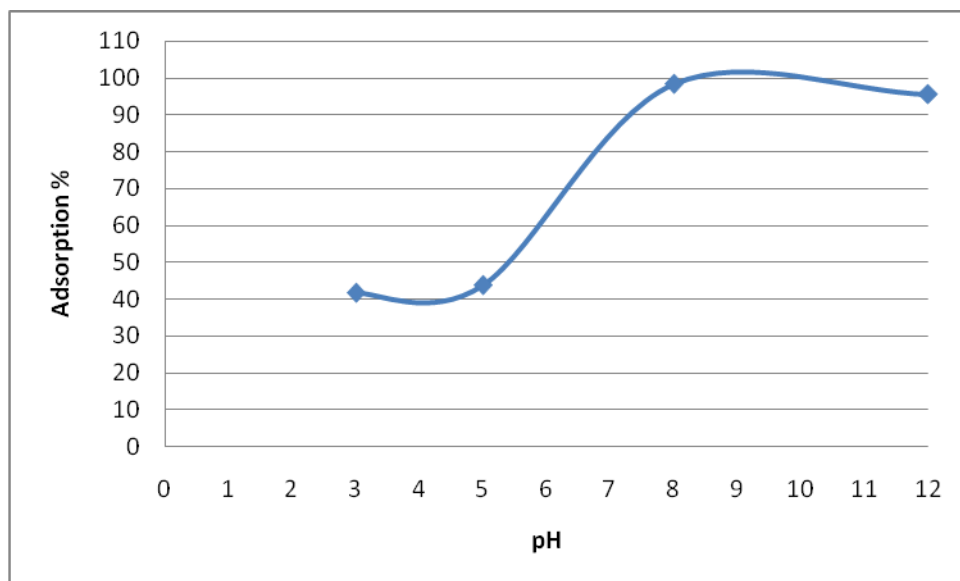


Figure (4.22) :The effect of pH on the percentage of adsorption of Cu^{+2} , Initial concentration of metal ion is 50 mg/L, CNTs dosage 10mg/L and contact time 60 min .

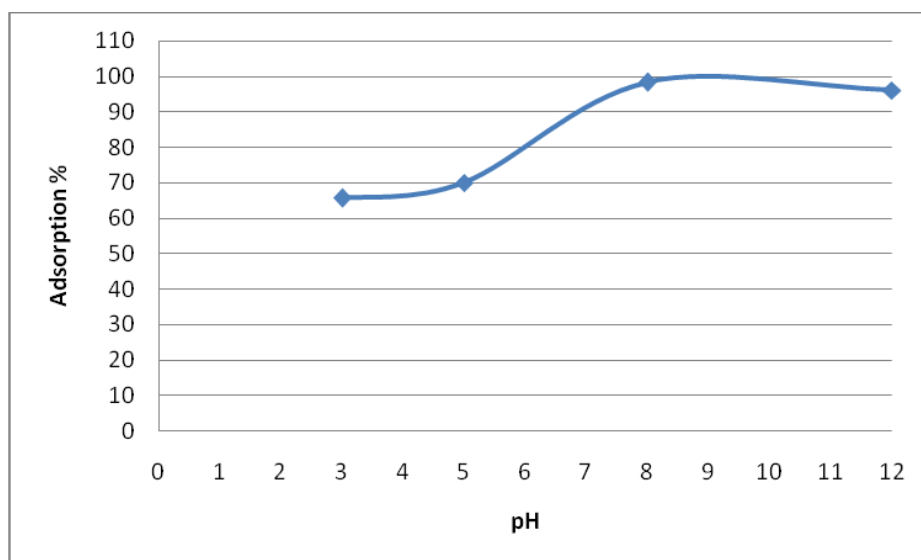


Figure (4.23):The effect of pH on the percentage of adsorption of Cu^{+2} , Initial concentration of metal ion is 50 mg/L, CNTs dosage 30mg/L and contact time 60 min .

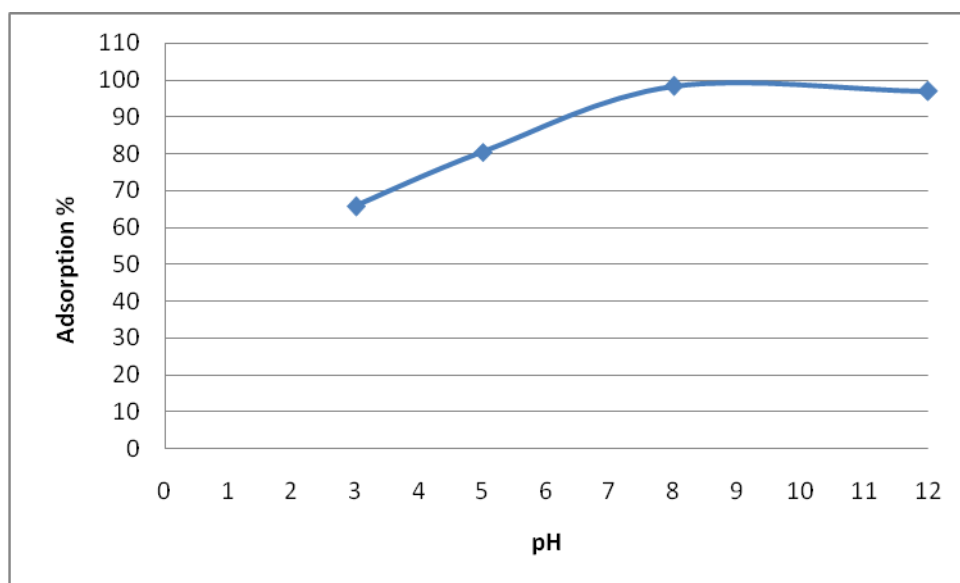


Figure (4.24) :The effect of pH on the percentage of adsorption of Cu^{+2} , Initial concentration of metal ion is 50 mg/L, CNTs dosage 50mg/L and contact time 60 min .

4-2-3 Effect of CNTs Dosage

The amount of carbon nanotubes in the water is one of the major factors, which affect the adsorption capacity. The batch adsorption experiments were carried out by using various amounts of CNTs of 10-30 and 50 mg/L. The results shown in Figs.(4.25) to (4.36) indicate that the adsorption capacity increases with increases in CNTs dosage. The perfect result is obtained when pH=8, C_0 (10, 30 and 50 ppm) and CNTs dosage of 50 mg at constant contact time (60 min).

The amount of adsorption for copper increases with adsorbent dose. This increase in loading capacity is due to the availability of greater amounts of active sites of the adsorbent^{[45][54]}.

These results are in good agreement with the results obtained by Muataz A., who found that the adsorption percentage increases with increasing the amount of carbon nanotubes^[55].

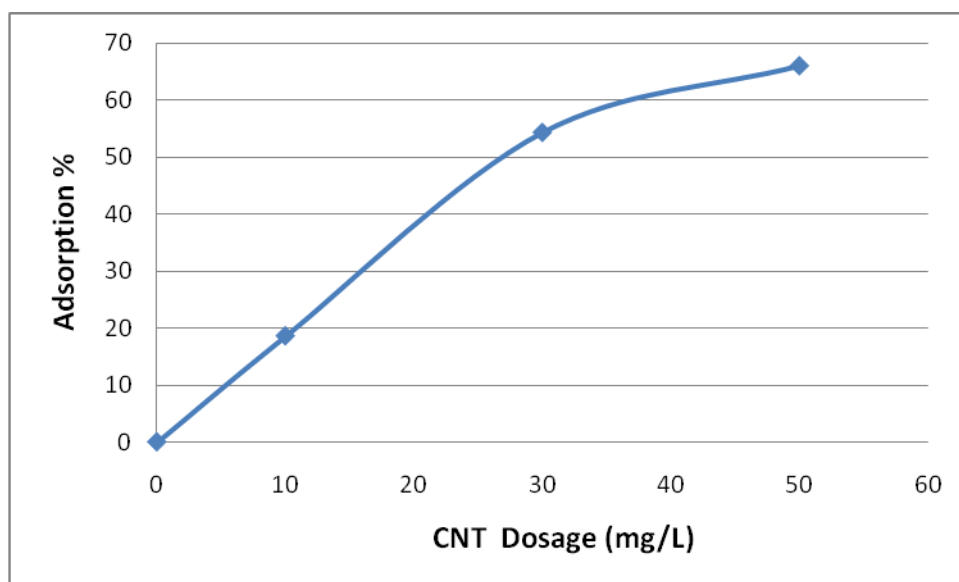


Figure (4.25) :The effect of CNTs dosage on percentage of adsorption of copper at $pH=3$, $C_0=10$ and time =60 min.

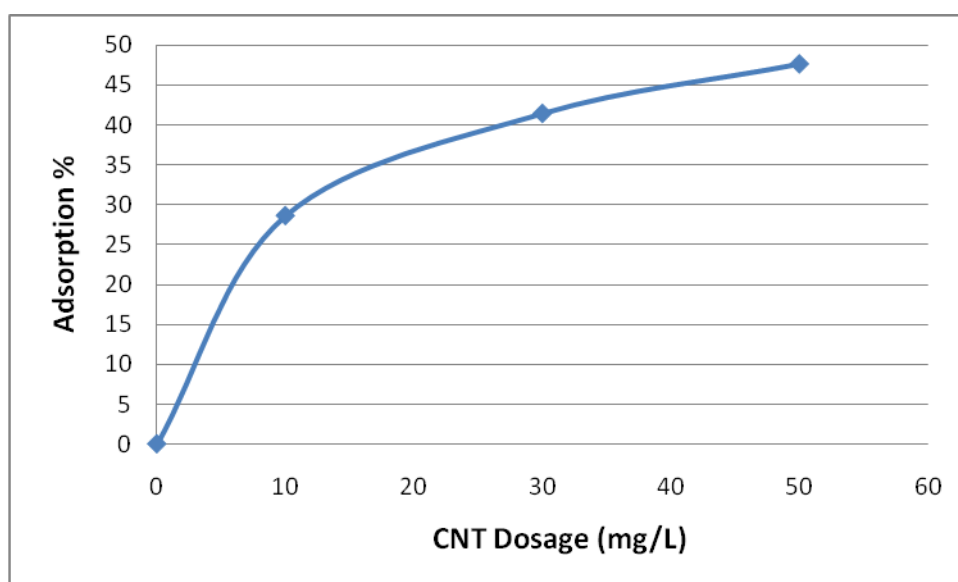


Figure (4.26) :The effect of CNTs dosage on percentage of adsorption of copper at $pH=3$, $C_0=30$ and time =60 min.

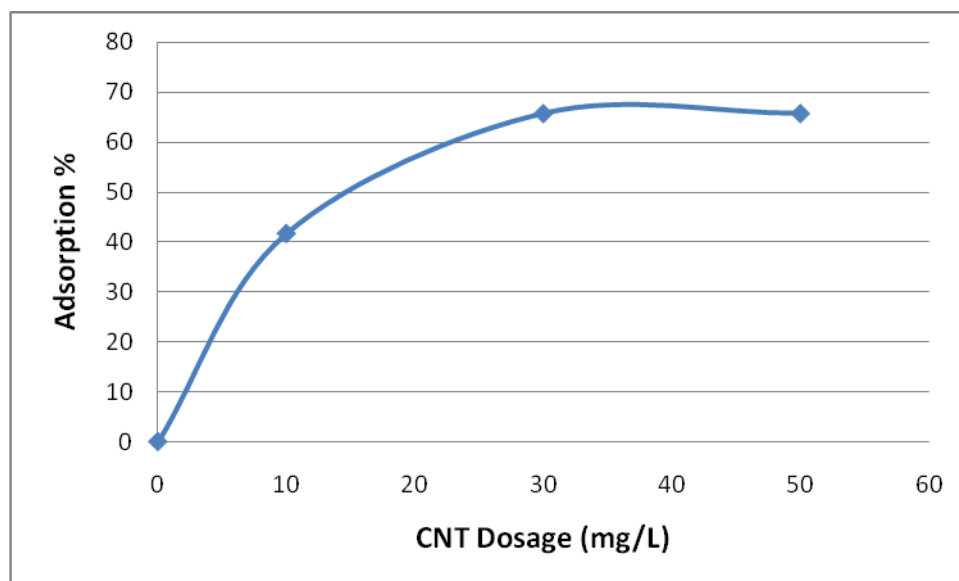


Figure (4.27) :The effect of CNTs dosage on percentage of adsorption of copper at $pH=3$, $C_0= 50$ and time =60 min.

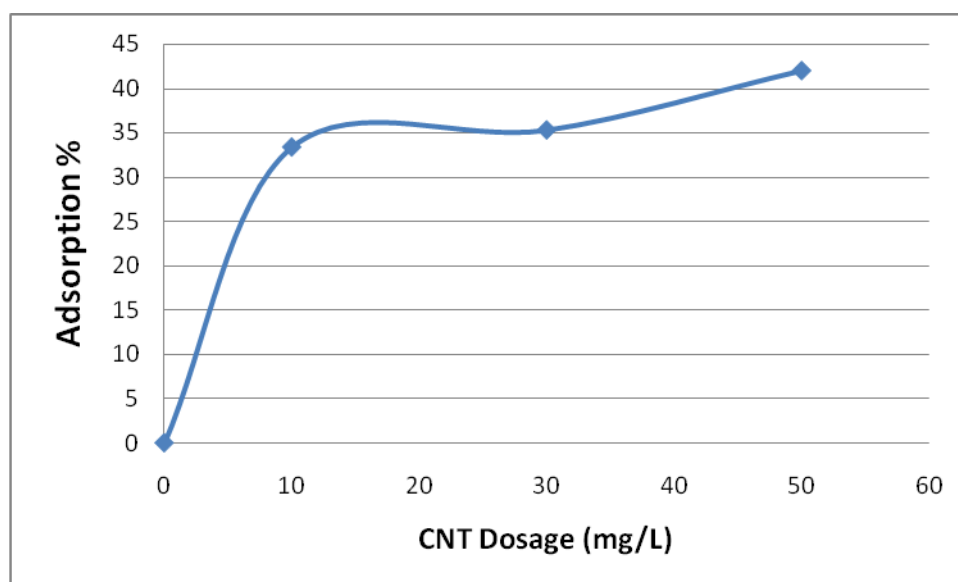


Figure (4.28) :The effect of CNTs dosage on percentage of adsorption of copper at $pH=5$, $C_0= 10$ and time =60 min.

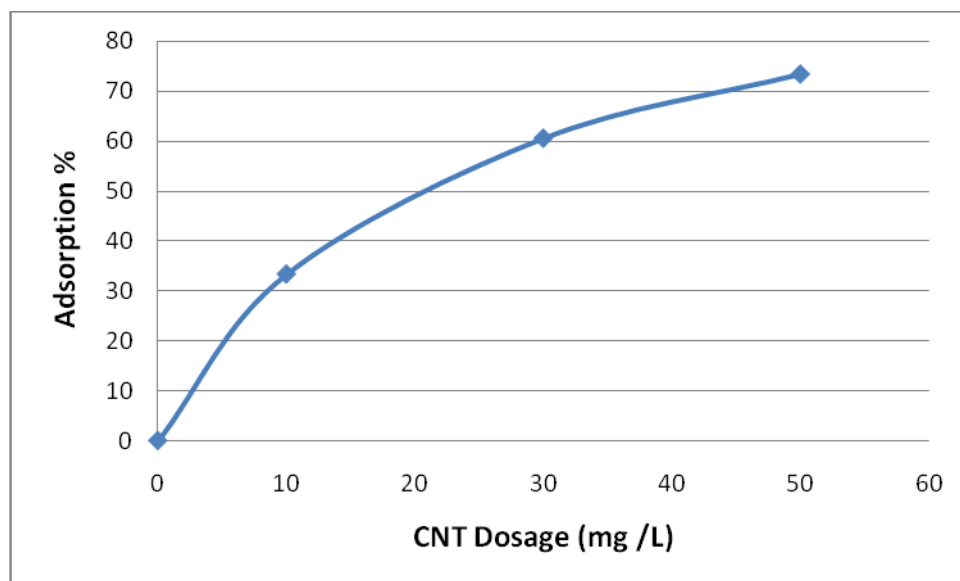


Figure (4.29) :The effect of CNTs dosage on percentage of adsorption of copper at pH=5, $C_0=30$ and time =60 min.

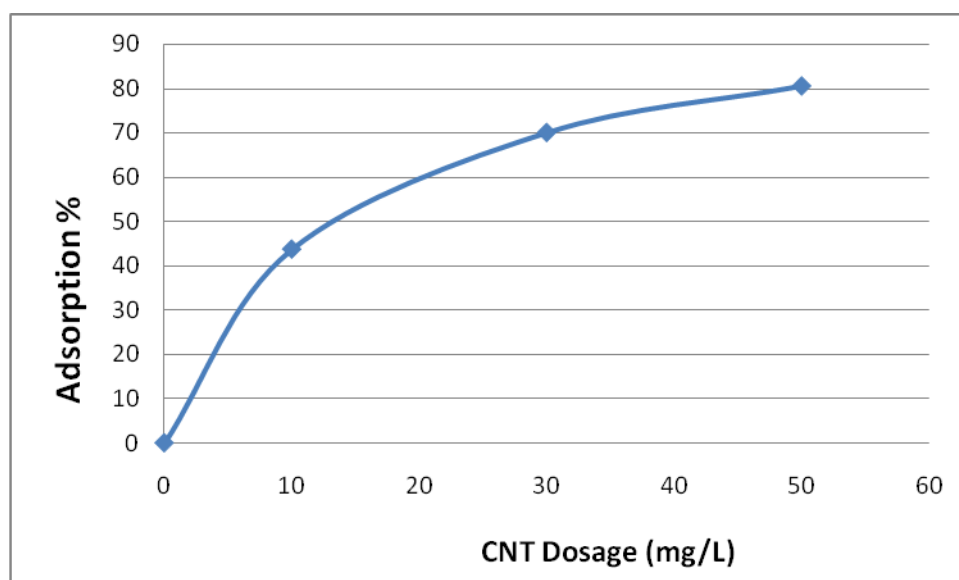


Figure (4.30) :The effect of CNTs dosage on percentage of adsorption of copper at pH=5, $C_0=50$ and time =60 min.

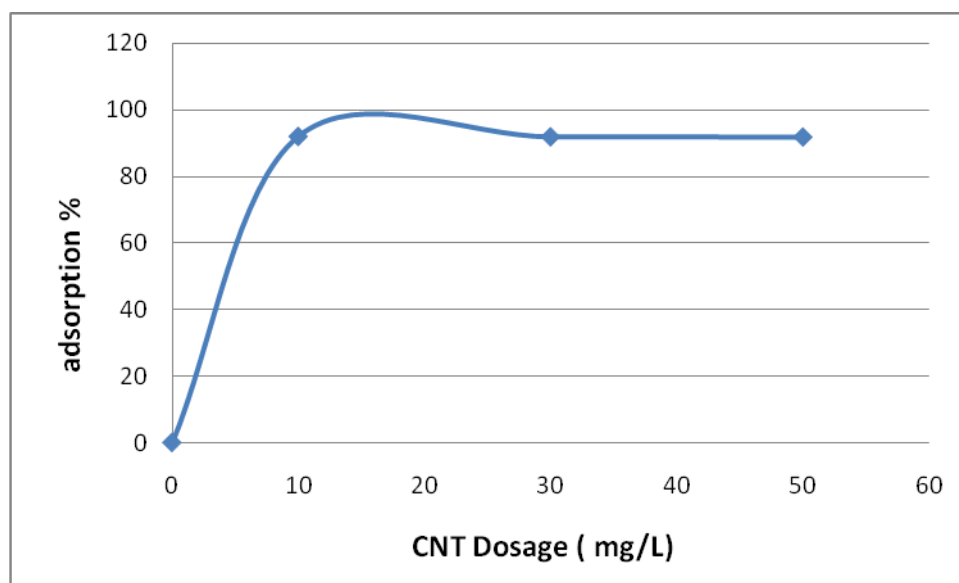


Figure (4.31) :The effect of CNTs dosage on percentage of adsorption of copper at pH=8, $C_0=10$ and time =60 min.

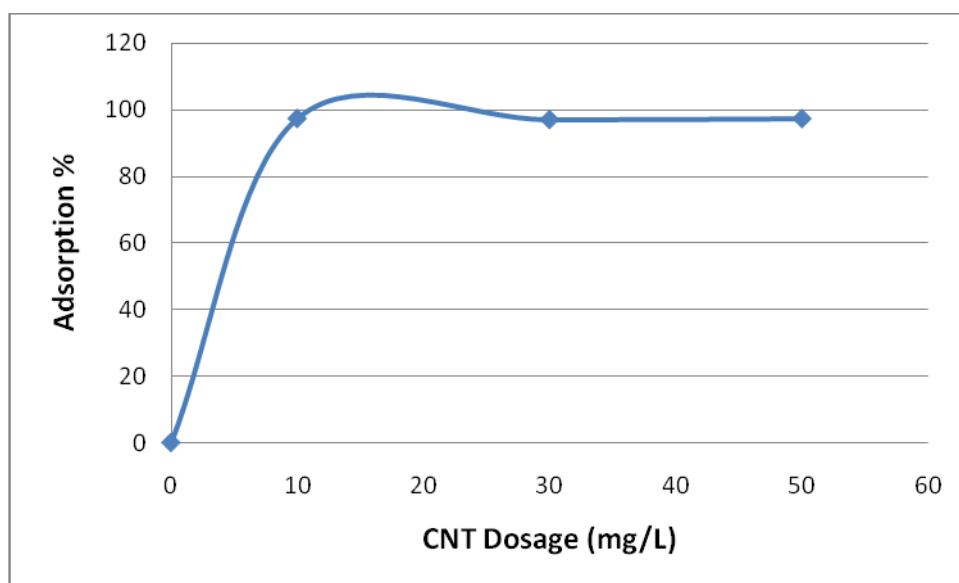


Figure (4.32) :The effect of CNTs dosage on percentage of adsorption of copper at pH=8, $C_0=30$ and time =60 min.

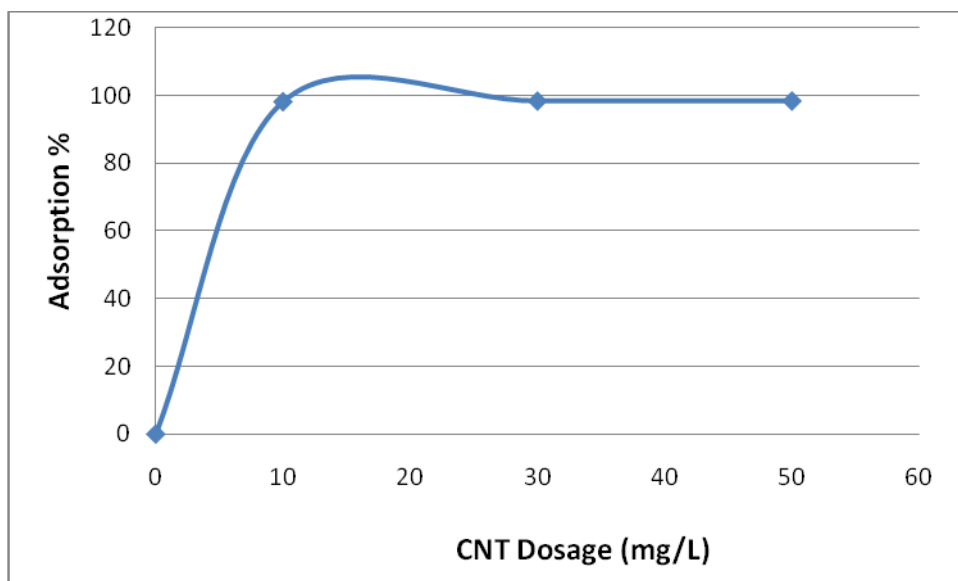


Figure (4.33) :The effect of CNTs dosage on percentage of adsorption of copper at $pH=8$, $C_0= 50$ and time =60 min.

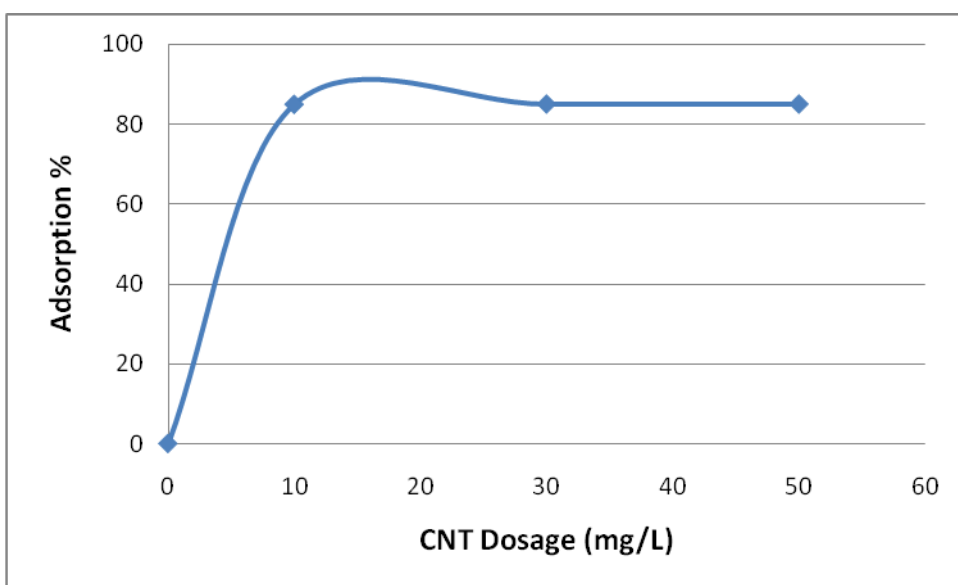


Figure (4.34) :The effect of CNTs dosage on percentage of adsorption of copper at $pH=12$, $C_0= 10$ and time =60 min.

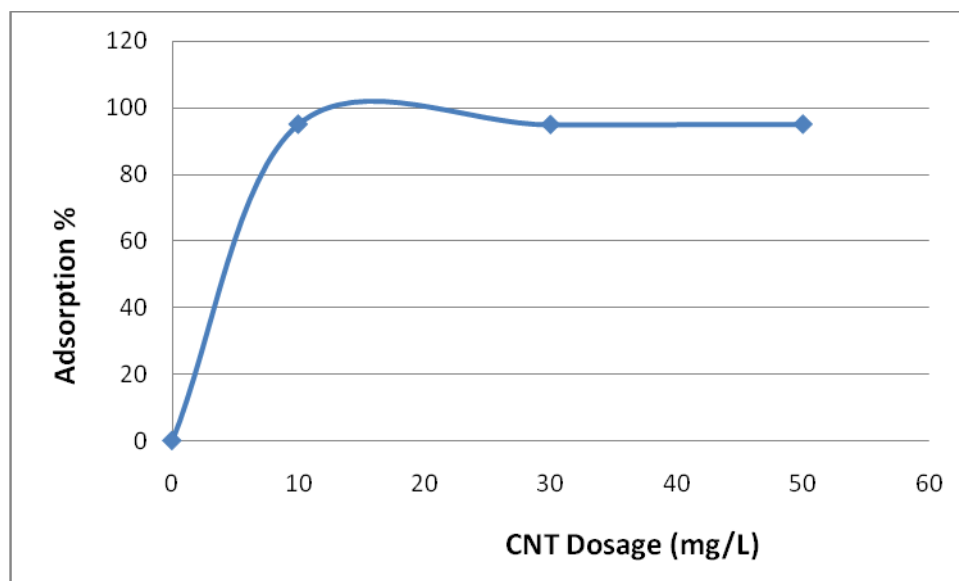


Figure (4.35) :The effect of CNTs dosage on percentage of adsorption of copper at $pH=12$, $C_0=30$ and time =60 min.

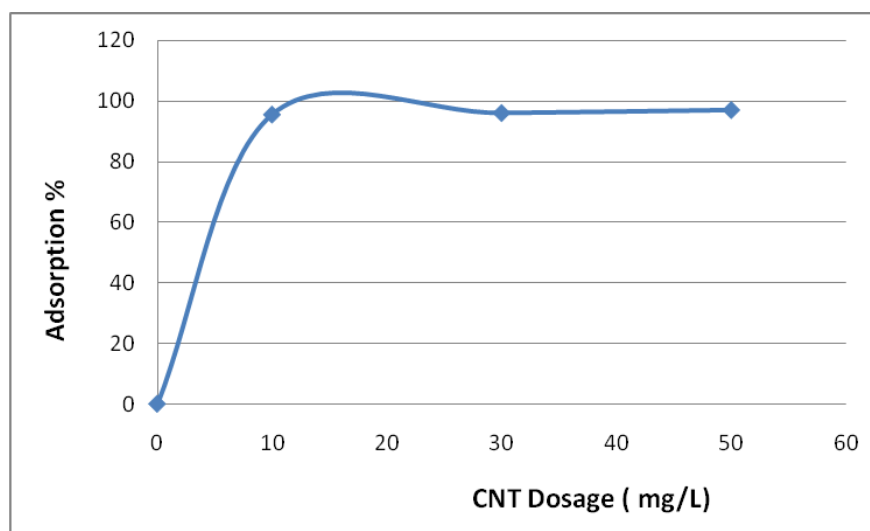


Figure (4.36) :The effect of CNTs dosage on percentage of adsorption of copper at $pH=12$, $C_0=50$ and time =60 min.

4-2-4 Effect of Copper Concentration

Various concentrations of Cu^{+2} solutions of (10, 30, 50) ppm were used to study their effect on the percentage removal of Cu^{+2} keeping the other parameters constant.

Figs.(4.37) to (4.48) show the percentage removal of Cu^{+2} at different concentration. It is clearly shown that the percentage removal of Cu^{+2} increases by increasing the concentration using the same dosage of CNTs. More metal ions were left unadsorbed in the solution due to saturation of the binding sites. The higher adsorption was at pH=8 as shown in Figs.(4.43) to (4.45).

Metal ion adsorption is attributed to different mechanisms of ion exchange as well as to the adsorption. This effect on ion adsorption can be explained, as follows at low metal ion/adsorbent ratios, metal ion adsorption involves more energy sites. As metal ion/adsorbent ratio increases, more energy sites are saturated and adsorption begins on fewer energy sites, resulting in low increasing of metal ion adsorption.

These results are in good agreement with the results obtained by Omid Moradi, who found that the adsorption percentage increases with increasing the initial concentration for copper^[28].

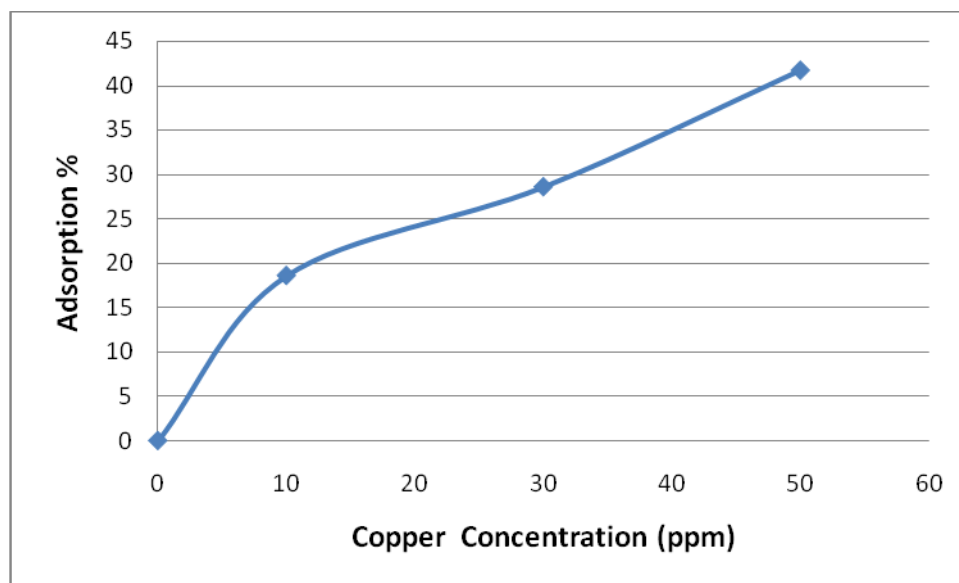


Figure (4.37) :The percentage removal of Cu^{+2} at different concentrations (ppm), pH=3, contact time=60 min and CNT dosage= 10 (mg/ L).

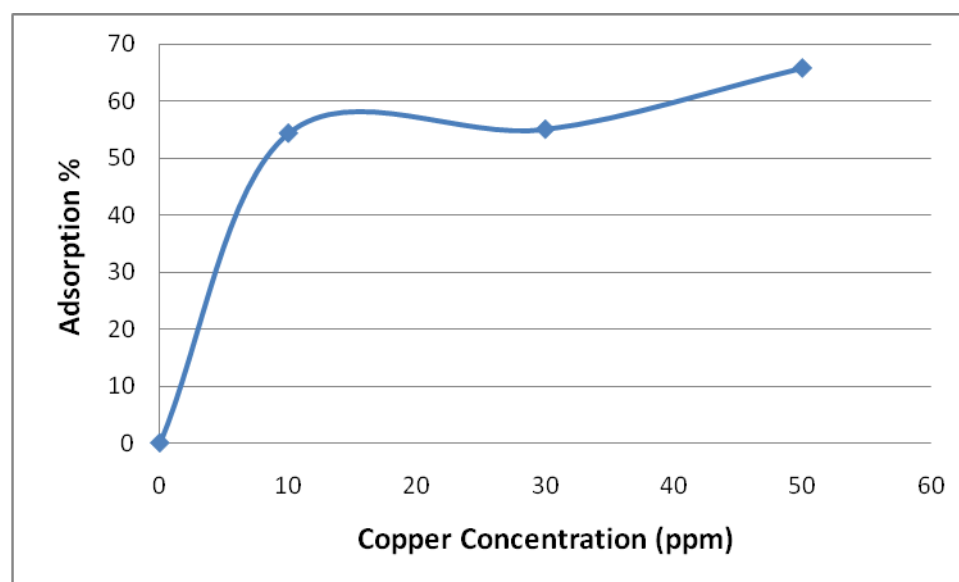


Figure (4.38) :The percentage removal of Cu^{+2} at different concentrations (ppm), pH=3, contact time=60 min and CNT dosage= 30 (mg/ L).

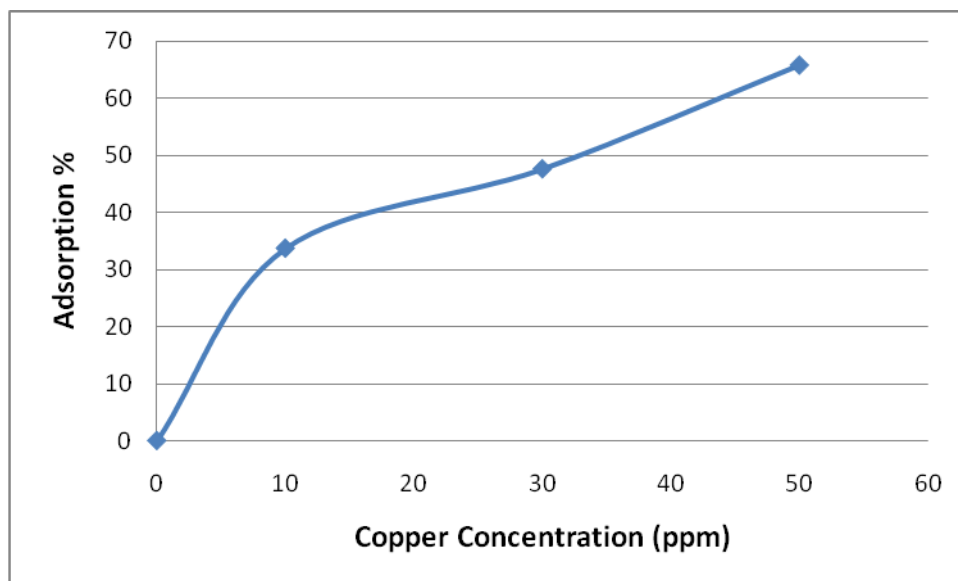


Figure (4.39) :The percentage removal of Cu^{+2} at different concentrations (ppm), pH=3, contact time=60 min and CNT dosage=50 (mg/ L).

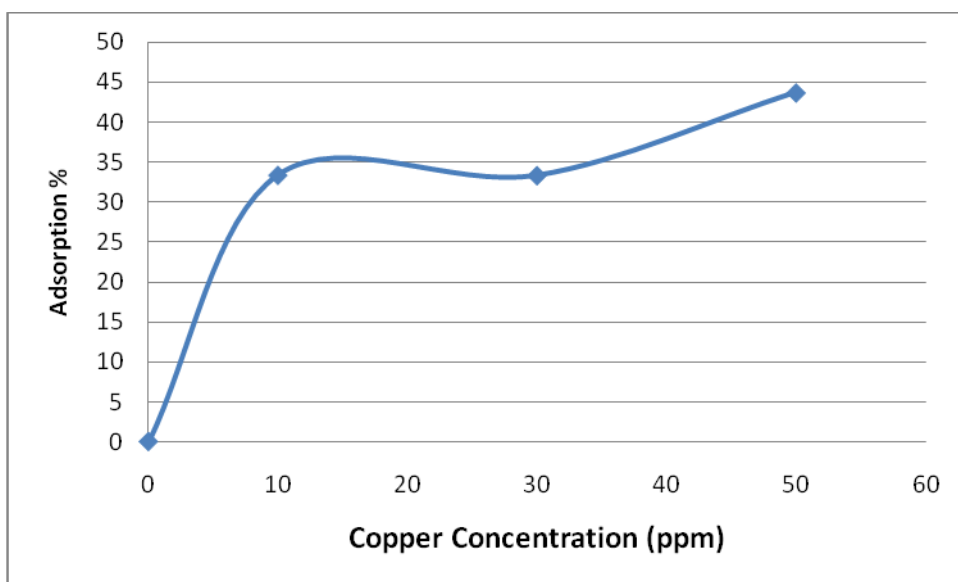


Figure (4.40) :The percentage removal of Cu^{+2} at different concentrations (ppm), pH=5, contact time=60 min and CNT dosage=10 (mg/ L).

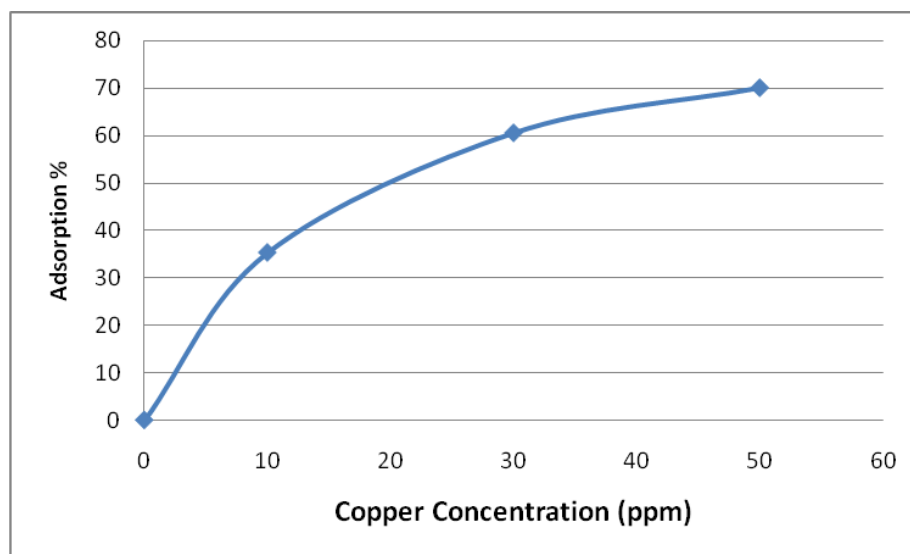


Figure (4.41) :The percentage removal of Cu^{+2} at different concentrations (ppm), pH=5, contact time=60 min and CNT dosage=30 (mg/ L).

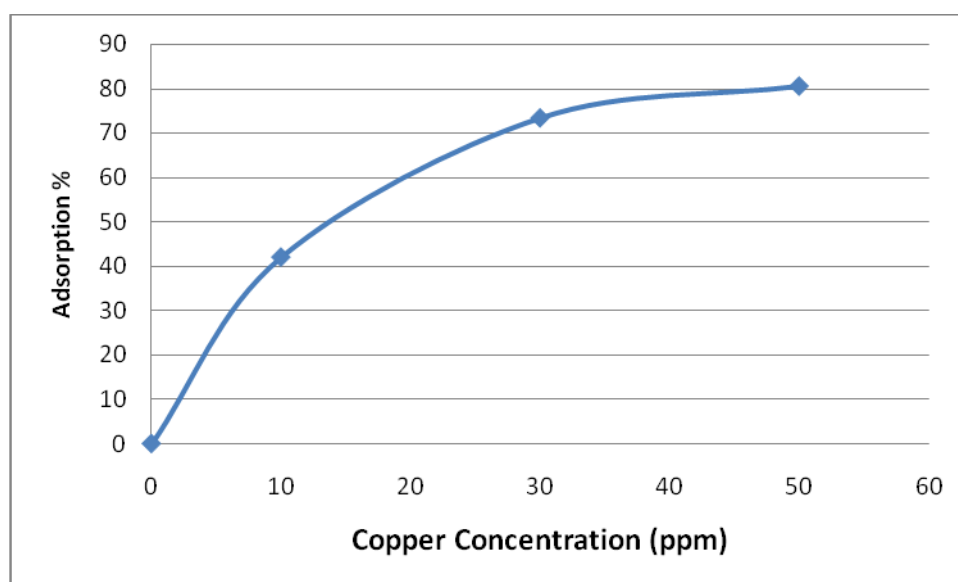


Figure (4.42) :The percentage removal of Cu^{+2} at different concentrations (ppm), pH=5, contact time=60 min and CNT dosage=50 (mg/ L).

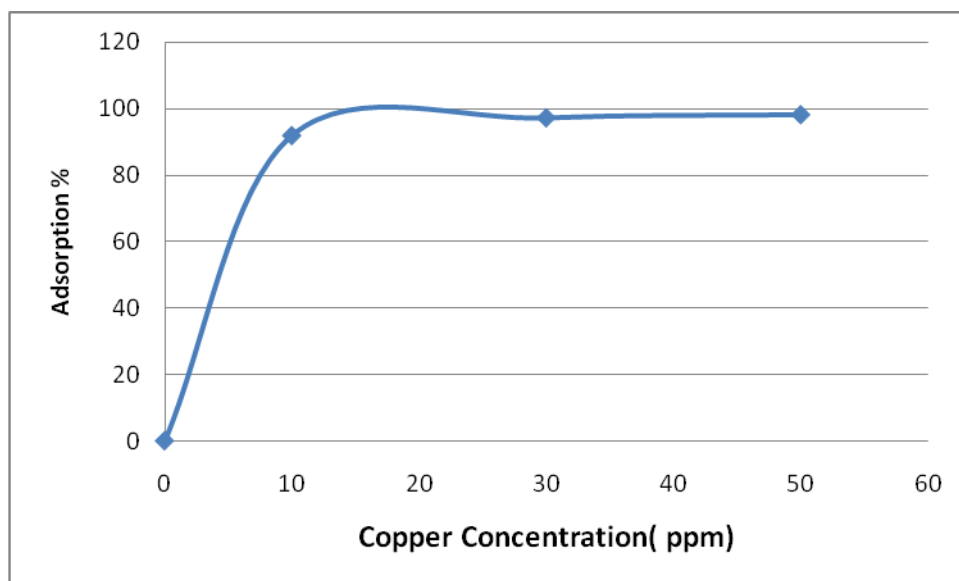


Figure (4.43) :The percentage removal of Cu^{+2} at different concentrations (ppm), $\text{pH}=8$, contact time=60 min and CNT dosage= 10 (mg/ L).

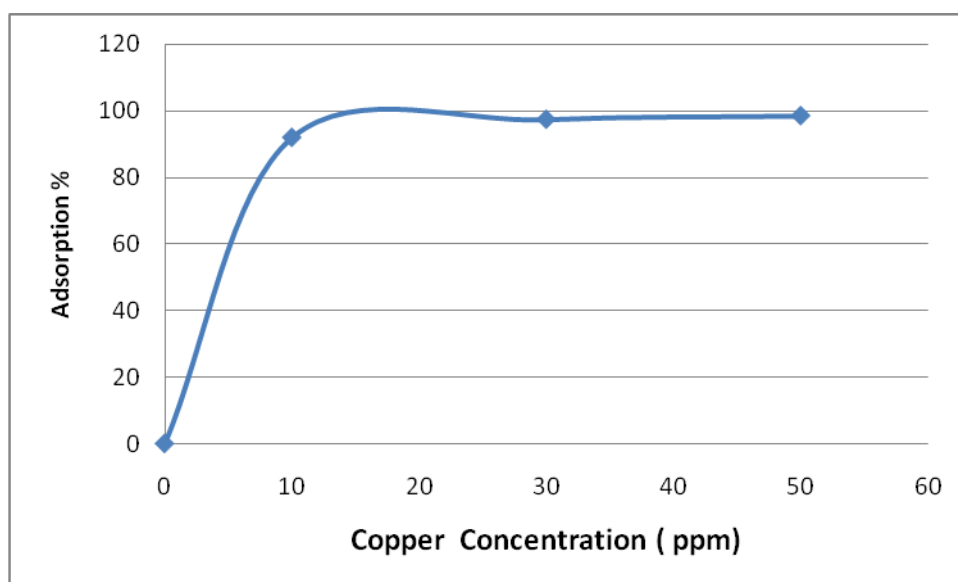


Figure (4.44) :The percentage removal of Cu^{+2} at different concentrations (ppm), $\text{pH}=8$, contact time=60 min and CNT dosage= 30 (mg/ L).

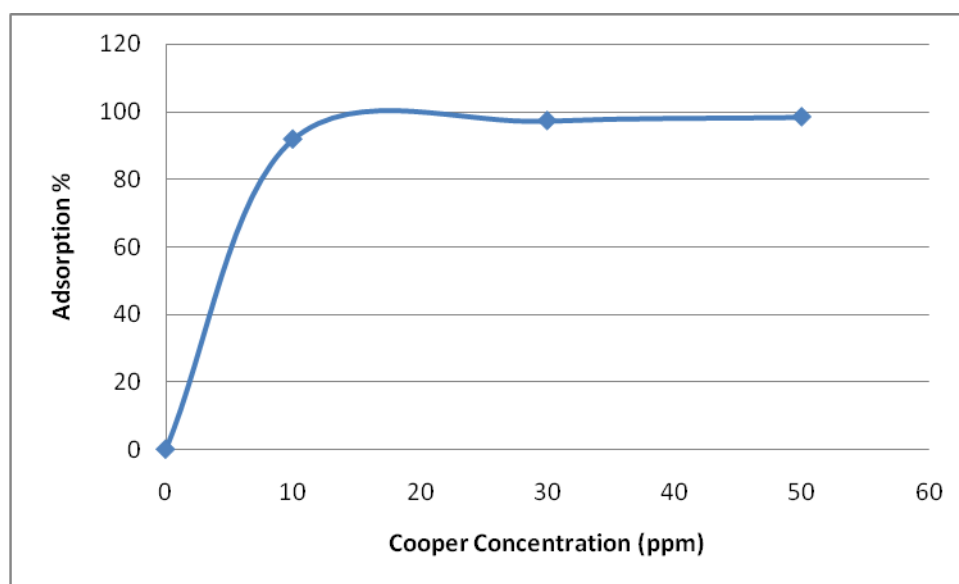


Figure (4.45) :The percentage removal of Cu^{+2} at different concentrations (ppm),pH=8,contact time=60 min and CNT dosage=50 (mg/ L).

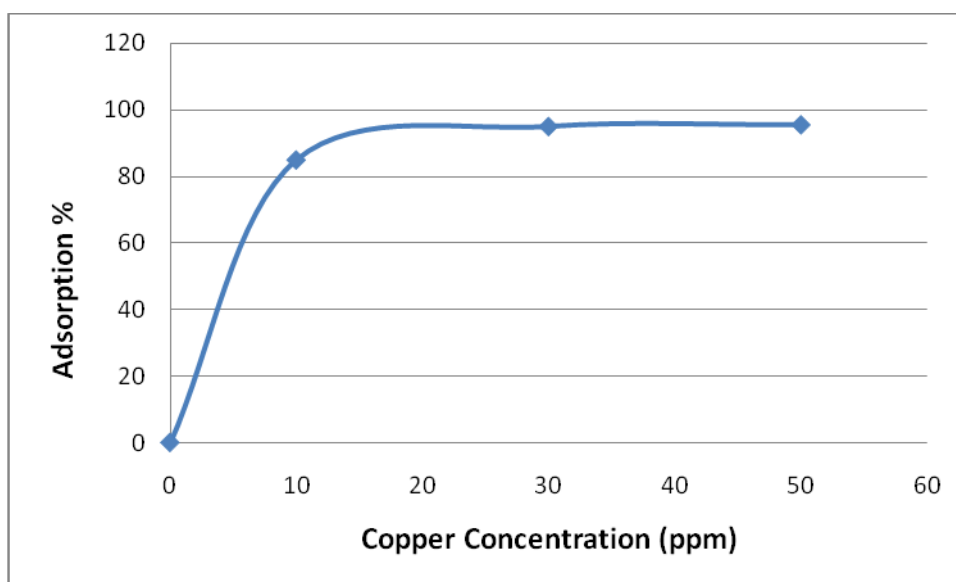


Figure (4.46) :The percentage removal of Cu^{+2} at different concentrations (ppm),pH=12,contact time=60 min and CNT dosage=10 (mg/ L).

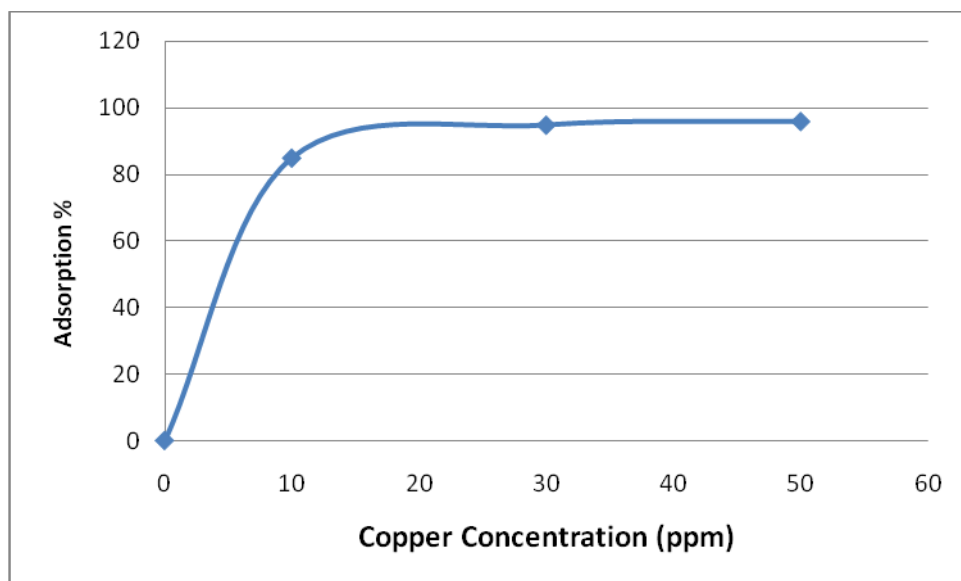


Figure (4.47) :The percentage removal of Cu^{+2} at different concentrations (ppm), pH=12, contact time=60 min and CNT dosage=30 (mg/ L).

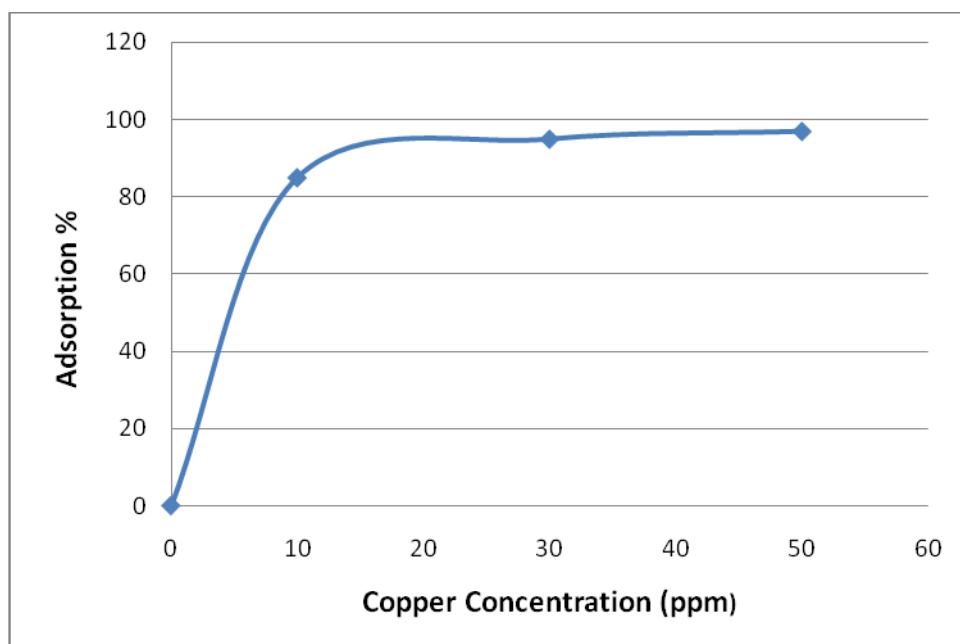


Figure (4.48) :The percentage removal of Cu^{+2} at different concentrations (ppm), pH=12, contact time=60 min and CNT dosage=50 (mg/ L).

4-3 Adsorption Isotherms

The distribution of adsorbates between aqueous phase and adsorbent is a measure of the position of equilibrium in an adsorption process and can be investigated through various models such as the Langmuir and Freundlich isotherms. The linear forms of the two models are^[60]:

$$\text{Langmuir} \quad \frac{C}{q} = \frac{1}{(K_L q_m)} + \frac{C}{q_m}, \quad \text{----- (4.1)}$$

$$\text{Freundlich} \quad \log q = \frac{1}{n} \log C + \log K_F \quad \text{----- (4.2)}$$

The equilibrium adsorption is important in the design of adsorption systems. Equilibrium studies in adsorption indicate the capacity of the adsorbent during the treatment process. It should taking into account that the percentage removal is the highest at pH=8.

The Langmuir isotherm equation is used to estimate the maximum adsorption capacity of the CNTs under the conditions of 298⁰K, pH 8.0, 1hour contact time and 30 gm/L adsorbent dose while varying initial Cu⁺² concentration from 10 to 50 mg/L. The values of the isotherm constants and R² are given in Table (A.13). The linear plot Fig.(4.49) of C/q versus C along with low value correlation coefficient indicates that Langmuir isotherm provides a poor fit with the equilibrium data.

The adsorption data when fitted to the Freundlich isotherm i.e. the plot of log (q) versus log (C) Fig.(4.50) ,shows that Langmuir isotherm gives a poor fit to the experimental data as compared to Freundlich isotherm.

The isotherm parameters as derived from the slope and intercept of the plots are listed in Table (A.13).

The values of the isotherm constants and R^2 are given in Table (A.13). The linear plot Fig.(4.49) of C/q versus C along with low value of correlation coefficient indicates that Langmuir isotherm provides a poor fit with the equilibrium data. The adsorption data when fitted to the Freundlich isotherm i.e. the plot of $\log(q)$ versus $\log(C)$ Fig.(4.50) shows that Freundlich isotherm gives a better fit to the experimental data as compared to Langmuir isotherm.

When Langmuir and Freundlich isotherms are compared, Freundlich Isotherm shows better fitting model with higher correlation coefficient of ($R^2 = 1$) compared Langmuir Isotherm of ($R^2 = 0.75$). Therefore, this indicates the applicability of monolayer coverage of Cu(II) ions to the surface of the adsorbent. This is due to the fact that CNTs have greater surface area for metal adsorption. The good correlation coefficient of Freundlich isotherm also indicates that Cu(II) ions strongly adsorb to the surface of CNTs. Therefore, it is verified that CNTs have great potential to be a good adsorbent for the removal of Cu(II) ions in water treatment.

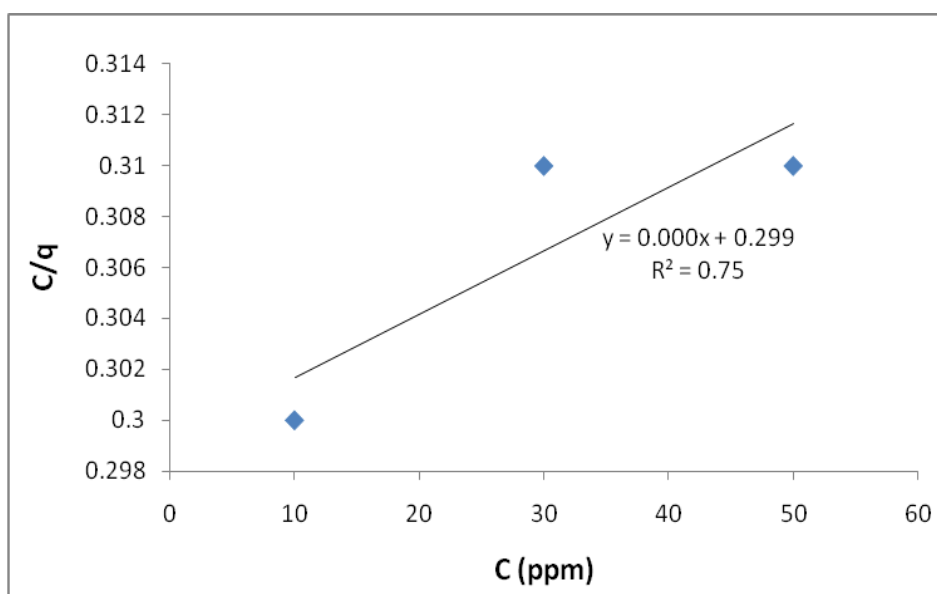


Figure (4.49): Adsorption isotherm Langmuir model for copper (II) .

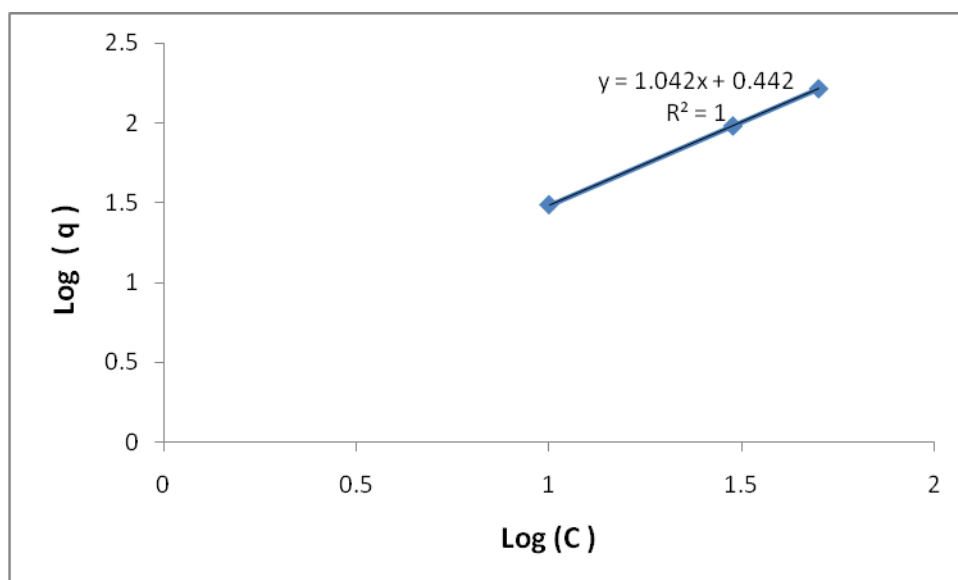


Figure (4.50): Adsorption isotherm Freundlich model for copper (II) .

The essential characteristics of Langmuir isotherm can be described by a separation factor or equilibrium constant R_L , which is defined as:

$$R_L = (1 + K_L \cdot C_0)^{-1} \quad \text{-----(4.3)}$$

The separation factor R_L indicates the isotherm shape and whether the adsorption is favorable or not, as per the criteria given below.

R_L values	Adsorption
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

From calculation, $R_L = 0.985, 0.957, 0.93$ for initial concentration of metal (10, 30, 50) ppm, respectively. values lie between 0 and 1 for all three concentrations, it is seen that the adsorption of heavy metal ions is favorable.

Chapter Five

Conclusions and Recommendations

5-1 Conclusions

From this study, the following main conclusions can be obtained:

1. The carbon nanotubes which was prepared in this study was found to be efficient for the adsorption of Cu^{+2} in aqueous solution.
2. Characterization of CNTs by SEM spectroscopy shows a domination of CNTs structure.
3. Functionalization of CNTs identified by FTIR clearly is shows the presence of functional groups of (-COOH) at 1701.22 cm^{-1} as well as hydroxyl groups. Such groups offer free active sites and consequently increase cation exchange capacity.
4. In general, the adsorption of Cu^{+2} onto CNTs increases with the increase in pH range from pH=1 to pH=8, reaches a maximum in the pH range of 8 and decreases at a pH of 12. The contact time to reach equilibrium is 60 min for CNTs. The percentage of removal increases with increase in the contact time. The maximum percentage of adsorption at pH= 8, CNT= 50 mg/L is 98.39%.
5. Removal percentage increases with increase in CNTs dosage and Initial concentration. Short time is needed to reach equilibrium as well as the high adsorption.
6. Freundlich adsorption model is better fitted for the adsorption of Cu(II), the good correlation coefficient of Freundlich isotherm indicates that Cu^{+2} ions are strongly adsorbed to the surface of CNTs.

5-2 Recommendations for Further Study

The researcher puts forward the following future study:

1. Studying parameters which affect yield of CNTs production process.
2. Studying parameters which affect CNTs purification, functionalization and ionic strength.
3. Removal of other heavy metals like Zn^{+2} , Pb^{+2} and Hg^{+2} .
4. Studying other parameter which affect removal percentage of Cu^{+2} such as solution temperature.
5. Using TEM technique to identify the type of CNTs.

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Appendix A

Table (A.1): The value of initial Cu^{+2} concentration C_0 (mg/l) vs time (min) at $pH=3$ and $CNT=10$ (mg/ L).

Time (min)	$C_0=10$		$C_0=30$		$C_0=50$	
	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)
0	0	0	0	0	0	0
10	2.86	2.87	4.76	14.3	31.886	159.43
20	18.6	15.7	14.33	43	34.92	174.6
30	18.6	15.7	28.6	85.8	41.72	208.6
40	18.6	15.7	28.6	85.8	41.72	208.6
50	18.6	15.7	28.6	85.8	41.72	208.6
60	18.6	15.7	28.6	85.8	41.72	208.6

Table (A.2): The value of initial Cu^{+2} concentration C_0 (mg/l) vs time(min) at $pH=3$ and $CNT=30$ (mg/ L).

Time (min)	$C_0=10$		$C_0=30$		$C_0=50$	
	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)
0	0	0	0	0	0	0
10	14.3	4.16	10	10	51.44	85.73
20	23	7.659	18.2	18.18	54.286	91.34
30	42.86	14.27	41.14	41.125	65.72	109.42
40	54.3	18.082	41.14	41.125	65.72	109.42
50	54.3	18.082	41.14	41.125	65.72	109.42
60	54.3	18.082	41.4	41.125	65.72	109.42

Table (A.3):The value of initial Cu^{+2} concentration C_0 (mg/l) vs time(min) at $pH=3$ and $CNT = 50(mg/ L)$.

Time (min)	$C_0=10$		$C_0=30$		$C_0=50$	
	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)
0	0	0	0	0	0	0
10	10	20	33.33	20	42.12	42.12
20	14.3	25.72	42.8	25.72	40.58	40.58
30	33.7	25.72	47.6	25.72	65.72	65.72
40	33.7	25.72	47.6	25.72	65.76	65.72
50	33.7	25.72	47.6	25.72	65.76	65.72
60	33.7	25.72	47.6	25.72	65.76	65.72

Table (A.4):The value of initial Cu^{+2} concentration C_0 (mg/l) vs time (min) at $pH=5$ and $CNT=10(mg/ L)$.

Time (min)	$C_0=10$		$C_0=30$		$C_0=50$	
	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)
0	0	0	0	0	0	0
10	33.25	33.25	16.66	50	33	165
20	33.375	33.375	18.33	55	37	185
30	33.375	33.375	33.33	100	43.7	218.5
40	33.375	33.375	33.33	100	43.7	218.5
50	33.375	33.375	33.33	100	43.7	218.5
60	33.375	33.375	33.33	100	43.7	218.5

Table(A.5):The value of initial Cu^{+2} concentration C_0 (mg/l) vs time (min) at $pH=5$ and $CNT=30(mg/L)$.

Time (min)	$C_0=10$		$C_0=30$		$C_0=50$	
	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)
0	0	0	0	0	0	0
10	10	3.33	12	11.988	33	56.61
20	15.2	5.0616	25	25	40	66.6
30	25.07	8.348	50.5	50.45	41	68.265
40	35.3	11.755	60.5	60.44	70	116.55
50	35.3	11.755	60.5	60.44	70	116.55
60	35.3	11.755	60.5	60.44	70	116.55

Table (A.6):The value of initial Cu^{+2} concentration C_0 (mg/l) vs time (min) at $pH=5$ and $CNT =50(mg/L)$.

Time (min)	$C_0=10$		$C_0=30$		$C_0=50$	
	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)
0	0	0	0	0	0	0
10	11.2	2.24	22	13.2	30	30
20	17.77	3.55	23	13.8	40	40
30	26.7	5.34	66.66	40	43	43
40	23.4	4.6	73.33	44	80.5	80.5
50	40.5	8.1	73.33	44	80.5	80.5
60	42	8.4	73.33	44	80.5	80.5

Table (A.7): The value of initial Cu^{+2} concentration C_0 (mg/l) vs time (min) at $\text{pH}=8$ and $\text{CNT}=10(\text{mg/L})$.

Time (min)	$C_0=10$		$C_0=30$		$C_0=50$	
	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)
0	0	0	0	0	0	0
10	91.985	91.982	97.3	291.97	98.27	491.35
20	91.985	91.982	97.32	291.97	98.27	491.35
30	91.985	91.982	97.32	291.97	98.27	491.35
40	91.985	91.982	97.32	291.97	98.27	491.35
50	91.985	91.982	97.32	291.97	98.27	491.35
60	91.985	91.982	97.32	291.97	98.27	491.35

Table (A.8): The value of initial Cu^{+2} concentration C_0 (mg/l) vs time (min) at $\text{pH}=8$ and $\text{CNT}=30(\text{mg/L})$.

Time (min)	$C_0=10$		$C_0=30$		$C_0=50$	
	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)
0	0	0	0	0	0	0
10	91.79	30.6	97.3	96.33	98.39	164
20	91.8	30.568	97.3	96.33	98.39	164
30	91.87	30.57	97.3	96.33	98.39	164
40	91.87	30.57	97.3	96.33	98.39	164
50	91.87	30.57	97.3	96.33	98.39	164
60	91.87	30.57	97.3	96.33	98.39	164

Table (A.9): The value of initial Cu^{+2} concentration C_0 (mg/l) vs time (min) at $\text{pH}=8$ and $\text{CNT}=50(\text{mg/L})$.

Time (min)	$C_0=10$		$C_0=30$		$C_0=50$	
	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)	Ads. capacity (mg/g)	Ads.%
0	0	0	0	0	0	0
10	91.8	18.362	97.28	58.368	98.39	98.4
20	91.8	18.362	97.28	58.368	98.39	98.4
30	91.8	18.362	97.28	58.368	98.39	98.4
40	91.8	18.362	97.28	58.368	98.39	98.4
50	91.8	18.362	97.28	58.368	98.39	98.4
60	91.8	18.362	97.28	58.368	98.39	98.4

Table (A.10): The value of initial Cu^{+2} concentration C_0 (mg/l) vs time (min) at $\text{pH}=12$ and $\text{CNT}=10(\text{mg/L})$.

Time (min)	$C_0=10$		$C_0=30$		$C_0=50$	
	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)
0	0	0	0	0	0	0
10	84.89	85	95	285	95.5	477.5
20	84.93	84.925	95	285	95.5	477.5
30	84.93	84.925	95	285	95.5	477.5
40	84.93	84.925	95	285	95.5	477.5
50	84.93	84.925	95	285	95.5	477.5
60	84.93	84.925	95	285	95.5	477.5

Table (A.11): The value of initial Cu^{+2} concentration C_0 (mg/l) vs time (min) at $\text{pH}=12$ and $\text{CNT}=30(\text{mg/L})$.

Time (min)	$C_0=10$		$C_0=30$		$C_0=50$	
	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)
0	0	0	0	0	0	0
10	85	28.28	94.9	95	96	161.5
20	85	28.28	94.9	95	96	161.5
30	85	28.28	94.9	95	96	161.5
40	85	28.28	94.9	95	96	161.5
50	85	28.28	94.9	95	96	161.5
60	85	28.28	94.9	95	96	161.5

Table (A.12): The value of initial Cu^{+2} concentration C_0 (mg/l) vs time (min) at $\text{pH}=12$ and $\text{CNT}=50(\text{mg/L})$.

Time (min)	$C_0=10$		$C_0=30$		$C_0=50$	
	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)	Ads.%	Ads. capacity (mg/g)
0	0	0	0	0	0	0
10	84.75	16.95	95	57	97	97
20	85	17	95	57	97	97
30	85	17	95	57	97	97
40	85	17	95	57	97	97
50	85	17	95	57	97	97
60	85	17	95	57	97	97

Table (A.13): Coefficients of Langmuir and Freundlich isotherms.

Isotherm model	Correlation Coefficients R^2	Constants
Langmuir	0.75	$K_L = 0.0015$ (Langmiur constant) (L/mg) $q_m = 2222$ (maximum adsorption capacity) (mg/g)
Freundlich	1	$K_F = 3.1$ (Freundlich constant) (mg/g)(mg/L) ^{-1/n} n=1 (dimensionless)

AppendixB

Table B.1 Exothermic peak maxima, T_p , and total heat of reaction, ΔH_{tot} of DGEBA curing with aromatic amine

β ($^{\circ}\text{C min}^{-1}$)	T_p (K)	ΔH_{tot} (J/g)	Average ΔH_{tot} (J/g)
2.5	417	576	563.5
5	430	565	
8	440	559	
10	448	554	

Table B.2 Activation energy E_a of epoxy DGEBA with phenylenediamine from multiple scanning rate methods.

model	exponential factor	E_a (kJ mol^{-1})
Ozawa	21.36	70.7
kissinger	7.22	63.6

AppendixB

Table B.3 Data of $\ln(\beta)$ and T for DGEBA/m-phenylenediamine at different conversions.

β ($^{\circ}\text{C min}^{-1}$)	Conversion T (k)			
	0.2	0.4	0.6	0.8
10	425	436	446	459
8	416	427	435	447
5	407	417	426	437
2.5	397.5	406	414	425

Table B.4 activation energy of curing epoxy DGEBA with m-phenylenediamine at different conversion

Conversion	Ea (kJ/mol)
0.2	68
0.4	65.5
0.6	64.7
0.8	63.9

AppendixC

Table C.5 Total heat of reaction, ΔH_t of DGEBA curing with m-phenylenediamine from isothermal

T (°C)	ΔH (J/g)	ΔH average
110	507	475
100	493	
90	462	
80	439.5	

Table C.6. Time at maximum rate of reaction t_p and maximum rate of reaction r_p at different curing temperatures.

T (°C)	t_p (min)	r_p (s ⁻¹)
110	9.9	0.00075
100	17.5	0.00047
90	32	0.00029
80	48.9	0.00018

AppendixC

Table C.7. Kinetic parameters as determined from the autocatalytic kinetic model for epoxy (DGEBA) with m-phenylenediamineat various curing temperatures.

T (°C)	k_1 ($\times 10^5$ s^{-1})	k_2 ($\times 10^4$ s^{-1})	m	n	m+n	c
110	40.09	10.48	0.95	0.78	1.73	50.61
100	24.18	7.69	0.94	0.87	1.81	45.75
90	11.2	6.05	0.85	0.97	1.82	57.99
80	5.6	4.94	0.85	1.2	2.05	61.44
E_{a1} (kJ/mol)		$A_1(s^{-1})$	E_{a2} (kJ/mol)		$A_2(s^{-1})$	
75.31		15.877	28.12		1.9347	

Appendix D

Table D.8. Gel Time at Different Temperatures and the Activation Energy

Temperature (°C)	80	90	100	110
t_{gel} (sec)	2760	1200	810	300
E_a (KJ/mol)	79.07			
Pre-exponential factor (s^{-1})	9.19			

Table D.9. kinetic Parameters in viscosity model (2.28)

T (°C)	t_c (s)	k (s^{-1})
80	3600	0.23
90	1380	0.65
100	900	2
110	360	4.4
E_a (KJ/mol)	79.46	
Pre-exponential factor (s^{-1})	5.66	

AppendixE

Table E.10 Gelation and different cure temperatures obtained by rheological and thermal measurements

T (°C)	Gelation time(min) (rheology)	Gelation time(min) (DCS)
80	46	53
90	20	31
100	13.5	20
110	5	11

الخلاصة

يعتبر الكربون من الاصناف المهمة وواسعة الاستخدام في هندسة الممتزات. انابيب النانوكاربون له امكانيات عظيمة في التطبيقات.

في هذا العمل فأن انابيب النانوكاربون قد تم تحضيرها بطريقة الترسيب الكيميائي (CVD)، وتم دراسة قابليتها على امتزاز ايون النحاس من فضلات الماء. في منظومة (CVD) فقد تم انماء الانابيب النانوكربونية بتفكيك غاز الاستلين بمساعدة عامل مساعد بدرجة حرارة 750 مئوية ولمدة ساعة واحدة. كما استخدم غاز الاركون كمادة مانعة للتأكسد.

ان الانابيب النانوكاربونية المنتجة قد تم تنقيتها وتوظيفها كيميائيا بمعاملتها مع حامض النتريك. استخدمت تقنيات المجهر الالكتروني الماسح ومطياف الاشعة تحت الحمراء وتقنية قياس المساحة السطحية (BET).

لتشخيص انابيب النانوكاربون حيث تم الحصول على انابيب ذات اقطار بحدود 30 نانومتر واطوال تصل الى بضعة مايكرون. وكانت المساحة السطحية 53 (m^2/g). بينت تقنية (FTIR) ان انابيب النانوكاربون المحضر قد اظهر قمم امتصاص لمجموعة الكربوكسيل ما بين 1500 - 1700 (cm^{-1})، كما ظهرت اصرة كاربون- كاربون في منطقة الامتصاص 1554.3 (cm^{-1}) والعائدة الى انابيب النانوكاربون.

ان تأثير كل من : التركيز الابتدائي للمعدن (ppm)، مقياس ال pH، كميات الكربون النانوي (ملي غرام/لتر) و زمن التماس بالدقيقة على اداء عملية الامتزاز للكربون النانوي لأزالة معدن النحاس من فضلات الماء قد تم دراستها.

اظهرت النتائج ان (pH) واحد من اهم المتغيرات المسيطرة على امتزاز الايون على سطح الصلب – ماء. اعلى نسبة امتزاز للنحاس (II) عند pH=8، كمية الانابيب النانوكاربونية 50 (ملي غرام/لتر) والتركيز الابتدائي 50 (ppm) هو 98.39%.

إن ثوابت موديل لانكماير و فرنديل اخذت من قراءات عملية الامتزاز، وجد منها (correlation coefficients) لموديل لانكماير = 0.75 ولموديل فرنديل = 1، يُشير بأن موديل فرنديل أكثر ملائمة لوصف خصائص امتزاز Cu^{+2} في الكربون النانوي.



جمهورية العراق
وزارة التعليم العالي والبحث العلمي
الجامعة التكنولوجية
قسم الهندسة الكيميائية

أزالة النحاس(II) من فضلات الماء بأستخدام الكربون النانوي المعدل

أطروحة
مقدمة الى قسم الهندسة الكيميائية في الجامعة التكنولوجية
كجزء من متطلبات
نيل درجة ماجستير علوم في الهندسة الكيميائية

من قبل

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بأشراف

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أيلول
2012