



Ministry of Higher Education and
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University of Diyala
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**Preparation and Comparison of Carbon Nanotubes Produced By Flame
Deposition Method from Plant Sources and Adsorption Of Pb⁺²**

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Master of Science in Chemistry

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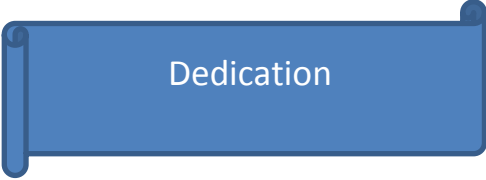
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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

"وانزل عليك الكتاب والحكمة
وعلمك ما لم تكن تعلم"

صدق الله العظيم
سورة النساء (١١٣)



Dedication

First of all I will dedicate this study to my Almighty God, who gave his strength and knowledge for me everyday life.

To my father

Mr. mohamad

and

Mrs. afrah

Whose affection, love, encouragement and prays of day and night make me able to get such success and honor, along with all hard working and respected Teachers.

To my brothers and sister, Abdullah, Noor, and Qusai for their eternal love.

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Supervisor Certification

I certify that this thesis (**Preparation and Comparison of Carbon Nanotubes Produced By Flame Deposition Method from Plant Sources and Adsorption Of Pb⁺²**) was carried out under our supervision in Chemistry Department, College of Education for Pure Science, Diyala University in partial fulfillment of the requirement for the degree of master of science in chemistry by the student.(**Athraa Mohamed Rashed**).

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ABSTRACT

In this study, multi walled carbon nano tubes were prepared by Chemical Flame Deposition Method (CFDM) from stem a Citrus aurantium and morus in Diyala province. The nano CuO was prepared by simple method using lemon leaves extract and copper chloride hexahydrate ($\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$) (source of copper) with calcination at temperature at $550\text{ }^\circ\text{C}$. The Multi-Walled Carbon Nano Tubes (MWCNTs) and nano CuO as a binary composite were prepared by mixing a certain different ratio of MWCNTs and copper oxide nanoparticles by ultrasonic water bath.

FTIR spectroscopy, Raman spectroscopy, X-ray diffraction and Field-Emission Scanning Electron Microscope techniques (FESEM) were used to characterize the synthesized compounds.

Raman spectra revealed that many observed peaks on all MWCNTs prepared samples belong to D band at 1359 cm^{-1} and 1436 cm^{-1} , G band at 1444 cm^{-1} and 1582 cm^{-1} . XRD spectra reveals average particle size obtained is about (37.8) nm for CuO nanoparticle which agreed fairly well with FESEM.

Water pollution with heavy metal lead ion (Pb^{+2}) is a major damage environment. Therefore the MWCNTs, nano CuO and MWCNTs/ CuO prepared to remove lead ion from polluted water. In this field, many factors have been studied that affect the percentage removal of lead ion such as contact time, adsorbent quantity and temperature. The time required to remove (Pb^{+2}) ion to reach equilibrium was (40) min and the maximum removal of Pb^{+2} ion on the were MWCNTs of Citrus aurantium active and MWCNTs of morus active about (71%) is much higher than those on other adsorbents. The removal of lead ion was found to be well and increase with increasing the contact time and adsorbent quantity while, it reduced with increase temperature, which means

that the process is exothermic, and agreed with thermodynamic functions values.

The experimental data were fitted into the following kinetic models: pseudo-first order, pseudo-second order and intra-particle diffusion model. It was observed that pseudo-second order describe the adsorption with high correlation factor (R^2) better than any other kinetic models.

Calculated values of the thermodynamic functions (ΔG , ΔH , ΔS) of the adsorption declare that it is spontaneous, exothermic and randomness at lead ion on samples prepared.

Finally Langmuir isotherm was found to be the best one which can describe adsorption the Pb^{+2} , all these were noted from the correlation coefficients values. Langmuir isotherm was better than Dubinin–Radushkevich isotherm.

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List of Symbols and Abbreviations

Symbol or Abbreviation	Definition
A	Langmiur Constant related with Adsorption Capacity
AAS	Atomic Absorption Spectrophotometer
Avg	Average
B	Langmuir Constant related with Energy of Adsorption
C_0	Initial Concentration of Adsorbate
C_e	Equilibrium Concentration of Adsorbate
C_t	Concentration of Adsorbate after any Time
D	Crystallite Size
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
IR	Infrared Spectroscopy
K	Thermodynamic Equilibrium Constant
K	Equilibrium Constant
k_1	Pseudo-First Order Constant
k_2	Pseudo-Second Order Constant
k_i	Diffusion Constant
M	Weight of adsorbent
min	Minute
MWCNTsc	Multi Walled Carbon Nano Tubes citrus aurantium
MWCNTsca	Multi Walled Carbon Nano Tubes citrus aurantium activated
MWCNTsm	Multi Walled Carbon Nano Tubes morus
MWCNTsma	Multi Walled Carbon Nano Tubes morus activated
q_e	Quantity of adsorbate at equilibrium
LE	Lemon Extract
q_t	Quantity of adsorbate at any time
R	Gas constant
R%	Percentage removal of adsorbate
R^2	Correlation coefficient
T	Temperature

$t^{1/2}$	Square root of the Time
V	Volume of Solution
wt%	Weight Percentage
XRD	X-ray Diffraction
ΔG	Gibbs free Energy
ΔH	Enthalpy
ΔS	Entropy
Θ	Bragg's angle

Chapter One

(Introduction)

1.1. General Introduction

Nanotechnology is one of the most promising technologies of the 21st century. It is the ability to convert the nanoscience theory to useful applications by observing, measuring, manipulating, assembling, controlling and manufacturing matter at the nanometer scale. The National Nanotechnology Initiative (NNI) in the United States define Nanotechnology as “a science, engineering, and technology conducted at the nanoscale (1 to 100 nm), where unique phenomena enable novel applications in a wide range of fields, from chemistry, physics and biology, to medicine, engineering and electronics.”^[1] This definition suggests the presence of two conditions for nanotechnology.^[2]

The first is an issue of scale: nanotechnology is concerned to use structures by controlling their shape and size at nanometer scale. The second issue has to do with novelty: nanotechnology must deal with small things in a way that takes advantage of some properties because of the nanoscale. Here, it is important to distinguish between nanoscience and nanotechnology.^[3]

Nanoscience is a convergence of physics, materials science and biology, which deal with manipulation of materials at atomic and molecular scales; while nanotechnology is the ability to observe measure, manipulate, assemble, control, and manufacture matter at the nanometer scale.^[4]

Nanoparticles (NPs) are classified as a material in which at least one dimension is $<100\text{ nm}$ ^[5]. NPs are not new to the environment and occur naturally in the form of minerals, clays, and products of bacteria. Engineered nanoparticles are designed to have the properties which are not present in bulk samples of the same materials. Engineered nanoparticles are composed of a variety of materials and occur in different sizes and shapes with a suite of synthetic surface molecules, which makes them distinct from naturally

occurring materials. Metal and metal oxides nanoparticles exhibit different physiochemical properties are different than their native bulk compounds in several respects such as surface, optical, thermal, and electrical properties. Metal and metal oxide nanoparticles can be manufactured by addition of reducing or oxidizing/precipitating agents during their synthesis, respectively^[6].

Green chemistry is a modern branch of chemistry that aims to reduce waste from the chemical manufacturing processes to the lowest possible extent. It is also aims to invent new chemicals that are good for the environment and chemicals that work as alternatives to other chemicals of that manufacture processes that return negative results to the environment. Green chemistry is called sustainable chemistry that contribute in environmental protection^[7].

Carbon nanotubes (CNTs) In 1991 Iijima has discovered the carbon nanotubes (CNTs) and attract many researchers due to its remarkable properties. The CNT is an allotrope of carbon with thin cylinder and long-tube structure^[8]. The tensile strength and young's modulus of the CNT are greater than those of the metals such as steel, iron, etc. The CNT is classified into three types: single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and multi-walled carbon nanotubes (MWCNTs).^[9] SWCNTs are mainly used in electrical field such as sensors and wires due to its twisting properties^[8]. MWCNTs and DWCNTs provide greater mechanical strength than SWCNTs because of the presence of many layers of graphene; this structure helps in the field of composite material. The CNT has application in different fields such as electrical, mechanical, chemical and biological. In the electrical field, CNT is used in vacuum microelectronics; in electron field emission appliances, energy storage applications, namely fuel cells, batteries and electrochemical applications due to its smooth surface topography and surface specificity^[10]. CNT also has its uses in storage tanks in the chemical field for the storage of hydrogen because of its absorbing property of different gases under ambient conditions. In the mechanical field, light density and

greater mechanical strength, CNT help as the filler and reinforcement material in mechanical composites to reduce the weight. CNT synthesis involves different methods such as arc discharge, plasma rotating, chemical vapor deposition and hydrothermal processes.^[11]

Adsorption is a phenomenon that collects gas or liquid matter in molecules, atoms or ions on the surface of another solid substance, or is a physical or chemical association of material molecules in the active sites of a surface through the weak Vander Waals forces or by forming chemical bonds with effective sites on the surface. Adsorption can also include removal of dissolved solids in a solution by a solid surface or recovery of dissolved solvents by that surface process called blackmail (Desorption)^[12].

Heavy metals are defined as elements that have metallic properties and an atomic number >20. The most common heavy metal contaminants are Cr, Cu Zn, Pb, Cd, and Hg. Metals are natural components in soil, some of these are micronutrients and necessary for plant growth such as Zn, Cu, Mn, Ni, and Co, while Cd, Pd, and Hg have unknown biological function^[13].

Lead (Pb) It is one of the most hazardous heavy metals and is naturally present in the environment. Its concentration is highly elevated by anthropogenic sources^[14]. The acute lethal concentration in fish species ranged from 10-100 mg/L. The bioavailability of lead depends on the physicochemical properties of water as pH, alkalinity and hardness, and natural organic matter content in water. Although it enters fish bodies through diet, the gills are the central part of the body for lead precipitation reflecting two different responses, one of them considered as physiological compensatory mechanism while other responses including epithelial damage, desquamation and aneurism are the main pathological effects of chronic lead toxicity in *Clarias gariepinus*. In addition, Vacuole formation, shrinkage of lamella and fusion of tips of gill lamella was noticed in lead toxicity^[15]. Therefore, it is necessary to eliminate such hazardous heavy metal ion in wastewater before discharging it into the

ecosystem. The tolerance limits for heavy metal concentration in potable water and discharge into inland surface waters is shown in Table 1.1.^[16]

Table 1.1: Tolerance limits for Pb^{+2} metal ions concentration in drinking water and discharge into inland surface waters.

Heavy metal	Drinking water (mg/L)	Discharge in inland surface water (mg/L)	Discharge in public sewers (mg/L)	EPA Drinking water (mg/L)	WHO Drinking water (mg/l)
Pb^{+2}	0.05	0.1	0.1	0.015	0.01

1.2. Literature Review;

Single-walled carbon nanotubes (SWCNTs) consist of single graphene layer with diameter varying between 0.4 and 2 nm while, multiwalled carbon nanotubes (MWCNT) consist of many graphene layers of graphene. MWCNTs were first discovered by Iijima by Arc discharge method. This method is the most ancient method that used earlier for the production of carbon fibers^[17]

Y.Hsiou and co-workers 2004 obtained the carbon nanotubes in several structural forms: single-wall CNTs (SWCNTs), double-wall CNTs, and multi-wall CNTs. They are mainly produced by the chemical vapor deposition (CVD) the laser vaporization, and electric arc discharge methods The length of CNTs is in the form of micrometers with a diameter of about 100 nm^[18].

Thostenson and many researchers have reported the carbon nanotubes which are made using a chemical vapor deposition, arc, laser and plasma for certain applications. The standard CVD process requires some form of catalyst, which are held in a controlled environment consisting of some percentage of a carbon source such as a hydrocarbon gas (methane, acetylene, ethylene, a liquid vapor (hexane or benzene) or another carbon source such as an alcohol etc.)^{[19] [20] [21]}

In other hand ,many researchers have produced and described activated carbon from olive-seed waste residue and from a bituminous coal by chemical activation using KOH, NaOH and other chemical reagents were analyzed in detail, and studied the influence of several variables such as impregnation ratio and carbonization temperature.^{[22] [23] [24] [25]}

In 2014, Eatemadi and co-workers and Pandey in 2016 have reported a paper explaining the CNTs that synthesized by different method such as; Arc discharge evaporation method, Laser Ablation Method, Thermal Synthesis Process, Plasma Enhanced CVD (PECVD), Chemical vapor deposition (CVD).^{[26] [27]}

In related work TAN Win Hon and co-workers utilized premixed flame burner system to synthesize carbon nanotubes (CNTs). The morphologies of highly-graphitic carbon nanotubes were characterized by using transmission electron microscopy (TEM) and X-ray powder diffraction (XRD). The XRD analysis shows the spectrum of a typical CNT, while TEM imaging shows the physical structure of the carbon nanotubes. CNTs were grown effectively on a Ni-contained substrate in an elevated temperature environment. The flame synthesis of CNTs was high crystalline, multi-wall structure, and contains relatively less impurities and amorphous carbon. The CNT inter shell spacing values was calculated and determined using TEM and XRD are 0.317 nm and 0.344 nm respectively. CNTs produced from flame synthesis are based on the tip-growth model and vapor-liquid-solid (VLS) mechanism.^[28]

In 2020, Karthikeyan and co-workers prepared multi-walled carbon nanotubes (MWCNTs) using thermal catalytic chemical vapour deposition method. The synthesis of MWCNTs was made by breakdown of acetylene (C_2H_2) gas and Fe/MgO which acts as a catalyst. The surface morphology and structure of MWCNTs were characterized by scanning electron microscopy (SEM). Also phase identification and crystalline size of the nanopowder were determined by XRD. The particle size of MWCNTs was verified by SEM analysis and it was

in the range of 20–30nm and elemental analysis was carried out through energy dispersive analysis X-ray. Furthermore, thermal decomposition of the material property was studied by thermogravimetric analysis.^[22]

Lignin precipitated from black liquor was carbonized at a temperature of 600° C, the resulting charcoal was used as adsorbent for the removal of heavy metals from aqueous solutions (Pb^{2+} , Cd^{2+} , Hg^{2+} and Ni^{2+}). The particle diameters and the morphology of the prepared coal were investigated. The adsorption properties of charcoal from lignin were explored under batch conditions and the results were compared to a commercial homologue that used in water treatment. The kinetic study and compare of the adsorbent (lignin-based coal, CL), as well as that of the commercial substrate, was also performed. Then, the regeneration of the charcoal was achieved using diluted ethylene diamine tetra-acetic acid (EDTA) and nitric acid (HNO_3) as desorbing solution. In addition, the thermodynamic parameters, free energy of adsorption G° , entropy S° and enthalpy H° for the adsorption process were determined and the mechanism of the adsorption was studied by zeta potential measurement. It was concluded that the charcoal from lignin used as a high capacity and reusable sorbent material in heavy-metal removing processes.^[29]

Peir-An has reported that a single-walled carbon nanotubes (SWCNTs) and purified by ultrasonication and microwave-assisted acid digestion. The results show that the method efficiently eliminates impurities (Graphite, fullerenes) reduces solvent consumption, and prevents damage to the structure of the SWCNTs. The purified SWCNTs were given functionalization treatments with a nitric acid/sulfuric acid mixture. Acid-treated SWCNTs (A-SWCNTs) were then grafted with 3-isocyanatopropyl triethoxysilane (A-SWCNTs-Si). The A-SWCNTs and A-SWCNTs-Si were used to improve interfacial interactions with polymers and to produce a well-dispersed SWCNT composite.^[30]

In related work, Shu and co-workers have investigated the copper loaded on activated carbon (Cu-AC) which was prepared by impregnating with cupric nitrate followed by microwave heating and then used to remove dyes from wastewater. The Cu-AC was thoroughly characterized by N₂ adsorption and desorption isotherms. It has been proven that cupric nitrate was successfully loaded onto activated carbon with the resulting formation of copper, copper oxide, and cuprous oxide. The Cu-AC was used to treat five kinds of dyes in wastewaters such as Rhodamine B, MB, Amaranth, Congo red, and Eosin-Y. The comparison of the adsorption capacity of these five dyes wastewaters shows that copper and copper oxides have photocatalytic degradation ability and can improve dye removal efficiency.^[31]

Al-Khazraji and his group prepared multi-walled carbon nanotubes from the animal charcoal by chemical flame deposition method and MWCNT/ZnO composite were synthesized and used for the adsorption of organic dyes from wastewater.^{[32] [33]}

Salam^[34] used the multi-walled carbon nanotubes successfully for the removal of Copper(II), Lead(II), Cadmium(II), and Zinc(II) from aqueous solution and the results showed that the percentage of adsorption increased by raising the temperature this could be due to the endothermic nature of the adsorption process.

Horti and co-workers synthesized and characterized copper oxide (CuO) nanopowder by solid state co-precipitation technique.^[35]

On the other hand, Renuga and co-worker have prepared copper oxide nanoparticles and study their properties, the UV visible spectra shows a peak at 220 nm indicating the formation of copper oxide Nps. It is further confirmed using FTIR which shows a band at 620 and 686 cm⁻¹ corresponding to Cu-O bond. The size of the nanoparticles was calculated using XRD and found to be 26 nm. The surface morphology and shape of copper oxide nanoparticles were analyzed using FESEM. The purity of NPs was confirmed by EDAX technique.

The copper oxide Nps were synthesized using the green Method and exhibits excellent antifungal activity.^[36]

In related work, Li and co-workers have investigated the adsorption of Pb(II), Cd(II) and Cu(II) on multi-walled carbon nanotube-hydroxyapatite (MWCNT-HAP) composites in detail and explore the effects of the solid-to-liquid ratio, pH, the ionic strength, reaction time and temperature on adsorption. The results show that the adsorption on MWCNT-HAP follows Pb(II)>Cu(II)>Cd(II). With an increasing solid-to-liquid ratio, the adsorption quantity of Pb(II), Cd(II) and Cu(II) on MWCNT-HAP decreases, whereas the removal efficiency increases.^[37]

1.3 Aim of study

1. Synthesis of multi-walled carbon nanotubes (MWCNTs) using different plant sources by Chemical Flame Deposition method (CFDM)
2. Preparation of CuO nanoparticles using friendly environmentally method.
3. Preparation of binary composite MWCNTs/CuO.
4. Adsorption of Pb^{+2} ions from water pollution by prepared samples.

Chapter Two

(Theoretical Part)

2.1. Carbon Compounds

Carbon atoms can connect with each other and with other elements in different ways, however, many varieties of carbon compounds exist. Unlike other chemical elements, carbon has directly opposed properties. Carbon has allotropes that are used to prepare super-hard and super-elastic materials, transparent and black materials, semiconductors and semimetals, heat insulators and thermal conductors, diamagnetic and paramagnetic materials, dielectric materials and electric conductors^[38]. The list of known carbon allotropes has expanded during the last decades of the 20th century after the discovery of several new low-dimensional carbon forms. The novel materials comprised carbon nanotubes (CNTs), fullerenes and graphene and attracted high interest from science and industry, since these materials exhibited a wide range of outstanding and novel features as promising materials for numerous application fields. Based on these properties, they were repeatedly termed as “wonder materials” in the scientific literature.^[39]

2.1.1. Graphite

Graphite is the crystalline form of carbon and another one being diamond. The classification of natural graphite based on a multitude of properties, including not only grade, but also crystallinity, as well as grain (flake) size and shape. According to these attributes, graphite ores are classified to crystalline lump (vein), flake and microcrystalline^[40]. Graphite an allotrope of carbon, and in last years modified graphite materials are synthesized and studied on a large scale due their mechanical properties, thermal conductivity electrical conductivity^[41], optical properties and lubricity^[42], which make them a good component for producing polymer composite materials. Graphite has a layered structure, is called a graphene, all the carbon atoms are linked by strong

covalent bonds (sp^2 -hybridization) with a bond length of $1.42 \text{ \AA}$ (0.142 nm), forming strong, stable, honeycomb-like hexagonal rings. The graphite layers with the interlayer distance of $3.35 \text{ \AA}$ (0.335 nm) are bound together by weak van der Waals forces. There are two polymorph modifications of graphite: hexagonal and rhombohedral. The most widespread in the nature is the hexagonal modification. Physical and chemical properties of both modifications are very similar^[43]. See Figure .2.1.

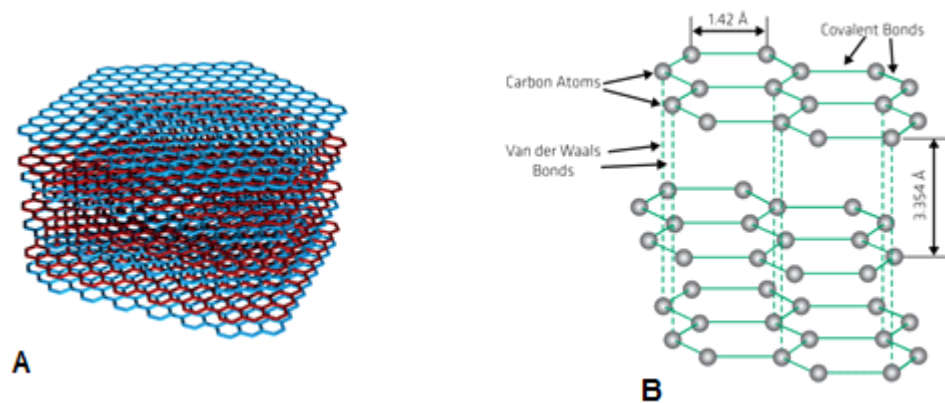


Fig 2.1. Show A) Multiple sheets of graphite. B) Graphite structure.^[44]

2.1.2. Graphene

Graphene can be described as a one-atom thick layer of graphite (Fig2.2.), with 2 dimensional properties. In graphene carbon atoms are densely in a regular sp^2 -bonded (hexagonal) pattern. It can also be considered as an indefinitely large aromatic molecule. It is known that carbon atoms at the edge of graphene sheets have special chemical reactivity and graphene has the highest ratio of edgy carbons in comparison with similar materials such as carbon nanotubes^[45]. There are several methods available for creating this material: cleavage of graphite mechanically, exfoliation of graphite via intercalation compounds CVD process, organic synthesis and more. The thermal conductivity of a suspended high quality CVD graphene was measured to exceed 2500 W/ (m.K) at a temperature of 350K . As filler in composites the graphene show a greater

enhancement of the overall conductivity of the composite compared to graphite and CNT, even at lower loading rates. This can be due to a low thermal resistance between the graphene and the matrix properties which make graphene an interesting material are its high thermal conductivity, great mechanical strength and small TEC. ^[46]

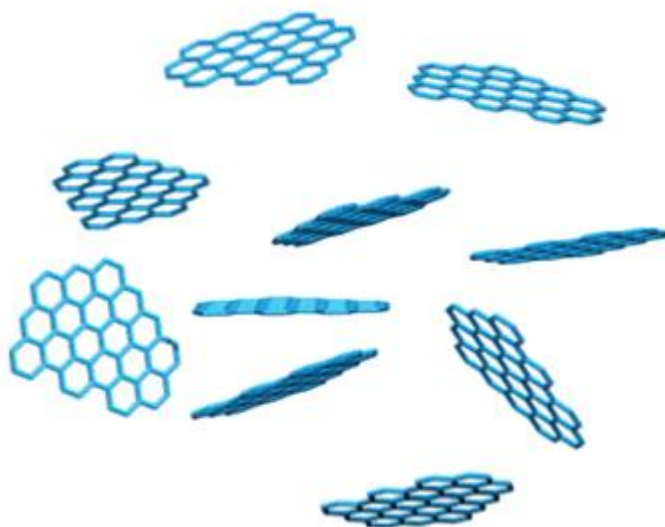


Fig.2.2. Shows The single- layer of graphene. ^[46]

2.1.3. Fullerenes

Fullerene is a carbon cage structure having fused ring system which consists of pentagons and hexagons ^[47]. C_{60} and C_{70} are the most famous members of fullerene family. The high symmetry found in this molecule is an important property. C_{60} molecule is composed of 60 carbon atoms which are arranged as 12 pentagons and 20 hexagons ^[48]. All rings are fused and double bonds are highly conjugated. The reason for high symmetry of this molecule is 120 symmetrical operations found in molecule like rotation around the axis and reflection in plane which maps the molecule onto itself. When a carbon atom is placed at each vertex of molecule which all valences satisfied by two single bonds and one double bond, stabilized by resonance gives structure of C_{60}

molecule, appears to be aromatic. There are many forms of fullerene^[49], such as Fullerane which is fully saturated fullerene for example, the hydrocarbon ($C_{60}H_{60}$) and Fullerooids are fullerene-like compounds be similar to fullerenes in structure but do not confirm the definition of a fullerene (example, Heterofullerens, Homofullerene, Norfulleres, Secofullerene).

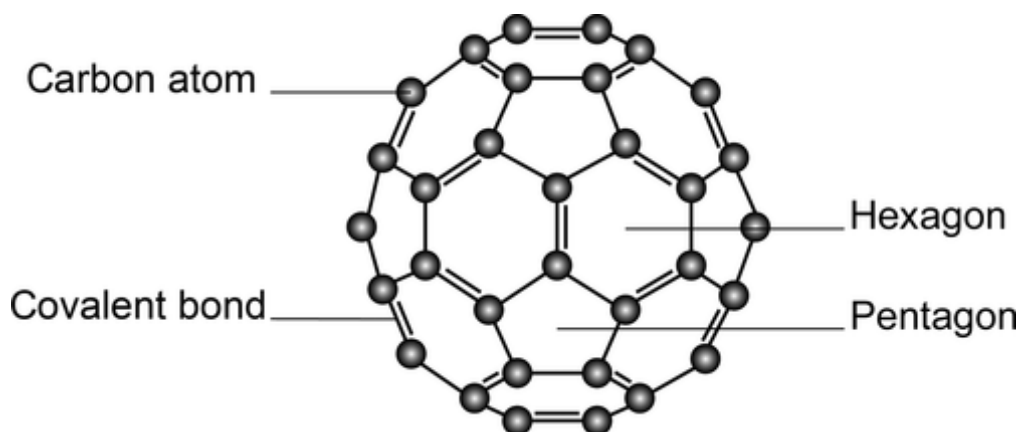


Fig.2.3. Shows The structure of fullerene C_{60} .

2.1.4. Carbon Nanotube

Carbon nanotubes (CNTs) are allotropes of carbon that have a nanostructure, which can have a length-to-diameter ratio more than 1,000,000 and it is derived from rolled graphene planes. CNTs have many interesting chemical and physical properties^[50], such as ultra-light weight, high aspect-ratio, tremendous strength^[51], high thermal conductivity and remarkable electronic properties ranging from metallic to semiconducting. CNTs have been used in biomedicine for their ability to bind with various biological molecules including drugs, proteins and nucleic acid to afford bio-functionalities^[52]. CNTs can be produced from other hydrocarbon-based materials such as paraffin wax candle, alcohols and polyethylene^[53] by different ways like chemical vapour deposition, arc discharge and laser ablation methods. Flame synthesis is an alternative method that can be used to produce CNTs at relatively low cost and short synthesis time^[54]. CNTs exist as single (SWNTs), and multi-walled (MWNTs) structures,

SWCNTs contain a single cylindrical carbon layer with a diameter in the range of 0.4-2 nm and have an ultra-high surface area as large as 1300 m²/g depending on the temperature, It was found that the higher the growth temperature of the carbon nanotubes, the greater the diameter of CNTs^[55]. Sp² is a hybridization for CNTs the bonding between carbon- carbon stronger than the bonds carbon in diamond that's have a sp³ hybridization. There are different mechanical properties of CNTs uses in many materials such as Young's modulus, TPa and tensile strength of 50–200 G Pa^[56]. These properties make CNTs the strongest and stiffest materials on earth.

2.2. Classification CNTs Based on Layers

Based on the number of layers, CNTs are classified into two types: single-walled carbon nanotubes) SWCNTs), Double-walled CNTs (DWCNTs) and multiwalled carbon nanotubes (MWCNTs), see figure2.5. The carbon atoms are arranged in a benzene rings to consist (CNTs) rolled up into a tubular structure^[57].

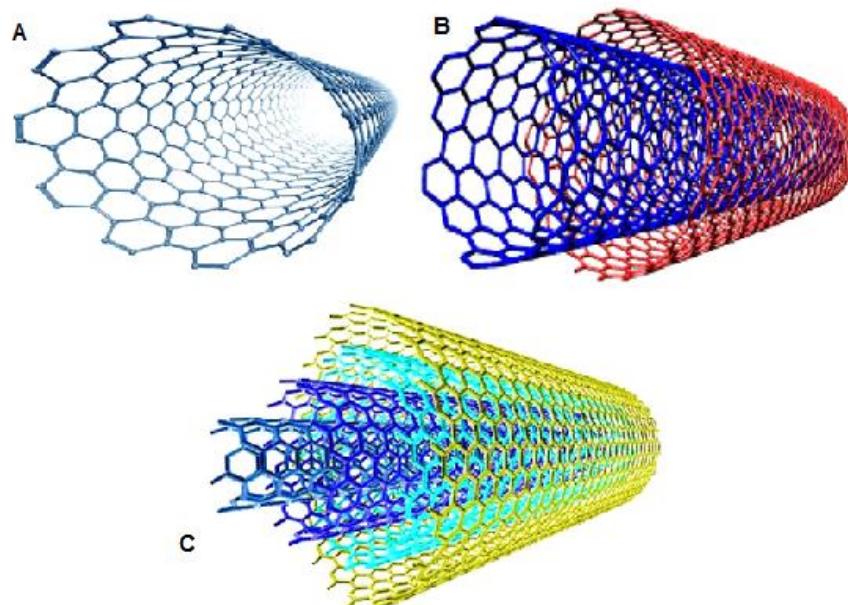


Fig.2.4. Show A) diagrams of single-walled carbon nanotubes (SWCNT) (B) Double-walled carbon nanotubes. (C) multi-walled carbon nanotubes (MWCNT).

The (SWCNTs) consist of a single graphene cylinder with 0.4 - 2 nm diameter, and usually occur as hexagonal close-packed bundles while Double-walled (CNTs) are made of two concentric carbon nanotubes in which the outer tube encloses the inner tube and (MWCNTs) consist of two to several coaxial cylinders, each made of a single graphene sheet surrounding a hollow core. The outer diameter of MWCNTs ranges from 2 -100 nm and the inner diameter is in the range of 1–3 nm to several μm .^[58]

2.3. Classification (SWCNTs) Based on Chirality

There are three types of SWCNTs basis on chirality, these are chiral, armchair, and zigzag. This chirality is a very important factor in determining the electrical properties of CNTs, figure 2.6.a.

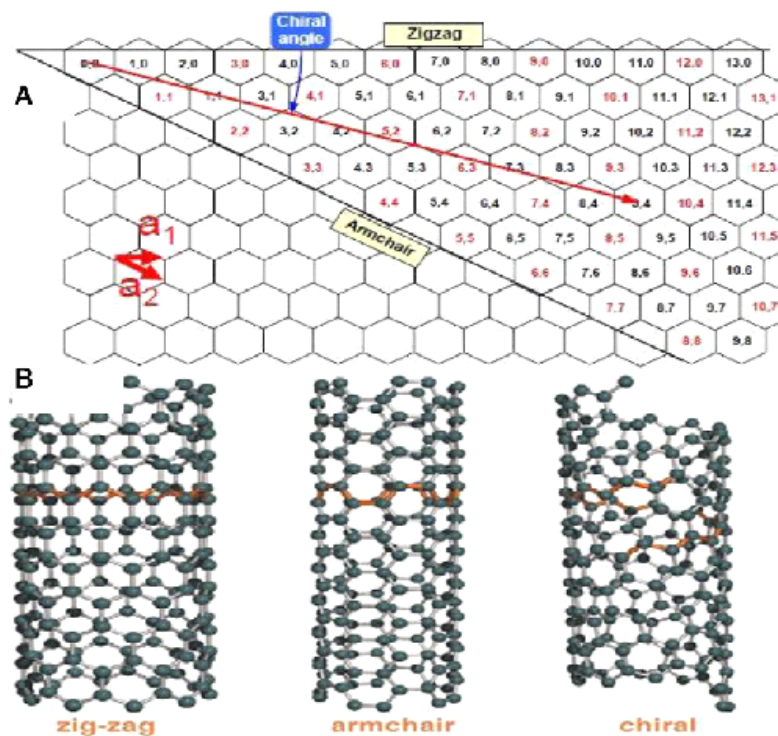


Fig.2.5. Show (A) The chiral vector C also determines the tube diameter. (B) Different forms of SWCNTs depending on chirality.

The SWCNTs have a pair of indices (n, m) describe the electrical properties of nanotubes, n and m considered as an integers, when $m = 0$ the nanotubes are named zigzag nanotubes; when $n = m$, the nanotubes are named armchair nanotubes, and other state are called chiral. The chiral vector $C = na_1 + ma_2$ finds out the direction of rolling a graphene sheet (a_1 and a_2 are the base cell vectors of graphite) also determines the tube diameter. Fig.2.6.b^[59].

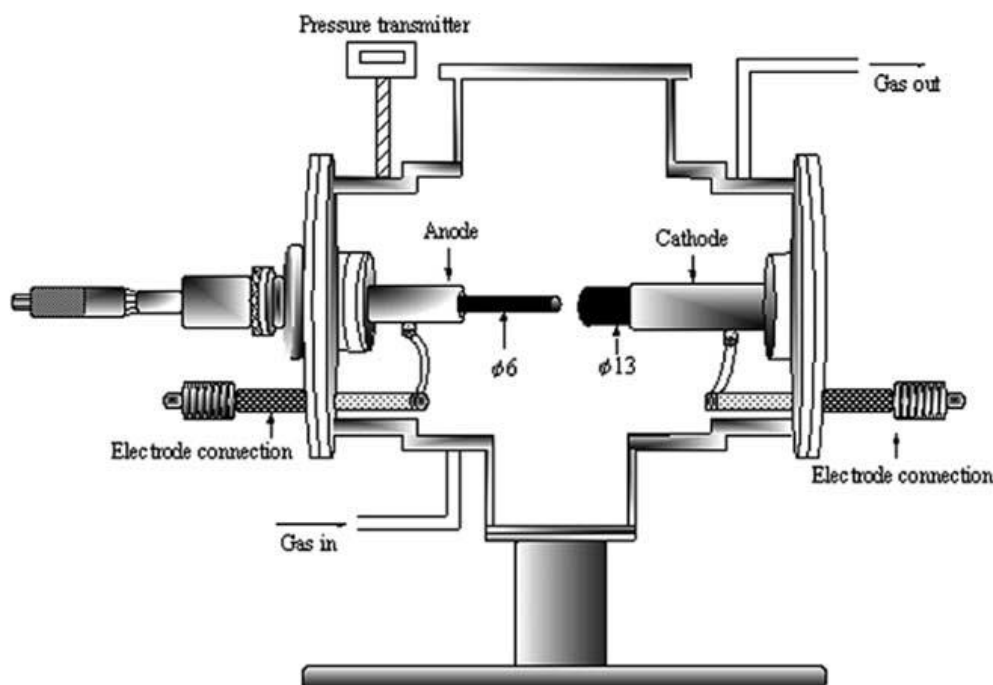
2.4. Methods of the Carbon Nanotube Synthesis

In the early sixties the (CVD) technique was used by R. Bacon for the carbon nanotube production, is the oldest technique method of CNTs production. In 1990 the CVD method was adapted by Krätschmer and Huffman to produce fullerenes in good yields after that was improved this method for the synthesis of multiwall (MWNT) and single-walled (SWNT) carbon nanotubes. Other methods such as laser evaporation/ablation and chemical vapour deposition (CVD) were also successfully used. The difference between the arc discharge method and laser evaporation process is the quality and purity of the obtained products.^[60]

2.4.1. Arc Discharge Method

In this technique two high-purity graphite electrodes use. The first pole (anode) is either pure graphite or contains metals. The metals are mixed with the graphite powder and introduced in a hole made in the anode center see fig (2.6). Arc-discharge technique uses higher temperatures (above 1,700°C) and carried out at low pressure (30-130 torr or 500 torr) in controlled atmosphere composed of inert and/or reactant gas (helium gas) for synthesis CNT. The high temperature in the inter-electrode zone made carbon sublimates from the positive electrode (anode) and there are Various kinds of products are formed in different parts of the reactor, large quantities of rubbery soot on the reactor walls, web-like structures between the cathode and the chamber walls, grey

hard deposit at the end of cathode and spongy collaret around the cathode deposit. Amorphous carbon, encapsulated metal nanoparticles, polyhedral carbon are also present in the product. Better results were obtained using bimetallic catalysts such as Fe, Ni, Co, Mo, Y, either alone or in mixture^{[61] [62]}. When no catalyst is used, only the soot and the deposit are formed. The soot contains fullerenes while MWNTs together with graphite carbon nanoparticles are found in the carbon deposit. The inner diameter of the MWNTs varies from 1 to 3 nm, the outer diameter varies in the range of 2–25 nm, the tube length does not exceed 1 μm , and the tubes have closed tips.



Scheme.2.6. Arc discharge apparatus.

2.4.2. Laser Ablation Method

The laser ablation method is similar to the arc discharge, both taking advantage of the very high temperature generated to vaporize a graphite target in an oven, which is filled with helium or argon gas to keep pressure^[63]. SWNTs were prepared by continuous wave carbon dioxide laser ablation without applying additional heat to the target. They found that the average diameter of SWNTs

produced by carbon dioxide laser increased with increasing laser power^[64]. The Nanotubes produced by laser ablation have higher purity (up to about 90% pure) and their structure is better graphitized than those produced in the arc process. The metal-graphite was placed in the oven (Figure 2.8.) in a high-temperature furnace (1200 °C). The laser beam (532 nm), was focused onto a metal-graphite and scans across the target surface under computer control to maintain a smooth, uniform face for vaporization. The soot produced by the laser vaporization was swept by the flowing air gas from the high-temperature zone, and deposited onto a water-cooled copper collector positioned downstream, just outside the furnace. Other impurities that have been detected include silicon and various hydrocarbons, which are probably due to impurities introduced from unknown sources. The metals were used: Co, Cu, Nb, Ni, Pt, Co/Ni, Co/Pt, Co/Cu, Ni/Pt mixed with graphite resulted in the best purity and yield of SWNTs of the configurations tested^[65].

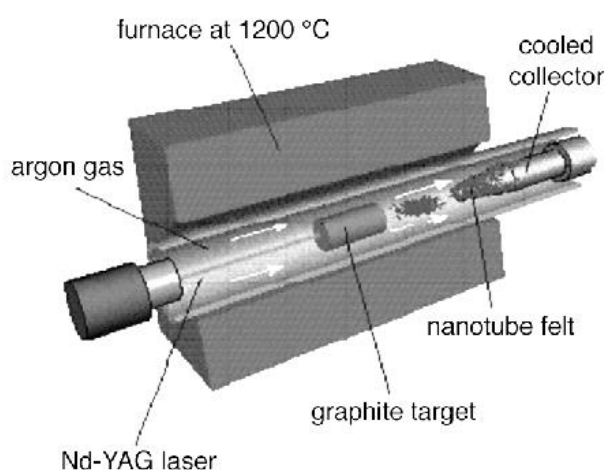
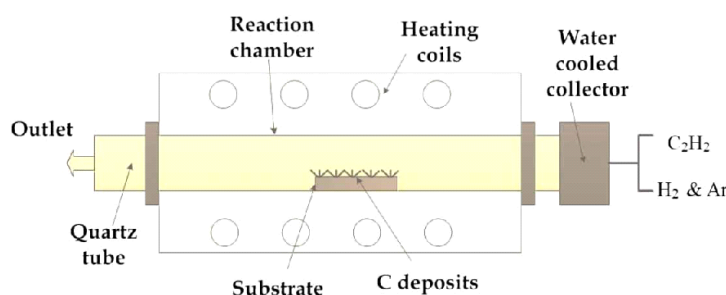


Fig 2.7. Schematic synthesis apparatus.

2.4.3. Chemical Vapor Deposition (CVD)

CVD method was discovered in 1996, for nanotube synthesis. This method is capable of controlling the growth direction on the substrate and synthesizing a large quantity of nanotube^[66]. Hydrocarbon molecules are often used as carbon sources such as (methane, ethane, ethylene, acetylene, xylene, eventually their mixture, isobutane or ethanol). The most frequently used catalysts are transition metals, primarily Fe, Co, or Ni. Sometimes, the traditionally used catalysts are further doped with other metals, e.g. with Au^[8]. The experiment is carried out in a flow furnace at atmospheric pressure. There are two types of furnace modality, one is a horizontal configuration, and the second is a vertical configuration (Figure 2.8). The horizontal furnace is the most popular; here the catalyst is placed in a ceramic or quartz boat which is put into a quartz tube. The reaction mixture containing a source of hydrocarbon and an inert gas is passed over the catalyst bed at temperatures ranging from 500 °C to 1100 °C while the vertical furnace is usually employed for the continuous mass production of carbon fibers/nanotubes. By varying the active particles on the surface of the catalyst, the nanotube diameter can be controlled. The length of the tubes depends on the reaction time; even up to 60 mm long tubes can be produced. The production of the carbon nanotubes by CVD method depend on the working conditions such as temperature, operation pressure, hydrocarbon type, volume and concentration of hydrocarbon, size of metallic catalyst , the nature of the support and the reaction time^[67].



Schem.2.8. Shows Chemical Vapor Deposition(CVD) method.

2.4.4. Flame Synthesis

In this method, hydrocarbon flames are utilized. Gases such as CO, CH₄, C₂H₂, C₂H₄, and C₂H₆, which are present in the post-flame area, are rich sources of carbon and these flames assist with the initiation to growth of CNTs. The reaction is exothermic and chemical energy released in the form of heat in the flame supports endothermic carbon deposition reactions. Catalysts are also required to provide reaction sites for the deposition of solid black carbon^[68]. The metal catalysts and transition such as iron (Fe), Nickel (Ni), Cobalt (Co), chromium (Cr), copper (Cu) and zinc (Zn) have been used in this method. A substrate coated with a catalyst layer is positioned at the appropriate location inside the flame. Catalyst nano-particles are formed on the substrate as a result of flame-substrate interactions. These particles further act as the nucleation site for nanotube growth. Stationary substrates have been typically used for synthesis of MWNTs because of the larger size of catalyst nano-particle (~20 nm). Catalyst can be injected inside a flame in the form of a vapor aerosol. Catalysts have been found to be very active towards a particular gas phase precursor of solid carbon, and hence structure and type of the catalyst play an important role in determining the growth rate as well as the structure of the CNTs^[69]. Figure 2.10.

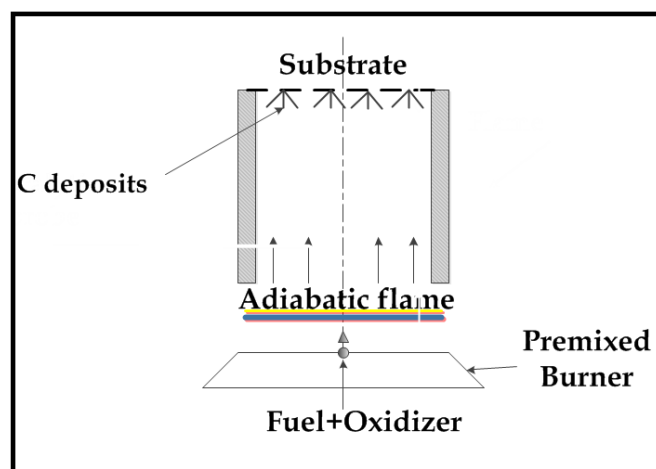


Fig.2.9. Shows Flame synthesis.

2.5. Copper Oxide Nanoparticles (CuO NPs)

Copper is an essential micronutrient, which is incorporated in many proteins and enzymes, therefore, playing a significant role in plant health and nutrition. Copper nanoparticles (Cu NP) are widely used in different commercial applications such as antimicrobial agent, gas sensors, catalysts, electronics, heat transfer fluids, batteries, etc.^[70]. There are some methods for preparation (CuO) such as, the sonochemical method, sol–gel technique^[71], a simple method from the corresponding salt using Fig leaves extracts^[72], and green synthesis approaches using natural extracts used to environmental remediation in terms of antimicrobial activity, catalytic activity, removal of pollutants dyes, and heavy metal ion sensing^[73]. Copper oxides were prepared by simple aqueous precipitation method with size 5-6 nm. The synthesized nanoparticles were characterized by XRD, SEM, TEM and PL spectrometer^[74]. The oxides of transition metals, copper oxide nanoparticles are of special interest because of their efficiency as nanofluids in heat transfer, in magnetic storage, solar energy transformation, electronics and adsorption heavy metals from polluted water application^[75].

2.6. Composites

Composite materials are formed by combining two or more materials that have quite different properties such as, Light weight, mechanical and chemical resistance, thermal and electrical insulation, design flexibility, and they do not dissolve or blend into each other. The different materials in the composite work together to give the composite unique properties^[76]. Newly, CNTs has been used a composite in polymers to improve properties, Al khazraji and his co-workers prepared MWNTs/polymer by add 0.1 wt% of MWCNTs were dispersed uniformly through the 0.3 wt% polymer matrix. The results supported with the help of physical analysis methods such as FTIR, Raman spectroscopy

and Atomic force microscope (AFM) showed an efficient dispersion of MWCNTs bundles in a polymer matrix was achieved and the polymer as a matrix has a clear effect on the diameters and longest carbon nanotubes by comparing with carbon nanotubes without polymer^[77]. Metal oxides such as MnO₂, ZnO, NiO, MgO, CuO and TiO₂ (titanium dioxide) have been used along with carbon as a potential electrode material for supercapacitors^[78].

2.7. Applications

2.7.1. Applications of CNTs

Nanotechnology can be used in different applications in various fields, including nano-medicine, energy, the environment, and in sensors^[79]. Although the fields of nanotechnology are vast and new materials come into use regularly, the potential of CNTs is most promising. CNTs are the most rapidly growing nanomaterials in the field of nanotechnology, due to their various applications. More attractive applications of CNTs can be achieved through the use of CNTs for applications that require conductivity and a high absorption capacity and for the creation of high-strength composites, fuel cells, energy^[17]. Many researchers used CNTs as fillers to form nanocomposites, it is the one of the most developed fields in nanotechnology. Mechanical, electrical and thermal properties were improved by injected of CNTs with polymeric and other materials. SWNTs/polyimide was prepared by addition of SWNT in a polyimide, The results showed that the mechanical properties of polyimide were enhanced^[80].

CNTs are excellent materials for use in electrochemical devices because it have a large surface area and high electrical conductivity^[81]. The first study showed that the MWNTs can be grown with sheet electrodes of pyrolytically, it is possible to achieve very high specific capacitances in individual cells in devices containing 38 wt% of H₂SO₄ as the electrolyte. Most important chemical

species such as metals, metal carbides, and oxides, can be introduced into CNT core by different methods, including chemical treatments, arc-discharge methods, solid state reactions and electrochemical techniques. CNTs can act as efficient gas and metal containers. The act process demonstrated that it is possible to introduce gaseous nitrogen inside MWNTs using a single-step process^[82]. Recent studies have revealed that is possibly adsorb hydrogen molecules by CNTs were proposed, including chemisorption, adsorption at interstitial sites, and the swelling of the nanotube array^[83]. Carbon nanotubes (CNTs) have exhibited great potentials in water treatment. The adsorption capacity of acid-refluxed by HNO₃ CNTs (11.2 mg/g) was higher than that of ACs (about 5.5 mg/g). The surface oxygen-containing functional groups were the most important factor for lead adsorption^[67].

2.7.2. Applications of CuO

Oxide nanoparticles have a challenging base for research as wide varieties of applications attract researchers to explore its properties especially due to their ability to alter the physical, optical and the electronic properties of compounds. Copper oxide nanoparticles gains special interest among the oxides of transition metals because of their efficiency as sensors nanofluids, antimicrobial applications, catalysis, super conductors, anticancer agent and as energy storage systems^[84]. CuO nanoparticles may have different applications depending on the various properties they manifest, which are highly influenced by their size, surface properties, optical and magnetic trait, the synthesis method being an important parameter for controlling all these and thus, their biological properties. Future biomedical applications of CuO NPs are focused intensively on disease detection and could present potential applications in many other areas, for example, in the detection of viruses in the human body^[85]. In a recent study, Li and co-workers developed a highly sensitive and selective method for the detection of H₁N₁ flu virus. Copper and copper-based compounds, due to

their potent biocidal properties, are now routinely used in pesticidal formulations^[86] and several health related areas applications are being explored and/or implemented.

2.7.3. Applications of Composites

Composites offer many benefits such as corrosion resistance, light weight, strength, lower material costs, improved productivity, design flexibility, and durability. Therefore, the wide range of industries uses composite materials and some of their common applications. Composite materials are being used in appliance and business equipment such as equipment panels, frames, handles and trims in appliances, power tools^[87]. Composites play a vital role in the manufacture of structures such as wind turbine blades it can help enable the use of wind and solar power and improve the efficiency of traditional energy suppliers. Composite materials offer wind manufacturers strength and flexibility in processing with the added benefit of a lightweight components and products^[88]. The marine industry uses composites to help make hulls lighter and more damage- resistant. With their corrosion resistance and light-weighting attributes, marine composite applications include boat hulls, bulkheads, deck, mast, propeller, and other components^[89].

2.8. Adsorption

The term pollutant, in a broad sense, refers to a substance that changes the natural quality of the environment by physical, chemical, or biological means. Thus, pollution may occur in air, water, and soil. Industrial, agricultural, and domestic activities of humans have affected the environmental system, resulting in serious problems such as global warming and the generation of wastewater containing high levels of pollutants. Adsorption refers to a process where a gas or liquid solute accumulates on the surface of a solid or a liquid, forming a molecular or atomic film. The material adsorbed is called the adsorbate or

solute and the adsorbing phase is the adsorbent^[90]. It is a simple and efficient method for the removal of organic and inorganic compounds in drinking water treatment. Among the various adsorbents, such as activated carbons (ACs), zeolites, CNTs, and resins, ACs are one of the most widely used type of adsorbents in water treatment^[91]. The reason for adsorption phenomenon is the existence of some unsaturated forces on the adsorbent due to the complete in coordination or insufficient material surface particles, like the liquid or solid phase adsorption which leads to saturate those forces on the adsorbent surface according to the thermodynamic relation^[92]:

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots (2-1)$$

during the adsorption process both surface free energy (ΔG) and entropy (ΔS) decreased, at the surface that the adsorption take place due to losing the degree of freedom possessed before adsorption. The decreasing of free energy (ΔG) and the entropy (ΔS) in the same time will cause decreasing in Heat content (ΔH).

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

- 1- Transport of solute molecules from the bulk of solution to the exterior surface of the adsorbent material.
- 2- Movement of solute molecules across the interface and adsorption onto external surface sites occurs.
- 3- Migration of solute molecules within pores of the adsorbent.
- 4- Interaction of solute molecules with available sites on the interior surfaces, bounding the pore of the adsorbent and capillary spaces of the adsorbent.

One or more of the previous steps may control the rate by the amount of solute adsorbed onto the solid particle.^[93]

2.9. Types of Adsorption

Forces of attraction exist between adsorbate and adsorbent. These forces of attraction can be due to Physical forces include Van der Waals and electrostatic forces, or the chemical forces result from a short inter-union rate involving the formation of internal compounds, which include a mechanism for the exchange of bonds and symbiotic bonds, and hydrogen bonds^[94]. On this basis adsorption can be divided into two types: The first is called natural adsorption or physical and the second type is called chemical adsorption or chemisorptions.

2.9.1. Physical Adsorption

This adsorption is also called Vander Waals adsorption or physisorption, which is a natural attraction between the surface of the atom and the atoms, particles or ions that adsorb on the surface see fig(2.10) Physical adsorption is not specific because the atom or molecule that suffers from physical adsorption is not chemically bound to the surface atoms but occupies a certain area of the surface^[95].

2.9.2. Chemical Adsorption

chemical adsorption is called chemisorptions. Hydrogen bonds are formed in this type between the surface and the atoms, molecules or ions that adsorb on the surface Chemical adsorption is characterized by privacy(specific)As happens in certain conditions and adsorption may not occur on another surface at the same conditions or on the surface itself when changing surrounding conditions chemical adsorption^[96].

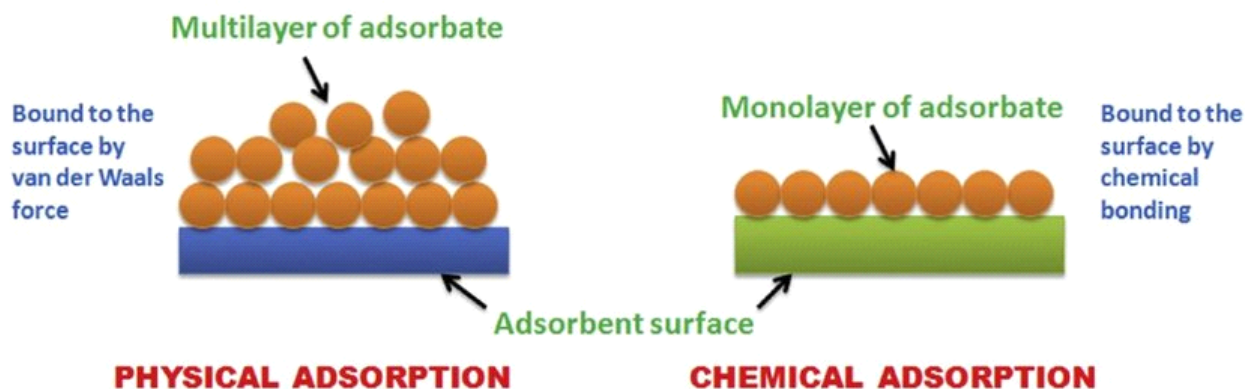


Fig.2.10. Shows Physical adsorption and Chemical adsorption

2.10. Factors Influencing Adsorption Processes

The main factors that affect the percentage of adsorption are:

2.10.1. Contact time

Contact time is one of the most effective factors in batch adsorption process. It can be defined as the longest time when the adsorption process complete and the balance or change is slight^[97]. Adsorption of heavy metals (Cr, Cd, Pb, Ni, and Cu) onto Activated Teff Straw (ATS) has been studied using batch-adsorption and effect of Contact Time on Adsorption^[98].

The changed from 20 to 120 minutes of adsorption show decreased for efficiency from 72 to 69% and further increased to 72 % and afterwards no change is observed. As time progresses the surface coverage of the adsorbent is high and further no adsorption take place^[99].

2.10.2. Nature of Adsorbate

The size of the ion plays an important role in the adsorption process, affecting the amount of adsorption of a certain ion on the surface of the atom with the presence of more than one ion of different size in the solution^[100]. Lead ion appear under certain conditions more intense from cadmium ion, this is because

of the large volume of lead ion. The solubility of the adsorbent in the solvent also has an effect on the adsorption process where the amount of the adsorbent is reduced by increasing its solubility in the solvent^[12].

2.10.3. Amount of Adsorbent

Many experiments were performed to increase the amount of the adsorbent. For example they using a 25 mL aqueous solutions of bromo- phenol blue (6.7 ppm), methylene blue (7.7 ppm), phenol red (3.5 ppm), alizarin red S (6.8 ppm), malachite green (4.6 ppm), ferrochrome black-T (2.3 ppm), methyl blue (4 ppm) and methyl violet (2 ppm) and were shaken together for 30 min adding different amount of charcoal. The absorbance of the filtrate was noted by the spectrophotometer at the λ_{max} of each dye. The results were that the adsorption of dyes increased with increasing the amount of charcoal and attained a constant value when equilibrium was established. The optimum amount was found to be 0.01 g, which was used for all further adsorption studies^[101].

2.10.4. Effect of Temperature

Since the adsorption is an exothermic process the adsorption decreases with increase in temperature. May also be explained for example that the solubility of the dyes is increased at higher temperature and adsorbate–adsorbent interactions decreased resulting into decreased adsorption. This also indicated that desorption steps increase at higher temperature than the adsorption. This type of adsorption is likely to be classified as reversible adsorption^[102].

2.11. Adsorption Isotherms

Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent. Distribution of metal ions between the liquid phase and the solid phase can be described by several isotherm models such as Langmuir, Freundlich, Temkin equation and Dubinin–radushkevich Isotherms.

2.11.1. Langmuir Isotherm

It is one of the oldest empirical models that describe adsorption isotherms and it is the most frequently used model in water treatment^[103]. The formulation is based on four assumptions that are monolayer adsorption, adsorption occurs only at finite number of sites, all adsorption sites are equivalent and adsorbed solutes do not interact with each other the Equation of Langmuir isotherm can be expressed as follow^[104]

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \dots\dots(2-2)$$

Where:

$q_e(\text{mg/g})$ is the amount of solute adsorbed.

$q_{max}(\text{mg/g})$ is the maximum monolayer on the adsorbent.

$b(\text{L/mg})$ is the Langmuir isotherm constant and $C_e(\text{mg/L})$ is the equilibrium concentration. The linear plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) (Figure 2.11) shows that the adsorption obeys the Langmuir model. The constants b and q_{max} relate to the energy of adsorption and maximum adsorption capacity, and their values are obtained from the slope and interception of the plot.

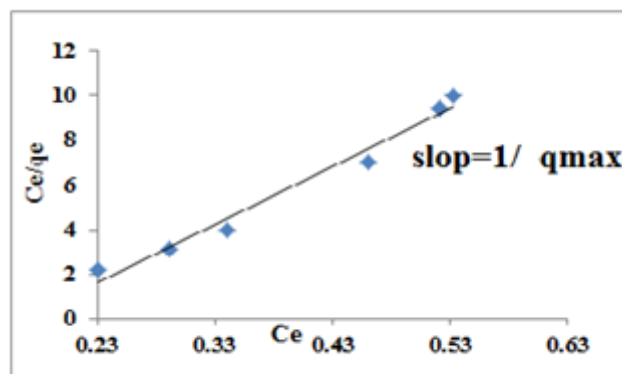


Fig. (2.11) The linear of Langmuir isotherm

2.11.2. Dubinin–Radushkevich (D–R) isotherm

The Dubinin–Radushkevich (D–R) isotherm model is more general than the Langmuir isotherm since it does not assume a homogeneous surface or constant sorption potential. It was applied to distinguish between the physical and chemical adsorption of metal ions^[105]. the equation are expressed, respectively by:

$$q_e = q_{max} \exp^{-(K_D)\varepsilon^2} \dots\dots(2-3)$$

where

q_e = is the amount of ions adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}).

q_{max} = the maximum adsorption capacity of the adsorbent (mg g^{-1}).

K_D = The constant K_D ($\text{mol}^2 \text{kJ}^{-2}$) gives the mean free energy E (kJ mol^{-1}) of adsorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution.

ε = polanyi potential constant given as $RT \ln(1 + 1/C_e)$, R the universal gas constant ($8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$).

The Dubinin–Radushkevich isotherm is the popular model that used to estimate the characteristic porosity and the apparent free energy of adsorption^[106]. The linear plot of specific adsorption $\ln q_e$ against the equilibrium concentration (ε^2) (Figure.2.12) shows that the adsorption obeys the Dubinin–Radushkevich model. The constants K_D and R^2 values are obtained from the slope and interception of the plot.

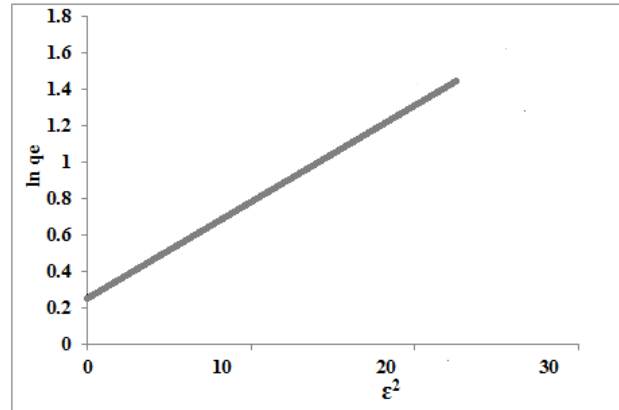


Fig. (2.12) The linear of Dubinin–Radushkevich isotherm

2.12. Adsorption Kinetics

Adsorption kinetics describes reaction pathways, as well as the time to reach the equilibrium. It also shows large dependence on the physical and chemical characteristics of the adsorbent material, which also influence the adsorption mechanism that can be either film or pore diffusion or due to the combination of both depending on the system hydrodynamics. From the many different kinetics models, the most common models in adsorption were observed to be: pseudo-first order, pseudo-second order, intraparticle diffusion model^[107].

2.12.1. Pseudo-First Order Model

The Lagergren pseudo-first order model is most commonly used to describe the adsorption of solute from a liquid solution. This adsorption takes place through physical forces. The pseudo-first order equation of Lagergren is given by^[108]:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \dots (2-5)$$

Where q_t and q_e are the amounts of phenol adsorbed at time t and equilibrium (mg/g) respectively, and k_1 is the pseudo-first order rate constant for the adsorption process (l/min).

2.12.2. Pseudo-Second Order Model

This model is using to fit the experimental data well, declares that adsorption mechanism is occurring through chemical means^[109]. When the adsorbate removal from a solution is due to physicochemical interactions between the two phases; the kinetics rate equation is express as^[110]:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \dots (2 - 6)$$

Where k_2 is the equilibrium rate constant of pseudo-second order equation (g/mg min). For the boundary conditions $t=0$, $t=t$, $q_t=0$ and $q_t = q_t$, the integrated form of Equation 2-6 becomes:

$$\frac{1}{q_e} - \frac{1}{q_t} = \frac{1}{q_e} + k_2 t \dots (2 - 7)$$

the integrated rate law for a pseudo-second order reaction. Equation (2-7) can be rearranged to obtain:

$$q_t = K_2 q_e^2 + \frac{t}{q_e} \dots (2 - 8)$$

Which has a linear form:

$$\frac{1}{q_t} = \frac{1}{h} + \frac{t}{q_e} \dots (2 - 9)$$

Where h (mg/g. min) can be regarded as the initial sorption rate($h=k_2q_e^2$).

2.12.3 Intraparticle Diffusion Model

Theoretical treatments of intraparticle diffusion yield rather complex mathematical relationships which differ in form as functions of the geometry of the biosorbent particle. A functional relationship common to most treatments of intraparticle diffusion is that uptake varies almost proportionately with the half-power of time, $t^{0.5}$, rather than t ; a nearly linear variation in the quantity biosorbed with $t^{0.5}$ is predicted for a large initial fraction of reactions controlled by rates of intraparticle diffusion. Good linearization of the data is observed for the initial phase of the reaction in accordance with expected behavior if intraparticle diffusion is the rate-limiting step^[111]. According to Weber and Morris (1963), if the rate-limiting step is intraparticle diffusion, a plot of solute sorbed against the square root of the contact time should yield a straight line passing through the origin^[112]. The most-widely applied intraparticle diffusion equation for biosorption system is given by:

$$q_t = k_i t^{1/2} + C \dots (2 - 10)$$

where k_i is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$)

$t^{1/2}$: the root of the time ($\text{min}^{1/2}$)

C : the thickness of boundary layer.

The diffusion constant was determined from the slope of the plot between q_t and $t^{1/2}$.

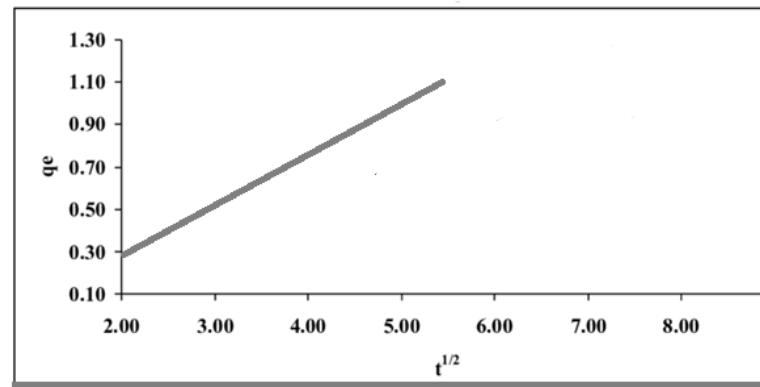


Fig.2.13. The linear of Intra particle diffusion model

2.13. Characterization of, Carbon Nanotube, Copper Oxide and Nano Composites

CNT, CuO and Nano- composites have many physic-chemical properties such as high mechanical strength, excellent thermal and electrical conductivity that made it important material for broad spectrum applications. There are different techniques to characterize these properties such as; SEM, XRD, FTIR and Raman spectroscopy. Raman spectroscopy were applied to analyze mixture of various carbon nanotube samples to presence of single-walled, double-walled and multi-walled carbon nanotubes (SWCNT, DWCNT, MWCNT, respectively)^[113]. FTIR were used to characterized the presence of functional groups in (CHIT and CHIT-MWCNT), and XRD to study the crystallinity, while SEM were used to study the morphology of the membranes^[114]

2.13.1. Raman Spectroscopy

Raman spectroscopy is a powerful tool to study vibrational and electronic properties, structures of CNT particularly for characterization of CNT's diameters, and quality of the samples^[115]. It can be analyses Various carbon materials including single-walled (SWCNT), double-walled (DWCNT) and multi-walled (MWCNT) carbon nanotube^[116]. There are three peaks in Raman spectroscopy Tangential modes—G or band, Disorder-induced D band through

which the structural composition and presence of pollutants in the sample. While the Radial Breathing Modes (RBMs) used to distinguish between graphene and CNT) when This peak indicates the presence of single-walled CNTs in the sample, but in graphene, this peak does not appear^[117]. Figure 2.14 shows the longitudinal optical (LO) phonon mode, occurring around 1580 cm^{-1} and is called the G band, and the other is dispersive Raman feature called the G' band (or 2D band). The G'-band frequency depends on the laser excitation energy, Elaser (dispersive behavior) and appears at 2700 cm^{-1} for Elaser $\frac{1}{4}$ 2.414 eV . D band appear in 1350 cm^{-1} for Elaser $\frac{1}{4}$ 2.414 eV ^[118] for disordered carbon in graphite atoms. The relative intensity of D to G provides a good indicator for determining the in-plane crystallite size or the amount of disorder in the sample^[119].

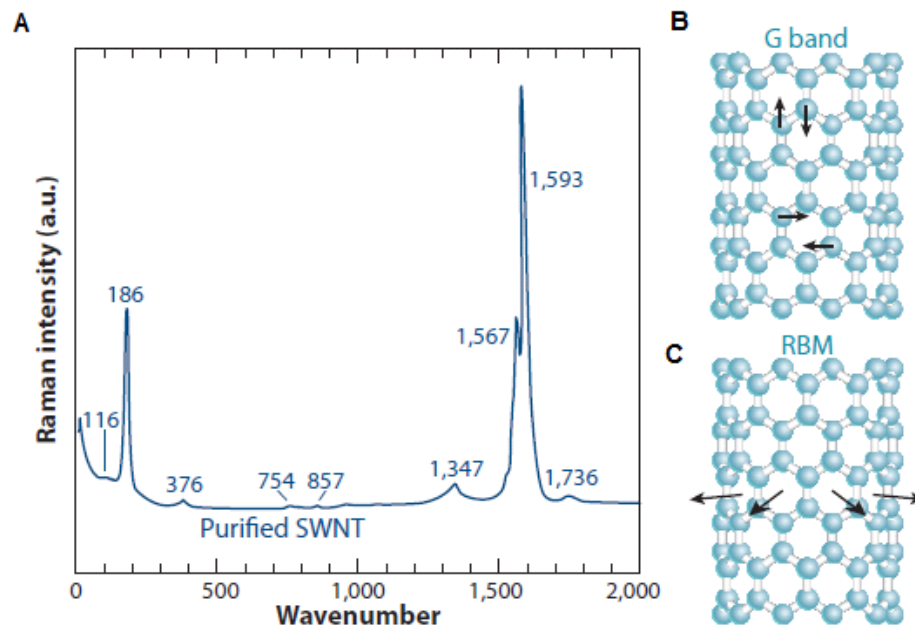


Fig.2.14. Shows A) Room-temperature Raman spectrum from a SWNT bundle grown by the laser vaporization method. B) The G-band eigenvectors for the C-C bond stretching mode^[120].

The G band is composed of up to six peaks that are allowed in the first-order Raman spectra. The vibrations are tangential to the tube surface, three along the tube axis (LO) and three along the circumference (TO). D) Eigenvectors for the radial breathing mode (RBM) that appears around 186 cm^{-1} .

2.13.2. X-Ray Diffraction (XRD)

The X-ray focused on a sample material to resolve structural information hidden in the crystal lattice. XRD have a monochromatic were produced from special tube called cathode-ray tube. Filtering of polychromatic X-rays through a monochromator generates monochromatic radiation (diameter $< 10\text{ }\mu\text{m}$), which hits onto the material atomic planes. Interactions of these incident X-rays with the sample atomic planes create diffracted, transmitted, refracted, scattered and adsorbed beams according to Bragg's law^[119], which is given below:

$$n\lambda=2d\sin\theta$$

n = is an integer that defines an order of the diffracted beam. λ = represents wavelength of the incident X-ray beam. d = the distance between near atomic planes, and θ = represents angle of an incidence X-ray. CNT diffraction peak intensities depend on CNTs morphological orientation. When X-ray beam strikes single wall of CNTs, it produces (002) peaks with some parallel (h k l) reflections. On the other hand, when X-ray beams pass through an empty central core of CNTs, it produces some extra hexagonal peak arrays (h ko). It may occur multiple times at different azimuths depending on the number of helix present^[121]. Rasel and his group provided a systematic presentation of X-ray powder diffraction application in carbon nanotubes characterization, which this could be used as a reference guide for the utilization of X-ray powder diffraction to probe the various features of carbon nanotubes and carbon nanotubes based materials^[122]. In Abboud^[123] work, reported an eco-friendly and convenient method for the synthesis of CONPs using brown alga

(*Bifurcaria bifurcata*) extract. No chemical reagent or surfactant template was required in this method, which consequently enables the bioprocess with the advantage of being environmental friendly.

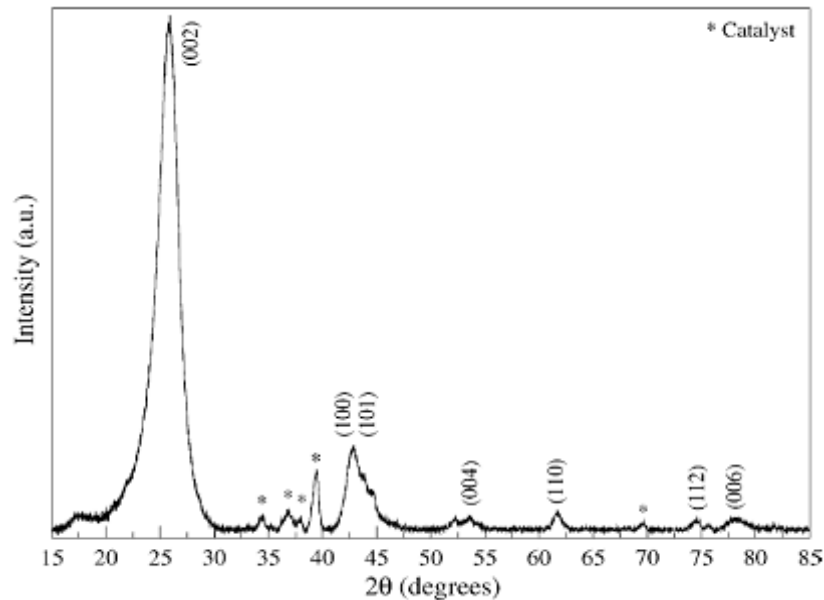


Fig.2.15. Shows XRD pattern of MWCNTs (60 nm in size and synthesized by chemical vapor deposition method). Here, incident X-ray wavelength (λ) = 0.154056 nm and Bragg peaks are obtained with Miller indices and presence of catalyst (Co and Mo) in CNT^[124].

2.13.3. Scanning Electron Microscope (SEM)

SEM is a tool at which invisible worlds of micro-space and nano-space can be seen. Details and complexity that is inaccessible by light microscopy can be revealed by SEM. This is all can be achieved through the following process^[125]. The SEM machine consists of the components and shown in fig.2.16 :

- A source to generate electrons of high energy between (100-30,000 electron volts). It is called electron gun.
- Column down for travelling the electrons (gun) through two or more electromagnetic lenses.

- Deflection system consists of scan coils.
- Electron detector for backscattered and secondary electron.
- A chamber for the sample.
- Computer system consists of viewing screen to display the scanned images and keyboard^[126]

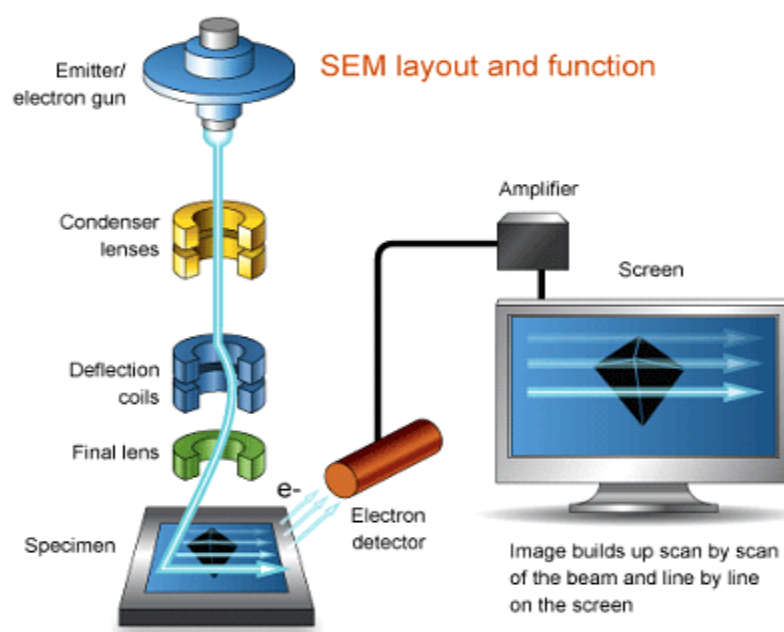


Fig.2.16. Show all Scanning Electron Microscope (SEM) components.

The SEM images polyindole/Ag–CuO exhibit spherical shapes with an average particle size of 290 nm. The images also show the porous nature of the polyindole. The CuO nanoparticles appeared as jasmine buds like at the magnification of 5 μm . Looking close up, it gave plenty of information regarding the structure and rearrangement. The average sizes of the spherical-shaped particles found to be in the range between 50 and 100 nm. It is important to note that the increased concentrations of polyindole (0.5%) and AgNO₃ (2.5%) in the nanocomposites (CA5) have produced significant changes in the morphology and structure^[127].

2.13.4. FT-IR Spectrometry (FTIR)

The IR region is lying between visible and microwave end of the electromagnetic radiation spectrum. It is basically divided into three main areas: near IR ($14000\text{--}4000\text{ cm}^{-1}$), mid-IR ($4000\text{--}400\text{ cm}^{-1}$), and far IR ($400\text{--}40\text{ cm}^{-1}$). IR spectroscopy is an advanced analytical tool and extensively used to investigate the structure of chemical compounds and identify the functional groups such as, C=O, C-H, N-H, C-C, C-H, C-O, O-H in the sample by irradiating with IR radiations. And this can be suitable to measuring all types of samples: solids, liquids, and gases. The molecules or sample absorbed the IR radiations and displayed an absorption spectrum. IR measured the amount of radiations absorbed by the molecule and their intensity. The absorption of the IR radiations causes various molecular motions in the molecule, which create a dipole moment^[128]. The FTIR measurements for the synthesized copper oxide NPs is given strong peaks observed at 3441 , 1633 , 1046 and 1403 cm^{-1} corresponds to O-H, C=C, C-O and aliphatic C-H stretching vibrations respectively. The peaks at 620 and 686 cm^{-1} corresponds to Cu-O vibration of copper oxide nanoparticles^[129].

2.14. Atomic Absorption Spectroscopy (AAS)

Atomic spectroscopy is the oldest instrumental method for the determination of elements. It is highly sensitive for elements that are difficult to excite (having a high excitation energy), since there are much more non-excited atoms in the flame than excited ones. Highly excited elements in a high-temperature flame emit radiation efficiently, so they can be detected with greater sensitivity by emission spectrometry. These techniques are introduced in the mid of 19th Century during which Bunsen and Kirchhoff showed that the radiation emitted from the flames depends on the characteristic element present in the flame. The potential of atomic spectroscopy in both the qualitative as well as quantitative

analysis were then well established. The developments in the instrumentation area led to the widespread application of atomic spectroscopy^[130]. Elemental composition of different parts including leaves, seeds and fruits have been determined by using Atomic Absorption Spectrophotometer (AAS). A total of 14 elements K^+ , Mg^{+2} , Ca^{+2} , Na^+ , Fe^{+2} , Co^{+3} , Mn^{+2} , Cu^{+3} , Cr^{+3} , Zn^{+2} , Ni^{+3} , Li^{+1} , Pb^{+4} and Cd^{+2} have been measured. Their concentrations were found vary in different samples. Medicinal properties of these samples of plant and their elemental distribution have been correlated^[131].

Chapter Three

(Experimental part)

3.1. Materials

3.1.1. The natural and Chemicals Materials

The properties of the chemicals and natural raw compounds which are used in this work are show in the table (3.1).

Table (3.1): The natural and chemicals materials

No	material	Source
1	Charcoal	 Sinsil Al-Tayeha village - Diyala – Iraq
2	Activated charcol	 Sinsil Al-Tayeha village - Diyala – Iraq
3	Lemon juice	 Lemon juice - Diyala province

4	Methanol (98.99%)	 India- Sigma
5	plant extract	 lemon leaves - Diyala province
6	hydrated copper chloride $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ 99%	 France
7	Sodium hydroxide NaOH 99%	 Germany

3.1.2. Instruments and Apparatus

The instruments and tools that are used in this study are tabulated with their details, origin, and location in **table (3.2)**.

Table (3.2): The instruments used in this study.

NO	Apparatus name	Details & Origin	Location
1	<i>Electric scal</i>	KERN ACJ/ACS,ACS 120-40, WB 12 AE 0308, max 120 g, d= 0.1 mg, (Germany)	Diyala University/College of Education for pure sciences
2	<i>Oven</i>	BINDER, Hotline International (20-360), (Germany)	Diyala University/College of Education for pure sciences
3	<i>pH- meter</i>	 Germany-Sigma	Diyala University/College of Education for pure sciences
4	<i>Centrifuge</i>	 USA	Diyala University/College of Education for pure sciences

5	<i>Ultrasonic device</i>	 Ningbo Runyes Medical Instrument Co. AC220V,F50Hz (China)	Diyala University/College of Education for pure sciences
6	<i>Electrical magnetic stirrer</i>	 Heidolph- MrHei-Standard- Germany	Diyala University/College of Education for pure sciences
7	<i>Infrared Thermometer</i>	 Germany-Sigma	Diyala University/College of Education for pure sciences
8	<i>FT-IR spectroscopy</i>	Japan	Diyala University/College of Education for pure sciences
9	<i>Atomic Absorption Spectroscopy Photometer</i>	Shimadzu AA-7000, (Japan)	College of Science, University of Baghdad, Iraq

	(AAS)		
10	X-ray Diffraction Spectroscopy (XRD)	College of Science/University Kashan	Iran
11	Raman Spectroscopy	College of Science/University Kashan	Iran
12	Scanning Electron Microscope (SEM)	College of Science/University Kashan	Iran

3.2. Preparation of carbon nanotubes (CNTs)

3.2.1. Preparation the source of carbon and activated carbon

The charcoal was obtained from the *Sinsil Al-Tayeha village-Diyala-Iraq* by burning the stalk of the *Citrus aurantium* and *morus* using primitive methods as shown in the scheme 3. 1. Excavate a pit, put in the charge of wood and cover the pit with excavated earth to seal up the chamber. The earth forms the necessary gas-tight insulating barrier behind the carbonization can take place without leakage of air; this would allow the charcoal to burn away to ashes and give a charcoal, see fig.3.2.

Activated carbon, also called activated charcoal to have small low-volume pores that increase the surface area available for adsorption or chemical reactions. The *Citrus aurantium* or *morus* charcoal (100 g) was grinded well to became a powder. Drying the charcoal powder with air for 24 hours, after that, add 50 mL of the lemon juice to the charcoal powder with stirring to get a cohesive paste. The paste was covered and left for 24 hours, and it was placed

in an oven (150 °C) for 3 hours to obtain activated carbon or activated charcoal, fig(3.1)



Fig 3.1 The steps of preparation charcoal and activated charcoal in *Sinsil Al-Tayeha village - Diyala – Iraq*

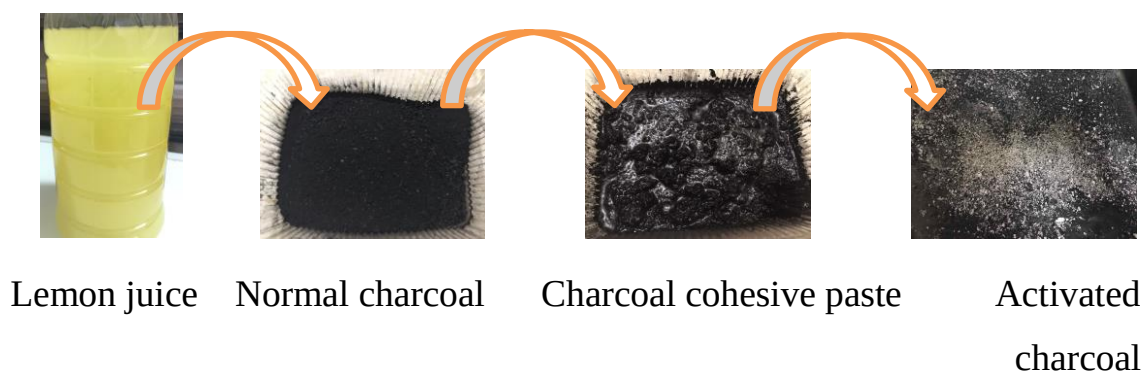


Fig.3.2 The steps of preproducing activated charcoal.

3.2.2. Preparation of Carbon Nanotubes

Multi walled Carbon nanotubes (MWCNTs) were produced by using Citrus Aurantium charcoal (normal and activated charcoal) and morus charcoal as a source of carbon at 120 °C under limit atmospheric oxygen. By chemical flame deposition CFD method were done *via* homemade reactor as shown in fig(3.3).

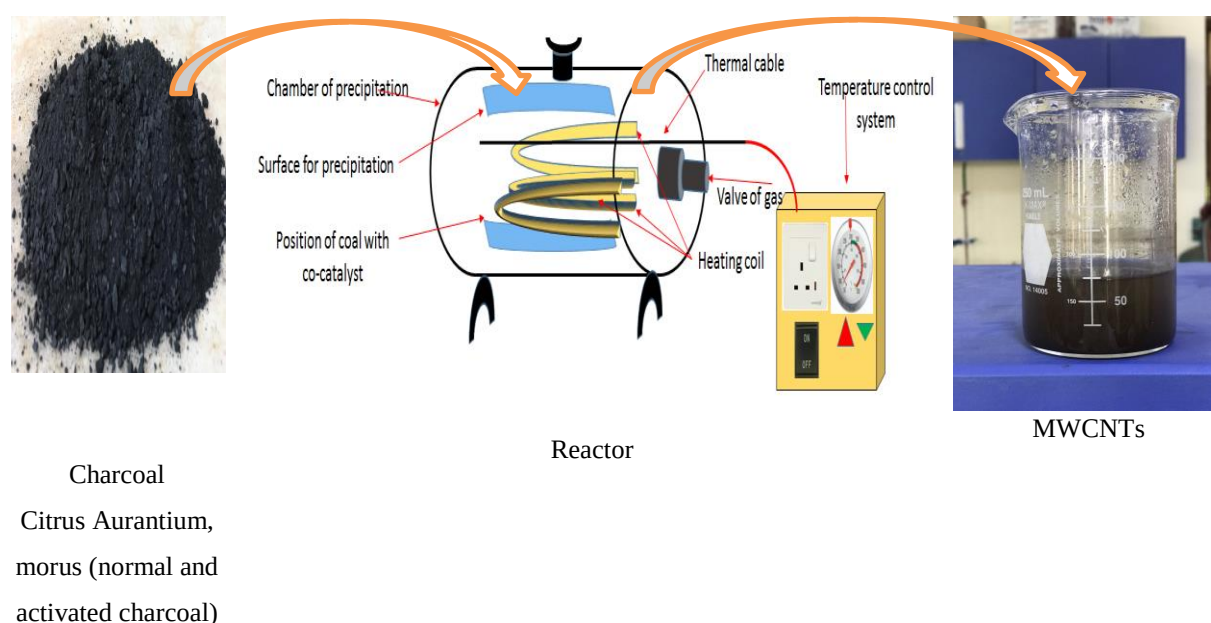


Fig.3.3. Reactor of chemical flame method (CFM)^[132].

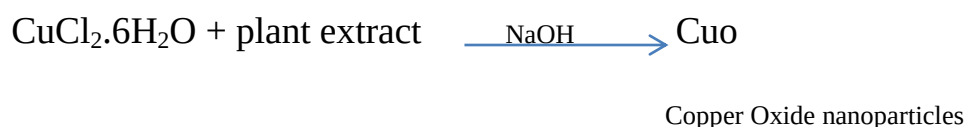
3.2.3. Preparation of copper (II) Oxide nanoparticles using lemon Leaves Extract

3.2.3.1. Preparation of Lemon Leaves extract

The lemon Leaves were collected from lemon trees in Diyala province, then cleaned from the suspended dirt by tap water then washed with distilled water and dried in shade .They were grinded with electric grinder then sifting them and stored away from wet, as shown in Figure (3.6) ,(5) g of powder leaves was added to (400) ml of deionized water and boiled for (30) min until the solution color change and then cool the mixture to room temperature and filtered it, centrifuge the filtrate at (1200) rpm for (2) min to remove biomaterials and store the extract at room temperature for use in the preparation of the copper oxide nanoparticles, as shown in Figure (3.6).

3.2.3.2. Preparation of copper (II) Oxide nanoparticles

Copper (II) chloride hexahydrate ($\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$) (0.3) g was dissolved in (50 mL) of deionized water with continuous stirring and then 10 mL) of plant extract is added gradually with continuous stirring at room temperature, raise temperature of solution to (80°C) and then adjusts pH of the solution by adding sodium hydroxide (0.1 M) approximately (10 mL) where precipitate with a light green color formed, then this was filtered and washed with deionized water several times and then with absolute ethanol to remove impurities and dry in an oven at (60°C) for (2) hours . The steps are shown in Figure 3.4 and the reaction equation is:



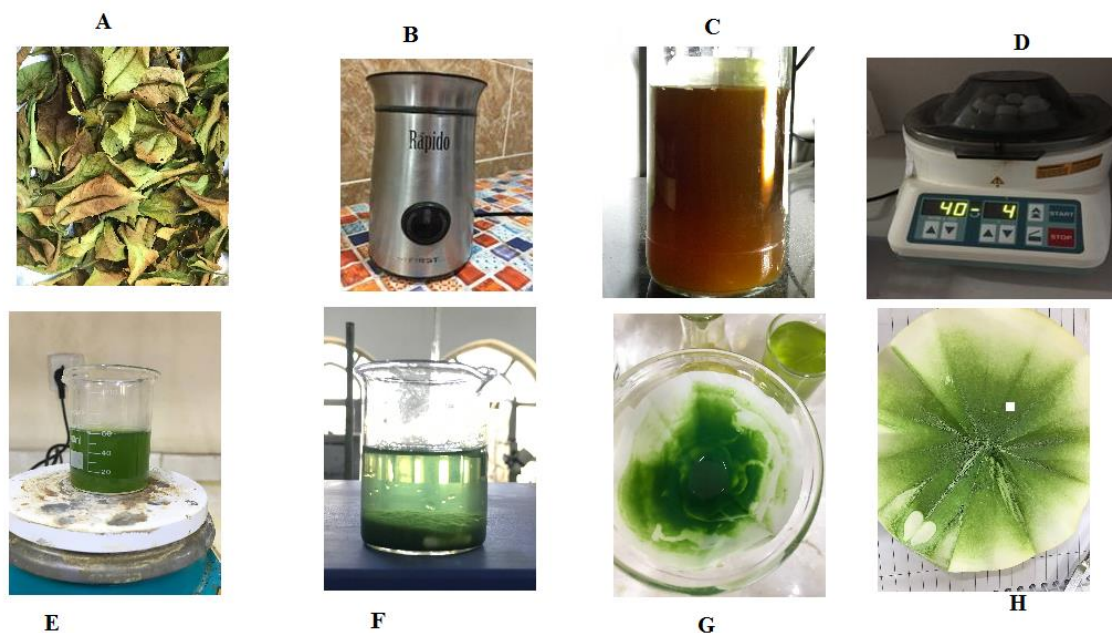


Fig.3.4. Steps of the preparation of copper (II) oxide nanoparticles(A-H) using lemon Leaves Extract.

3.2.3.3. Preparation CNT of citrus aurantium charcoal /CuO composite, CNT of citrus aurantium charcoal Active/CuO composite and CNT of morus charcoal /CuO composite

Using impregnation method the MWCNTsc/CuO compesites were synthesized (0.01g MWCNTsc : 0.03g nano CuO) . An impregnated solution was prepared by suspended (0.01g) MWCNTsc and (0.03g) CuO in ethanol (20 mL) at room temperature with constant stirring; the mixture was placed in water Bath apparatus. After 1.5 hour the nanoparticles are completely suspended and the solvent was evaporated to obtain a MWCNTsc /CuO as a binary compasite. The MWCNTsca/CuO, MWCNTsm/CuO and MWCNTsmc/CuO composed also prepared using same method.

3.3 Studying the factors affecting adsorption process

3.3.1. Effect of contact time on Pb^{+2} ion Adsorption

The time that is required for the adsorption process to reach equilibrium at temperature of 298 K and was determined by using five volumetric flasks with a volume of (100 mL) and containing (100 mL) polluted water contains a Pb^{+2} ion with initial concentration of (0.8523) mg/L.

Adsorbent amount of 0.1 g of (prepared MWCNTs or nano CuO or binary composite MWCNTs/CuO) was added into each flask and covered them with glass stopper and placed in a water bath shaker at constant temperature of (298) K at speed of (100) rpm at various time intervals (10, 20, 30, 40, 50, 60) min. Then filtered the solutions and finally measure the concentration of Pb^{+2} ion in polluted water to reach equilibrium using atomic absorption spectrophotometer at λ_{max} of (283.32) nm for Pb^{+2} ion.

3.3.2. Effect of quantity of samples adsorbent

The effect of adsorbent quantity was studied using (50, 100, 150, 200 and 250 and 300) mg from prepared MWCNTs or nano CuO or binary composite MWCNTs/CuO for the removal of Pb^{+2} ion using a fixed (100 mL) of (0.8523 mg/L Pb^{+2} ion), temperature at 298 K, stirring speed at 100 rpm. The contact time for adsorption was 60 min for all cases.

3.3.3. Effect of temperature.

Adsorption experiments are carried out at different temperatures (298, 308, 318, 323, 333 and 343) K to remove Pb^{+2} ion from polluted water in order to investigate the effect of temperature on adsorption. The adsorption equilibrium constant (K) calculate by using Van't Hoff equation following^[133].

$$\ln K = - \Delta H / RT + \Delta S / R \dots (3.1)$$

Where

k: The thermodynamic equilibrium constant, **ΔH**: The enthalpy change (kJ.mol⁻¹), **ΔS**: The change in entropy (kJ.mol⁻¹.K⁻¹), **R**: The gas constant (8.314 J.mol⁻¹.K⁻¹) and **T**: The absolute temperature (K).

3.4. Calculation of lead ion (Pb⁺²) Concentration after adsorption processes

Multi-walled carbon nanotubes and nano copper oxides and their composites have been extensively studied as an effective adsorbents for the removal of lead ion (Pb⁺²) from polluted water in environmental remediation. In present work, MWCNTs and binary composite MWCNTs/ nano CuO were synthesized and investigated for Pb⁺² ion adsorption.

The residual lead ion Pb⁺² concentrations in the polluted water was then measured by atomic absorption and the amount of adsorbed lead ion Pb⁺² were calculated as follows^[134]

$$q_e = v(C_o - C_t)/w \dots (3 - 2)$$

Where q_e is the amount of lead ion Pb⁺² adsorbed by the MWCNTs (mg/g), C_o is the initial metals ion concentration (mg/L), C_t is the final metal ion concentration after a certain period of time (mg/L), V is the initial solution volume (L) and m is the MWCNT dose (g) and W is the weight of the adsorbent in gram scale. The percentage of removed metal ions in solution was calculated using Equation:

$$\%Removed = \frac{C_o - C_t}{C_o} \times 100 \dots \dots (3 - 3)$$

3.5 Kinetic of adsorption of Pb⁺² ions

Kinetic experimental procedures were identical to the equilibrium tests. The effect of contact time on the amounts of adsorbed Pb⁺² ions on the adsorbent materials at any time, t, were calculated from the concentrations in solutions before and after adsorption. At any time, the amount of adsorbed Pb⁺² ions

(mg/g) onto the adsorbent materials was calculated from the mass balance equation as follows^[134]

$$q_t = v(C_0 - C_t)/w \dots (3.4)$$

where q_t is the amount of adsorbed Pb^{+2} ions on the adsorbent materials at any time (mg/g); C_0 is the concentration of metal ions before adsorption in mg/L, C_t is the concentration of metal ions after adsorption in mg/L, V is the volume of metal ions solution in liter scale, and W is the weight of the adsorbent in gram scale.

To study the kinetic of adsorption of lead ion, five volumetric flasks (50 mL) of Pb^{+2} ion with initial concentration of (0.8523) mg/L were used. Weight (100) mg of prepared MWCNTs or nano CuO or binary composite MWCNTs/ nano CuO was added to each flask which is then placed in water path shaker at (100 rpm) and a temperature 298 K under continuous shaking. The samples were withdrawn from the shaker at a regular time interval of (10, 20, 30, 40 and 50) min and was filtered to separate the adsorbent and then atomic absorption spectroscopy was used to measure the absorbance of the solutions to determine the concentration of lead ion. The previous procedure was repeated using the adsorbent at a temperature (298, 308, 318, 328, 338 and 348) K. The order of adsorbate – adsorbent interaction was investigated by using three kinetic models (Pseudo- first order model, Pseudo-second order model and Intraparticle Diffusion model).

Chapter Four

(Results and Discussion)

4.1. Characterization of the nanomaterials

4.1.1. Fourier Transform Infrared (FTIR) Spectra Analysis

The FTIR technique was used to confirm the synthesis of the normal charcoal, activated charcoal, normal carbon nanotube and activated carbon nanotube structure.

4.1.1.1. Fourier Transform Infrared Spectra Analysis (FTIR) of charcoal

The FTIR of normal charcoal and activated charcoal from citrus aurantium and morus sources are shown in figure (4.1) and figure (4.2) respectively. The FTIR spectrum of normal charcoal (citrus aurantium a source of charcoal) (Fig. 1. green spectrum) showed many main bands at $3417\text{--}3441\text{ cm}^{-1}$ assigned to O–H stretching and 1643 cm^{-1} refer to C=C stretching^[135]. Similarly, the activated charcoal (Fig 4.1. red spectrum) shows at 3429 cm^{-1} weak broad bands belong to O–H stretching, C–H bonds of the aromatic ring moderate intensity at $2927\text{--}2981\text{ cm}^{-1}$. Band at 1643 cm^{-1} and 1427 refers to C=O /C=C bonds, while 1049 cm^{-1} for the C–O bonds of the aromatic ring compound^[136].

On other hand, figure 4.2 black spectrum (morus source of charcoal) showed bands at $3414\text{--}3453\text{ cm}^{-1}$ assigned to O–H stretching and weak band at 1580 and 1597 cm^{-1} refers for C=C stretching, while red spectrum looks similar to the activated charcoal (Fig4. 1. red spectrum).

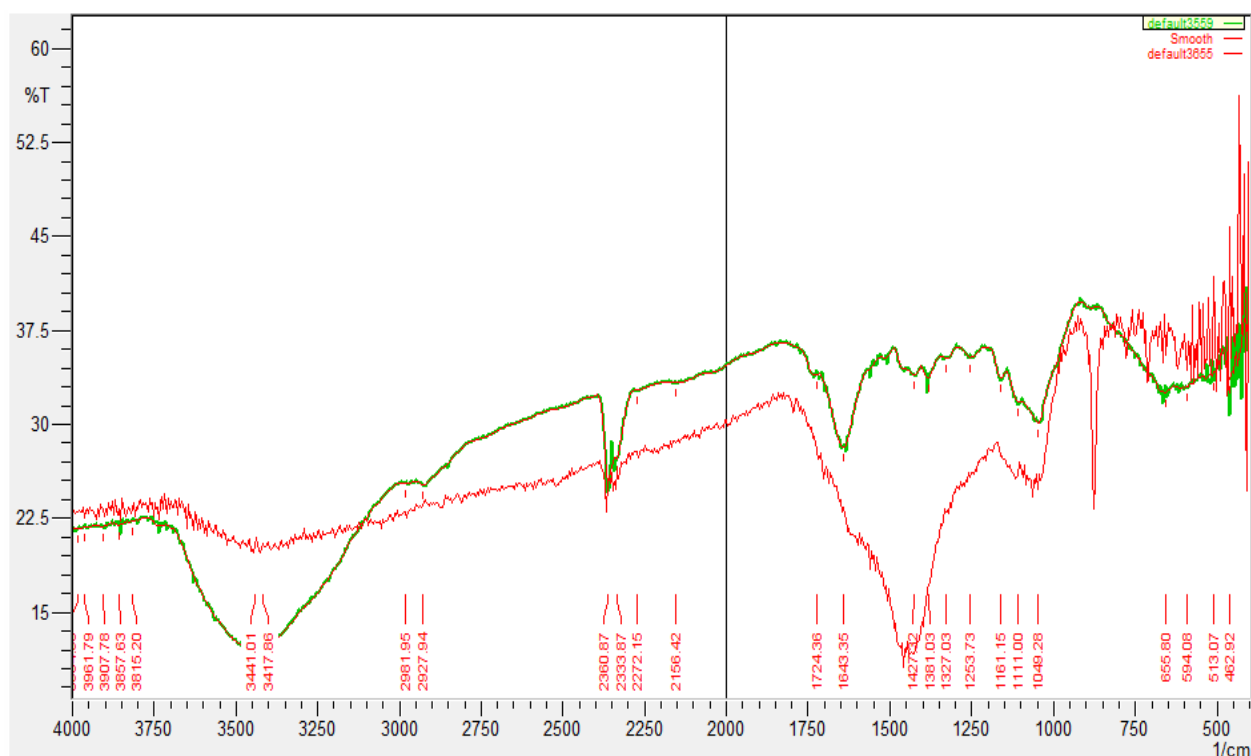


Fig4.1. FTIR spectra of normal charcoal from citrus aurantium a source (green spectrum) before and after activated (red spectrum)

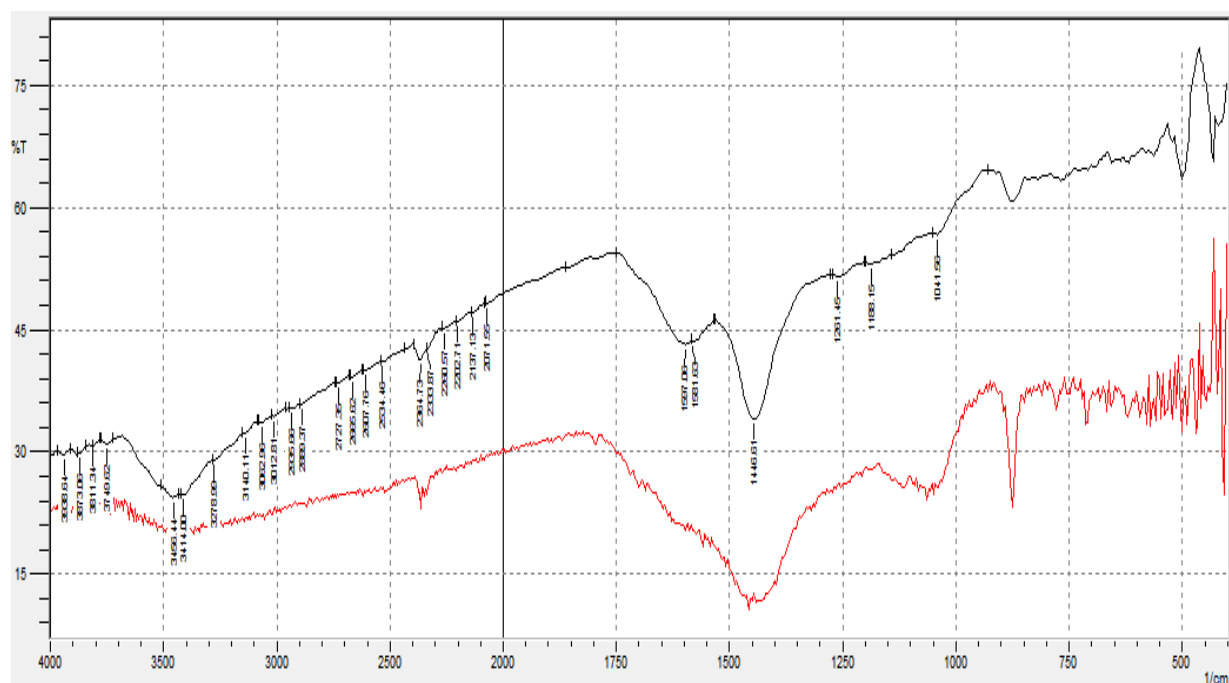


Fig4 . 2. FTIR spectra of normal charcoal from morus a source (black spectrum) before and after activated (red spectrum)

4.1.1.2. Fourier Transform Infrared (FTIR) Spectra Analysis of MWCNTs

The FTIR spectra of normal and activated MWCNTs from citrus aurantium and morus sources are shown in figure (4.3) and figure (4.4) respectively are shown. FTIR of normal MWCNTs (Fig.3. red spectrum) shows dominant peaks at $3180 - 3477\text{ cm}^{-1}$, 1622 , 1402 and 1122 cm^{-1} corresponds to O–H, C=O/C=C and C–O, respectively. While the FT-IR spectrum of activated MWCNTs shown in (Fig. 3. blue spectrum) gave different peaks at 3392 , 2924 , 1620 and 1071 cm^{-1} indicating the presence of a hydroxyl group O–H, aliphatic–CH, C=O and C–O stretching vibrations in alcohols, phenols and ether or ester groups.

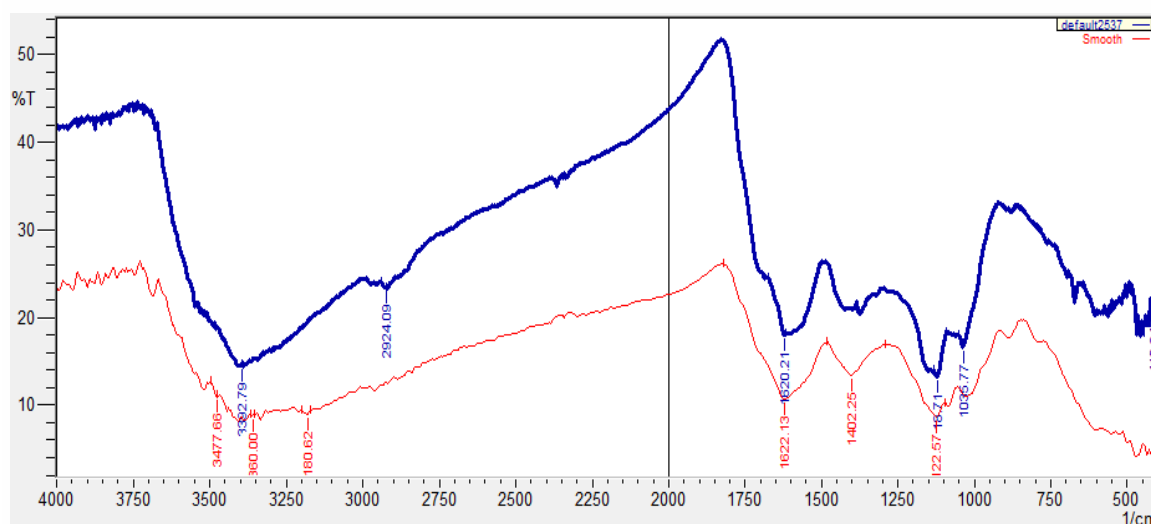


Fig4.3. FTIR spectra of normal MWCNTsc (red spectrum) and MWCNTsca (blue spectrum)

Figure 4.4 shows the FTIR spectra of normal (black spectrum) and activated (red spectrum) MWCNTs obtained from morus. As expected, the intensities of the FTIR absorption bands are weak, and the bands at 3410 cm^{-1} , 2960 cm^{-1} , 1472 cm^{-1} and 1107 cm^{-1} indicates the presence of a hydroxyl group O–H, aliphatic–CH, C=O and C–O stretching vibrations in alcohols, phenols, ether or ester groups observed in all the MWCNTs samples.^[137]

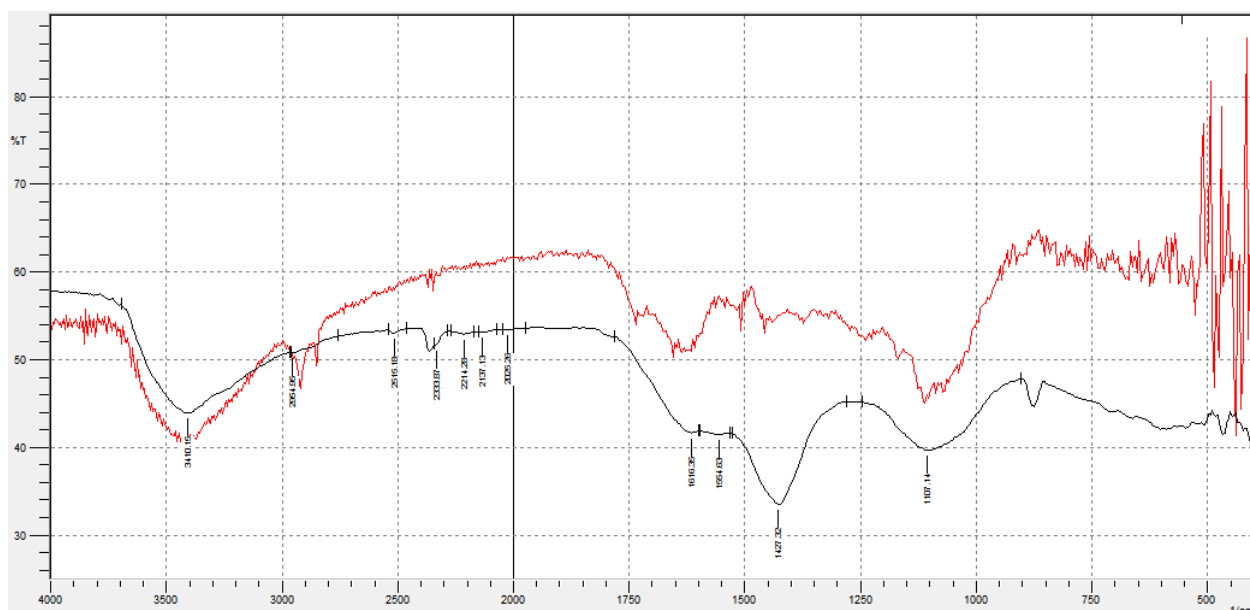


Fig4.4. FTIR spectra of normal MWCNTsm (black spectrum) and MWCNTsma (red spectrum)

4.1.1.3. Fourier Transform Infrared (FTIR) Spectra Analysis of CuO nanoparticles

The FTIR spectrums of synthesized cupric oxide nanoparticles are shown in figure 4.5. These spectra of nano-sized CuO samples are presented in two regions. In the first region, the observed bands between 500 and 1050 cm^{-1} are strong absorption, is the stretching of Cu–O^[138]. In the second region from 2800 to 3500 cm^{-1} , H₂O in the air and hydrated CuO samples are responsible for existence of such peaks. It is confirmed through the FTIR spectrum results that synthesized CuO nanoparticles compared to Cu(OH)₂ and CuCl₂.H₂O present pure.

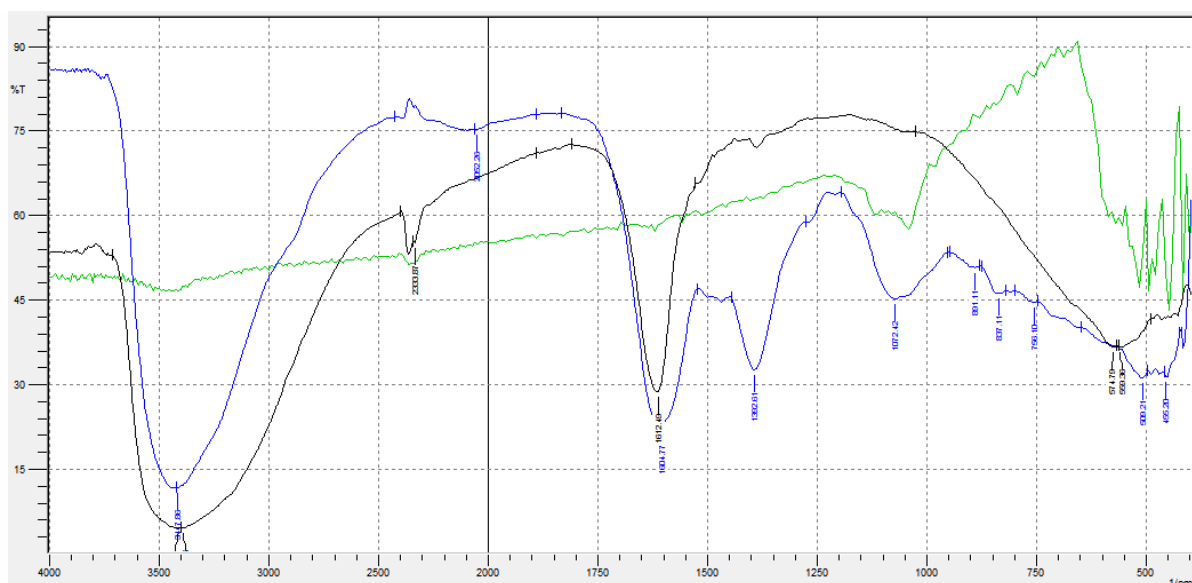


Fig4.5. FTIR spectra of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (blue spectrum), $\text{Cu}(\text{OH})_2$ (black spectrum) and CuO nanoparticles (green spectrum)

4.1.2. Raman spectroscopy of MWCNTs

Raman spectra of normal and active MWCNTs are presented in Figure 4.6. There are two peaks observed on all MWCNTs samples. In the normal MWCNTs (from citrus aurantium and morus) the D band corresponding to the degree of nanotubes structure disorder are observed at 1359 cm^{-1} , 1444 cm^{-1} and the G band corresponding to the degree of nanotubes graphitisation appeared at 1588 cm^{-1} , while in the active MWCNTs the D band observed at 1436 cm^{-1} and G band at 1582 cm^{-1} . In addition, the 2D band corresponding to stresses at 2972 and 3027 cm^{-1} were observed, which refers to normal and activated MWCNTs respectively. However, it is clearly shows that the use of activated charcoal as a source enhanced the disorder and the defects on the sidewall of tubes^[139], in which a larger D to G ratio indicates a higher defect density. The ratio of ID/IG of the normal MWCNTs (0.85) less than activated MWCNTs (0.91) and was around 0.6.

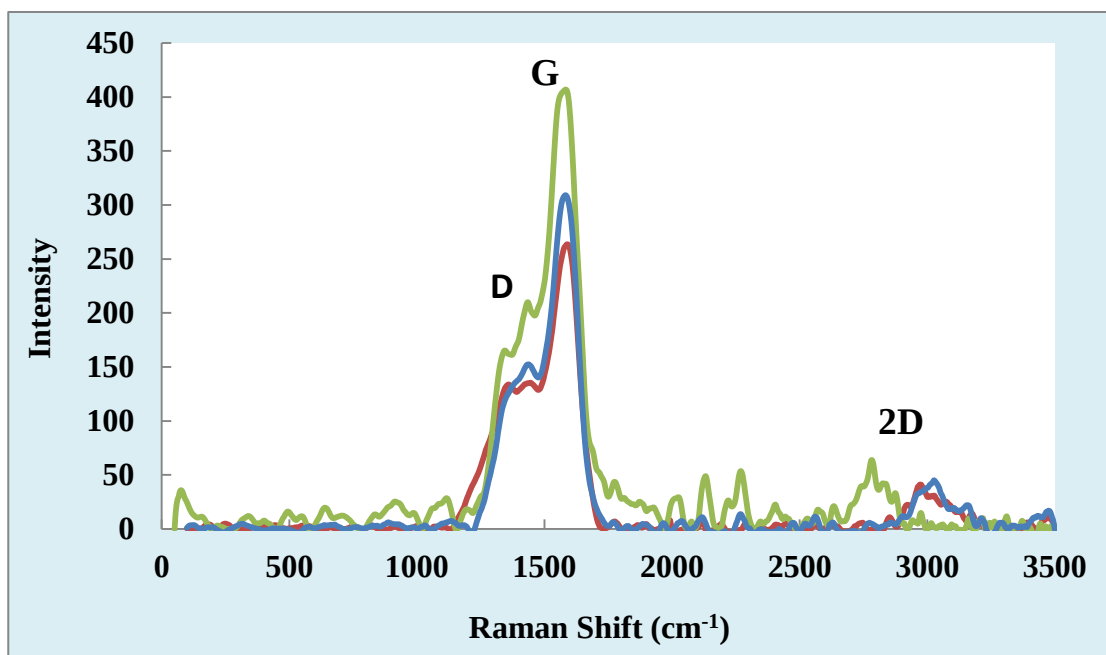


Fig4.6. Raman spectra of normal MWCNTsc (blue spectrum) and MWCNTsm (red spectrum) and activated MWCNTsca (green spectrum)

4.1.3. X-ray diffraction analysis

4.1.3.1. X-ray diffraction analysis of MWCNTs

The XRD results for the product MWCNTs were compared for all samples (MWCNTsc, MWCNTsm, MWCNTsca and MWCNTsma) and it shows that the peak point value has a negligible value of around ± 0.6 . There are only two peak point values achieved by XRD for prepared samples which are 24.07 and 42.5, see in Figure 4.7(a-d) respectively, which illustrates that MWCNTs produced are made up of tubes and are crystalline. This peak value shows the presence of carbon in the product.

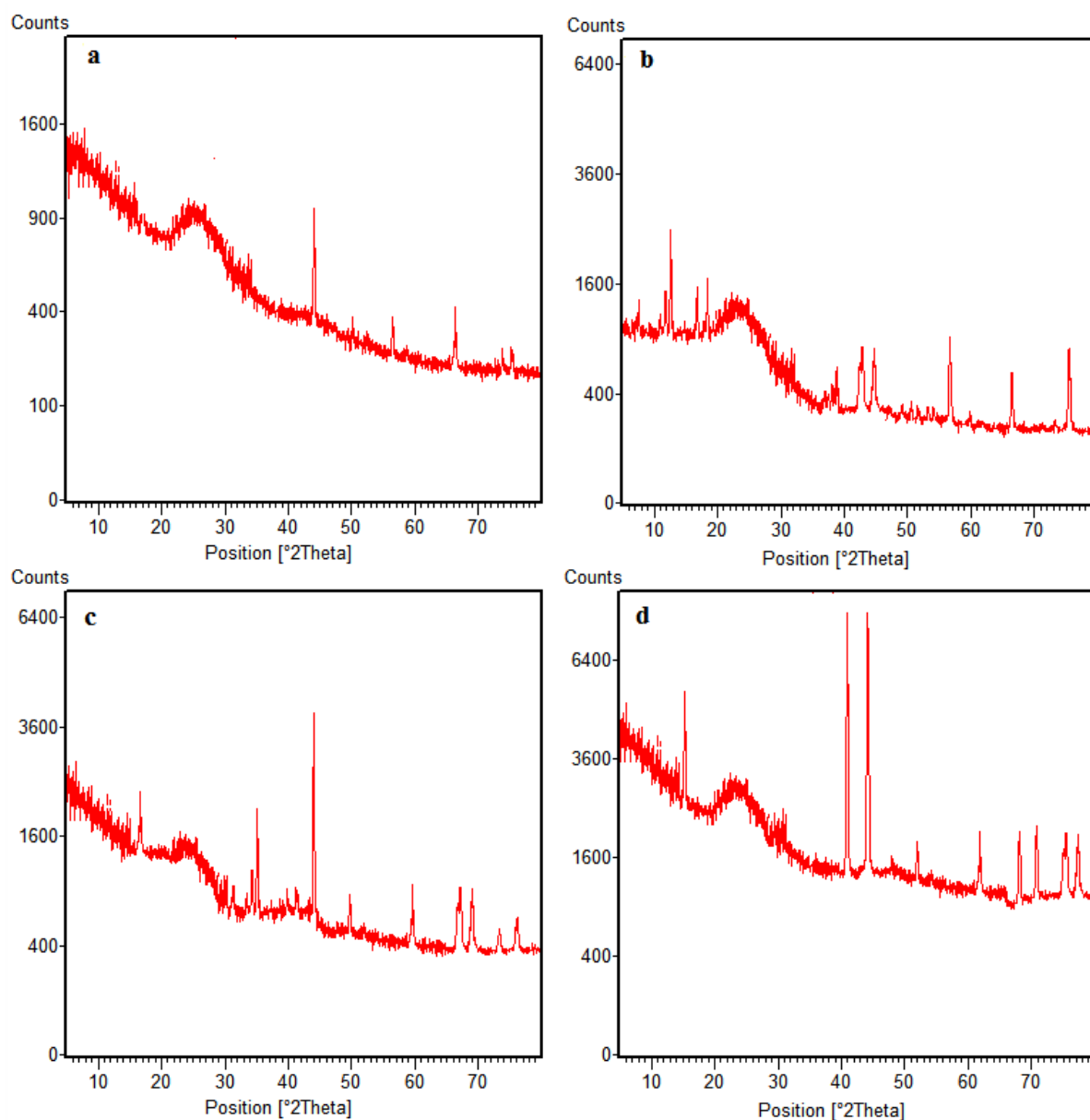


Fig 4.7. The XRD pattern of (a) normal MWCNTsc , (b) activated MWCNTsc, (c) normal MWCNTsm and (d) activated MWCNTsm

4.1.3.2. X-ray diffraction analysis of CuO nanoparticles

Figure 4.8 depicts the X-ray diffraction pattern of prepared CuO nanoparticles. The broad peaks witnessed in the diffraction pattern indicates the size of particles is of nanometer scale^[35, 140]. The average crystallite size has calculated by using the Scherrer equation; $D = K\lambda/\beta \cos \theta$ where; the symbols have their usual meaning:

D is the crystallite size, β the full-width at half maximum (FWHM) of the most intense diffraction peak in radians, θ the diffraction angle and λ the wavelength of X-ray radiation. The average crystalline size of CuO nanoparticles from the intense peaks is found to be around 37.8 nm.

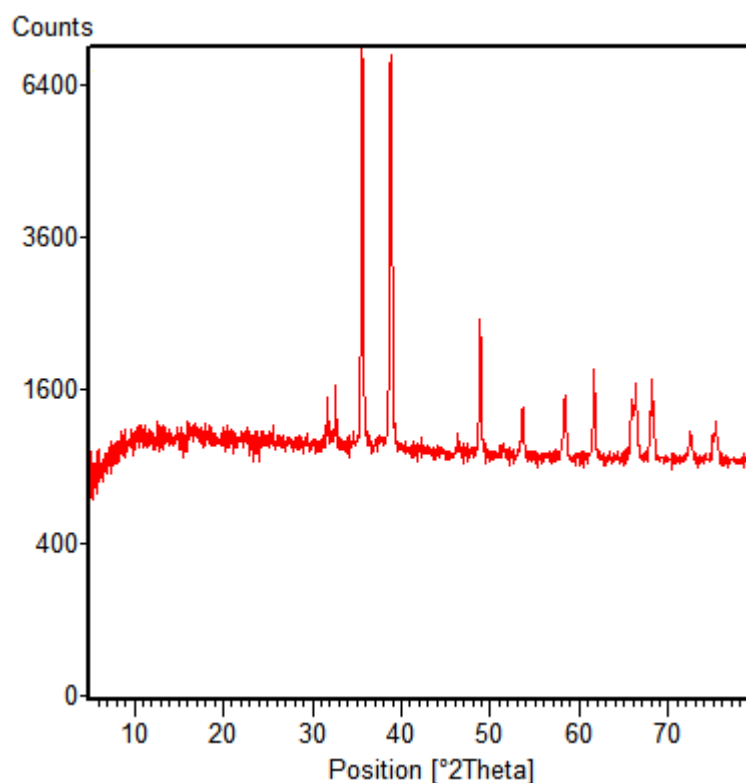


Fig4.8. XRD patterns of CuO nanoparticles

4.1.4. FESEM image

4.1.4.1. FESEM of normal and activated charcoal

The FESEM images of normal charcoal (Fig 4.9, 4.10), the products from citrus aurantium and morus respectively revealed that it have fewer nanopores than activated charcoal (Fig4.11, 4.12)^[141].

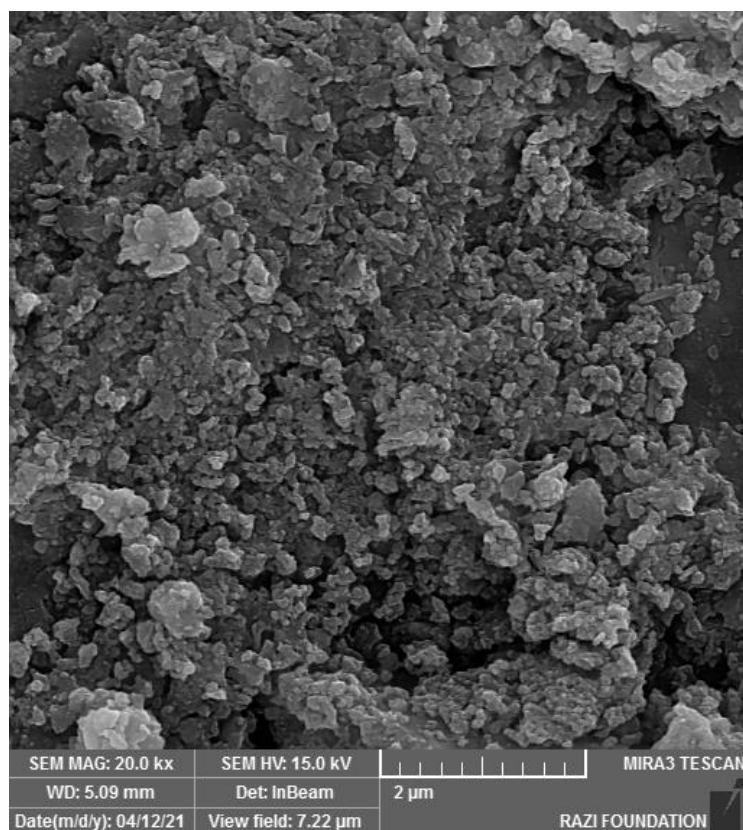


Fig4.9. FESEM images of normal charcoal from citrus aurantium as a source

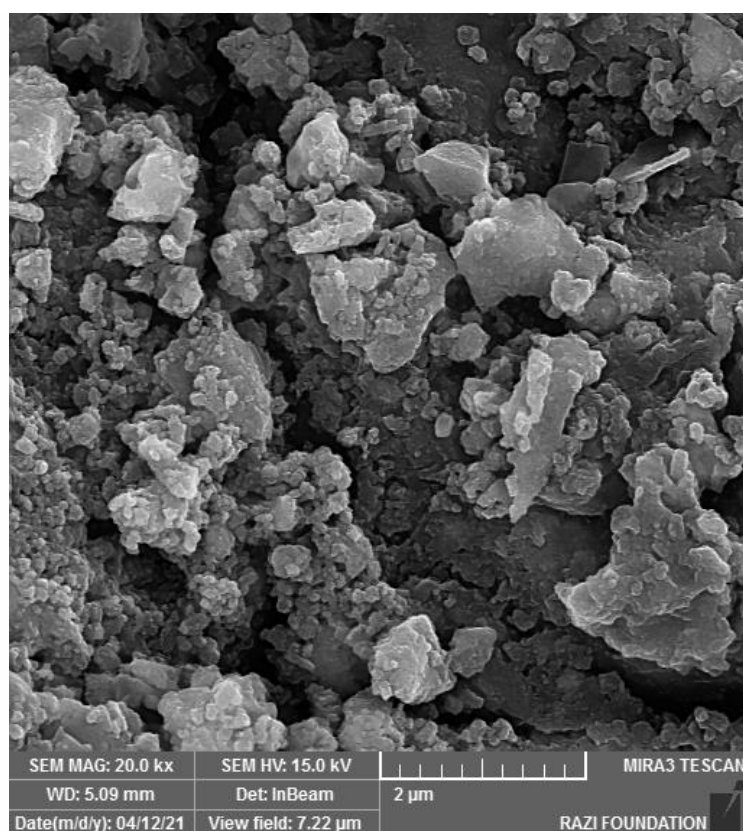


Fig4.10. FESEM images of normal charcoal from morus as a source

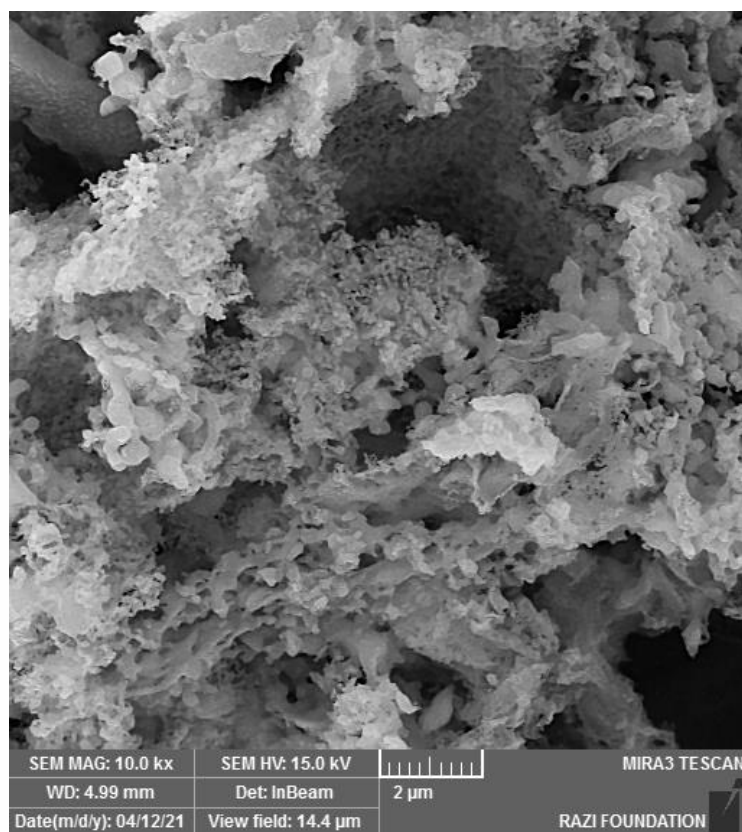


Fig4.11. FESEM images of activated charcoal from citrus aurantium as a source

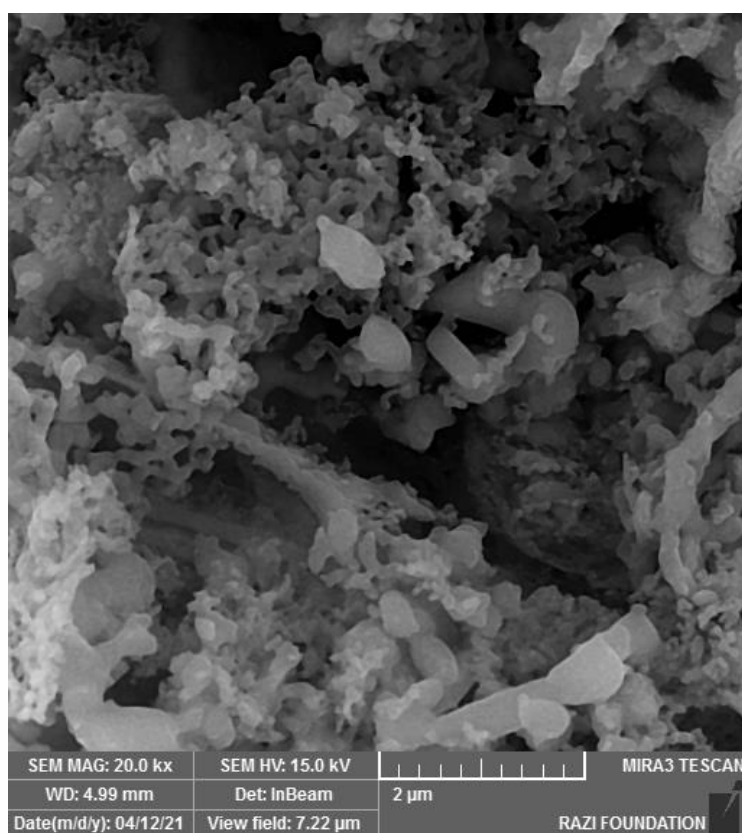


Fig4.12. FESEM images of activated charcoal from morus as a source

4.1.4.2. FESEM of normal and activated MWCNTs

The FESEM images (Fig 4.13-16) of the normal and activated MWCNTs shows few filament of carbon with average diameter 31-451 nm and length more than 1 μm with many species of unconverted carbon. In addition, the outer surface of the tubes of the normal (MWCNTsc) and (MWCNTsm) were rough, while the outer surface of the tubes of the activated (MWCNTsca) and (MWCNTsma) were smooth with some disfigurements. Moreover, it is clearly indicates that the diameter of the normal MWCNTs was a bit smaller than the activated MWCNTs. The activation process damaged some outer surface of the tubes of the MWCNTs which lead to some disfigurements on the outer layers of the activated MWCNTs.

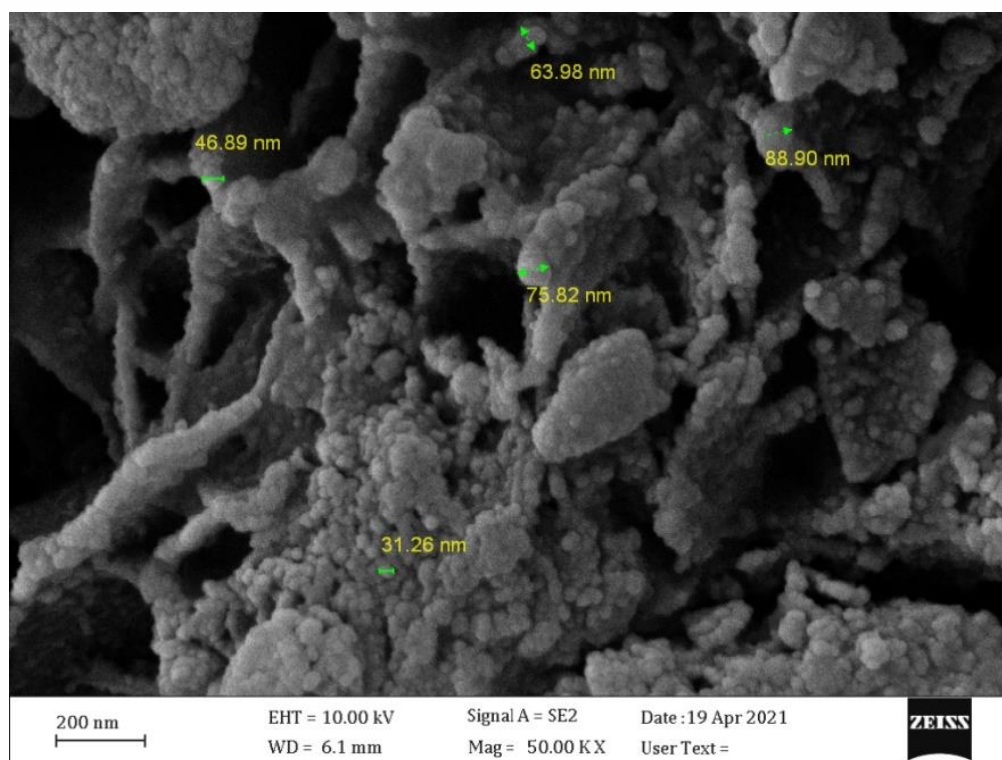


Fig4.13. FESEM images of normal MWCNTsc

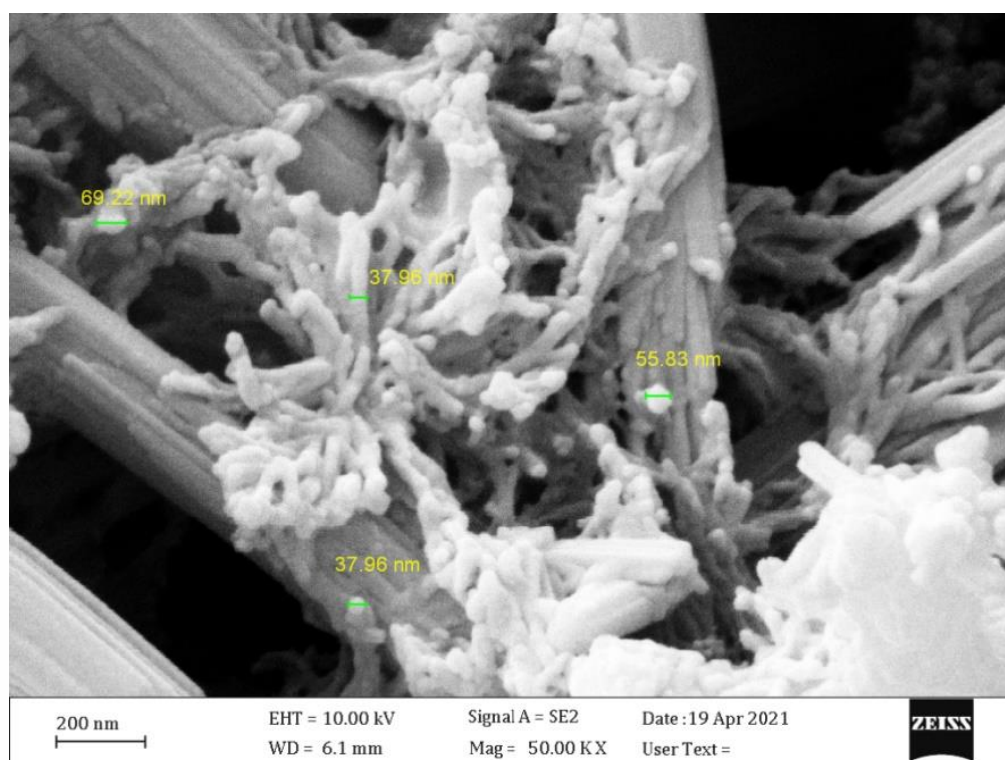


Fig4.14. FESEM images of activated MWCNTsca

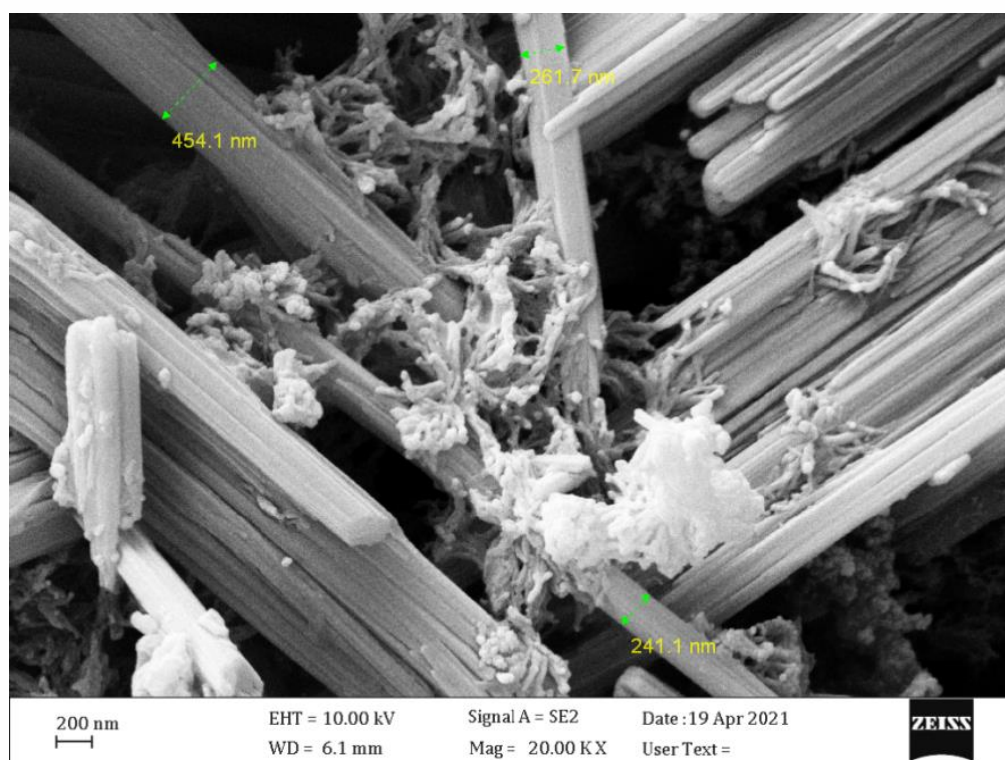


Fig4.15. FESEM images of normal MWCNTsm

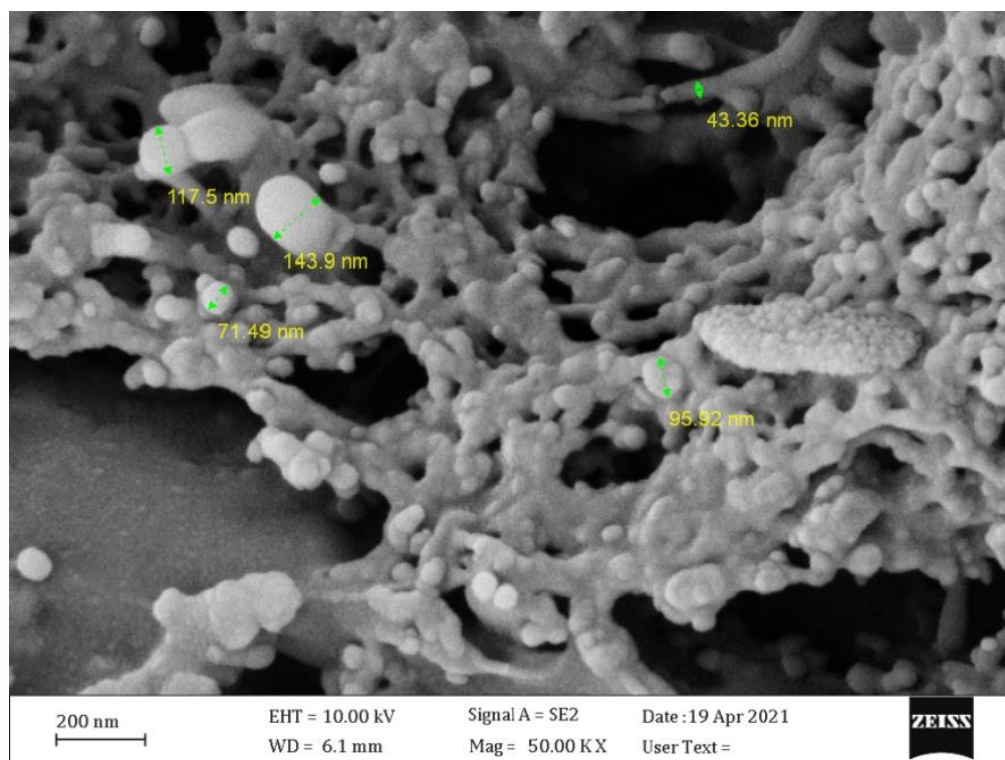


Fig4.16. FESEM images of activated MWCNTs

4.1.4.3. FESEM of CuO nanoparticles and binary composites MWCNTs/CuO

Surface morphology for the prepared CuO nanoparticle is studied using Field Emission Scanning Electron Microscopy. Figure 4.17 shows the FESEM image of a prepared CuO nanoparticle. It shows that the particles are in almost irregular shape and conglomerates some structures like islands are obtained. The close analysis of the diameter of islands gave average 71.662 nm.

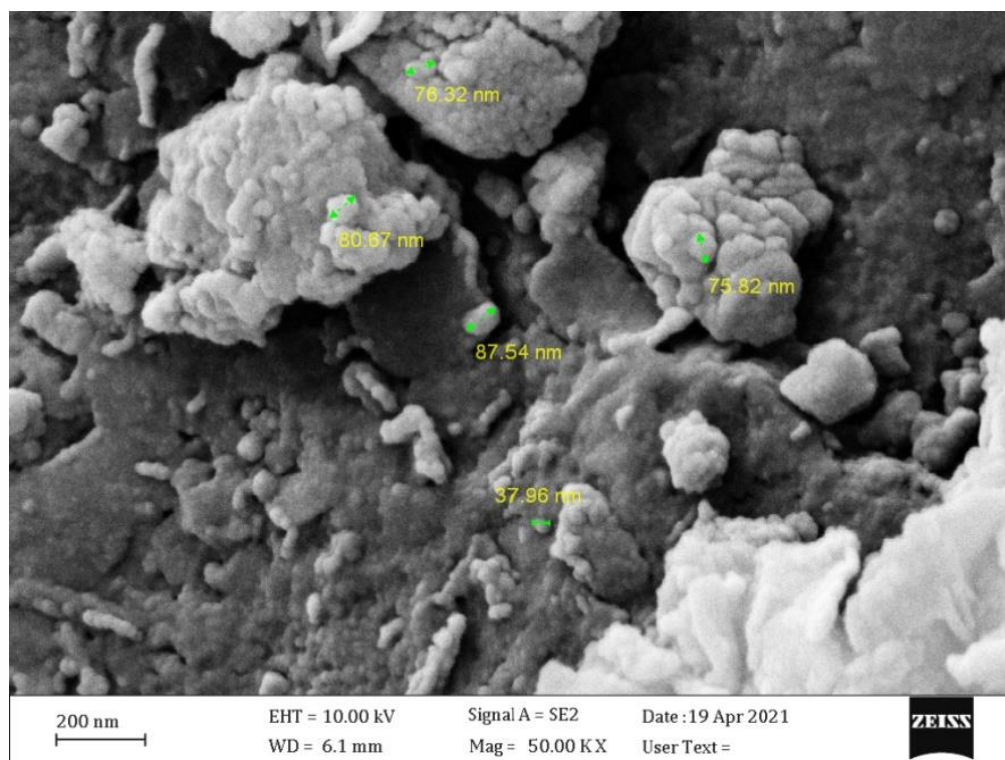


Fig4.17. FESEM image of CuO nanoparticles^[35]

Comparing Figures 4.13-17 with Figures 4.18-21, shows damage filament of carbon and they clearly tells that most of the synthesized carbon nanotubes looks completely covered with CuO nanoparticles and not like a tubular structures^[77]. The reason behind the spread of the synthesized CuO nanoparticles might be due to the fact that they have their spread within the matrix structure and this are the common characteristic for all matrixes with carbon nanotubes using flame method as illustrated in the figures below.

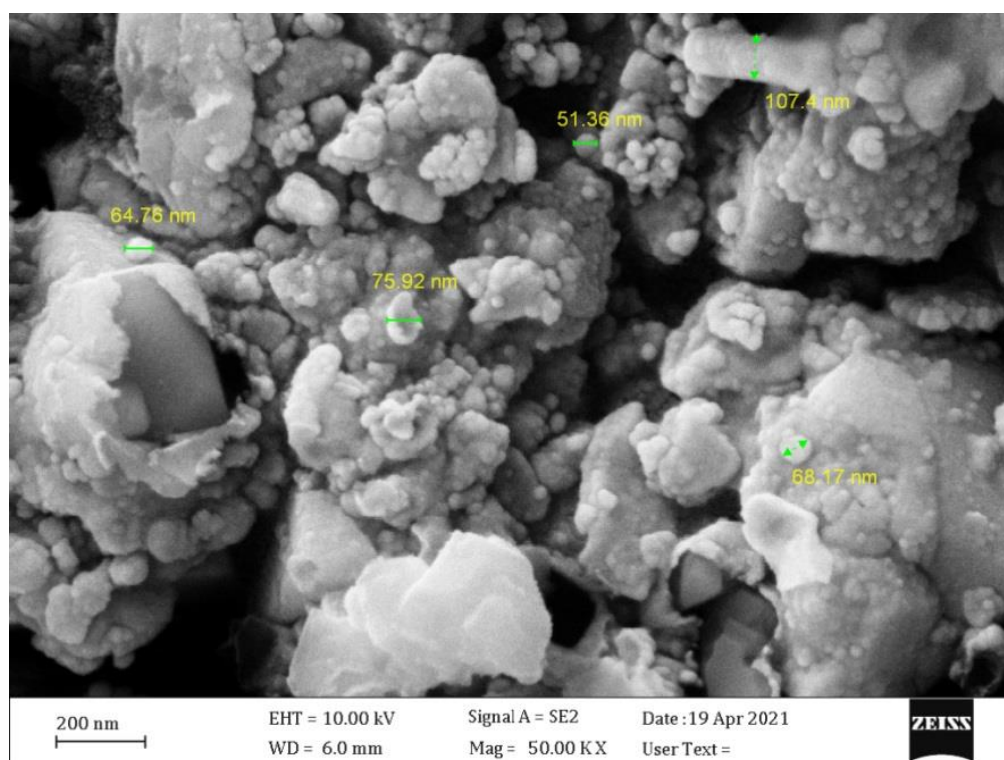


Fig4.18. FESEM image of normal MWCNTsc / CuO nanoparticles

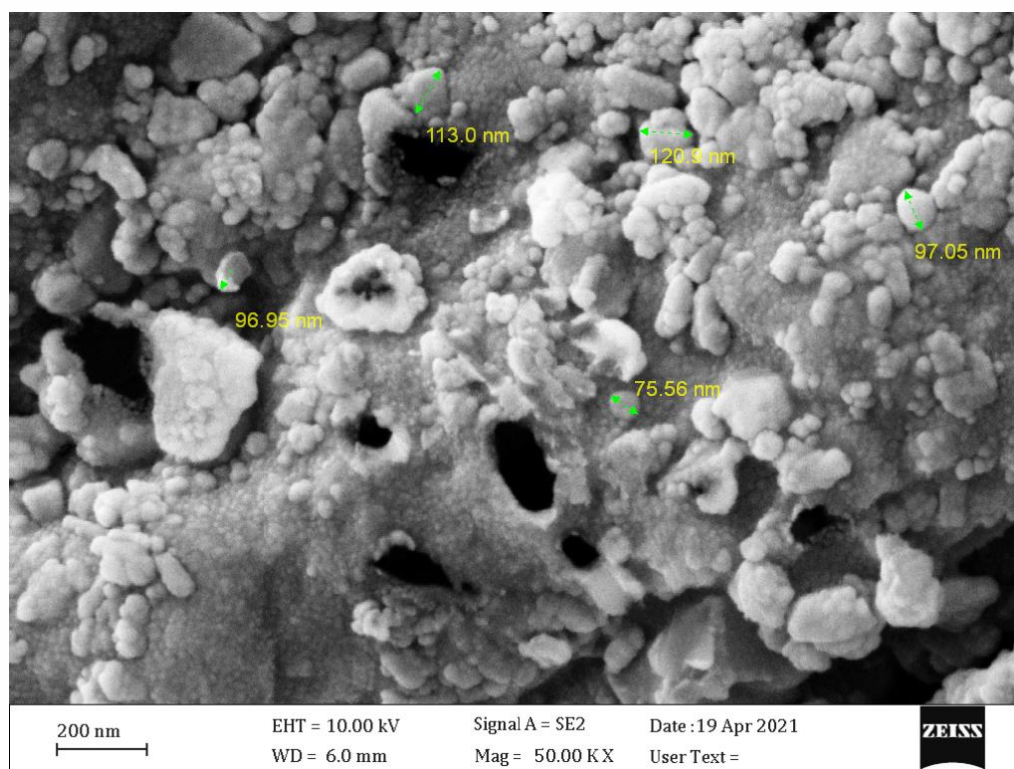


Fig4.19. FESEM image of activated MWCNTsca / CuO nanoparticles

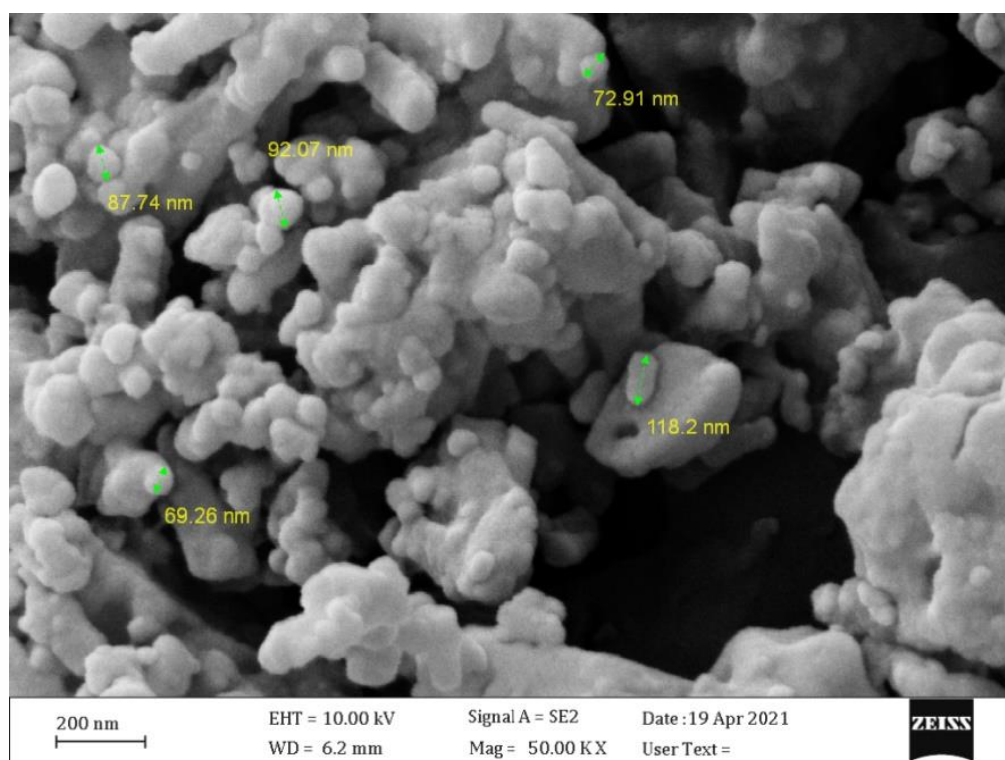


Fig4.20. FESEM image of normal MWCNTsm / CuO nanoparticles

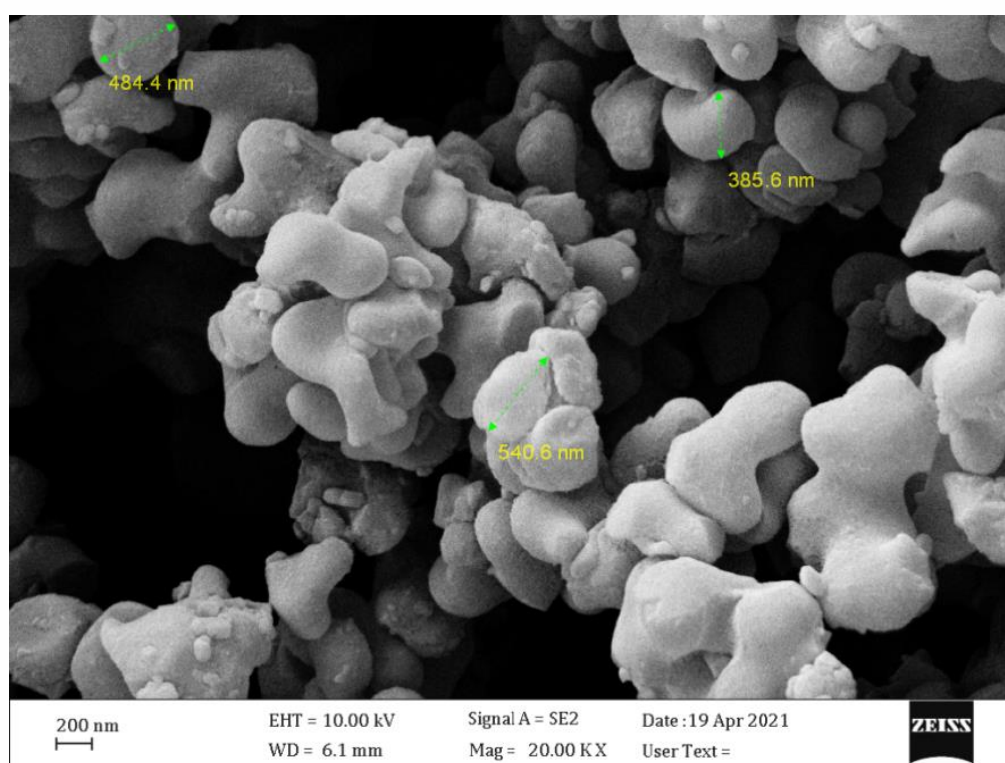


Fig4.21. FESEM image of activated MWCNTsma/ CuO nanoparticles

4.2. Adsorption of Pb^{+2}

The effect of contact time, adsorbent quantity and temperature effect on lead ion (Pb^{+2}) adsorption from polluted water was studied by multi walled carbon nanotubes that prepared from plant sources, in addition to copper oxide nanoparticles and the binary composite prepared from CuO nanoparticles/MWCNTs. Initial concentration of lead ion (Pb^{+2}) in polluted water before carrying out the adsorption process by atomic absorption was 0.8523 mg/L.

4.2.1. Effect of Contact Time on Adsorption

It is clear from table (4.1) and Fig 4.22 that the adsorption process was enhanced by the activated composite. The percent removal of Pb^{+2} increased from 60.92 to 70.01% for MWCNTsca/CuO, whereas for MWCNTsma/CuO, the percent removal increased from 63.39 to 71.019%. In the case of CuO, there was less change in the percent removed. The adsorption of Pb^{+2} with MWCNTsca/CuO and MWCNTsma/CuO were enhanced by raising the solution adsorption process. The Fig 4.22 also showed that the adsorption reached equilibrium after 40 min in the all cases^[34, 142]

Tables (4.1): Effect of contact time on the adsorption of Pb^{+2} ion at 298 K by all samples prepared

MWCNT _{sc}				MWCNT _{sm}			
t min	C ₀ mg/L	C _t mg/L	R%	t min	C ₀ mg/L	C _t mg/L	R%
10	0.8523	0.653	23.38379	10	0.8523	0.623	26.90367
20		0.4712	44.7143	20		0.4912	42.36771
30		0.421	50.60425	30		0.401	52.95084
40		0.311	63.5105	40		0.2701	68.30928
50		0.301	64.6838	50		0.261	69.37698
60		0.3001	64.78939	60		0.265	68.90766
MWCNT _{sca}				MWCNT _{sma}			
t min	C ₀ mg/L	C _t mg/L	R%	t min	C ₀ mg/L	C _t mg/L	R%
10	0.8523	0.753	11.65083	10	0.8523	0.693	18.6906
20		0.613	28.07697	20		0.6012	29.46146
30		0.521	38.87129	30		0.421	50.60425
40		0.331	61.16391	40		0.301	64.6838
50		0.322	62.21988	50		0.302	64.56647
60		0.333	60.92925	60		0.312	63.39317
CuO				MWCNT _{sc} /CuO			
t min	C ₀ mg/L	C _t mg/L	R%	t min	C ₀ mg/L	C _t mg/L	R%
10	0.8523	0.723	15.17071	10	0.8523	0.623	26.90367
20		0.5012	41.19442	20		0.5112	40.02112
30		0.421	50.60425	30		0.421	50.60425
40		0.3791	55.52036	40		0.361	57.64402
50		0.378	55.64942	50		0.368	56.82272
60		0.382	55.1801	60		0.362	57.52669
MWCNT _{sm} /CuO				MWCNT _{sca} /CuO			
t min	C ₀ mg/L	C _t mg/L	R%	t min	C ₀ mg/L	C _t mg/L	R%
10	0.8523	0.723	15.17071	10	0.8523	0.619	27.37299
20		0.6112	28.28816	20		0.473	44.50311
30		0.421	50.60425	30		0.401	52.95084
40		0.323	62.10255	40		0.2501	70.65587
50		0.331	61.16391	50		0.241	71.72357
60		0.332	61.04658	60		0.255	70.08096
MWCNT _{sma} /CuO							
t min	C ₀ mg/L	C _t mg/L	R%				
10	0.8523	0.709	16.81333				
20		0.613	28.07697				
30		0.401	52.95084				
40		0.264	69.02499				
50		0.245	71.25425				
60		0.247	71.01959				

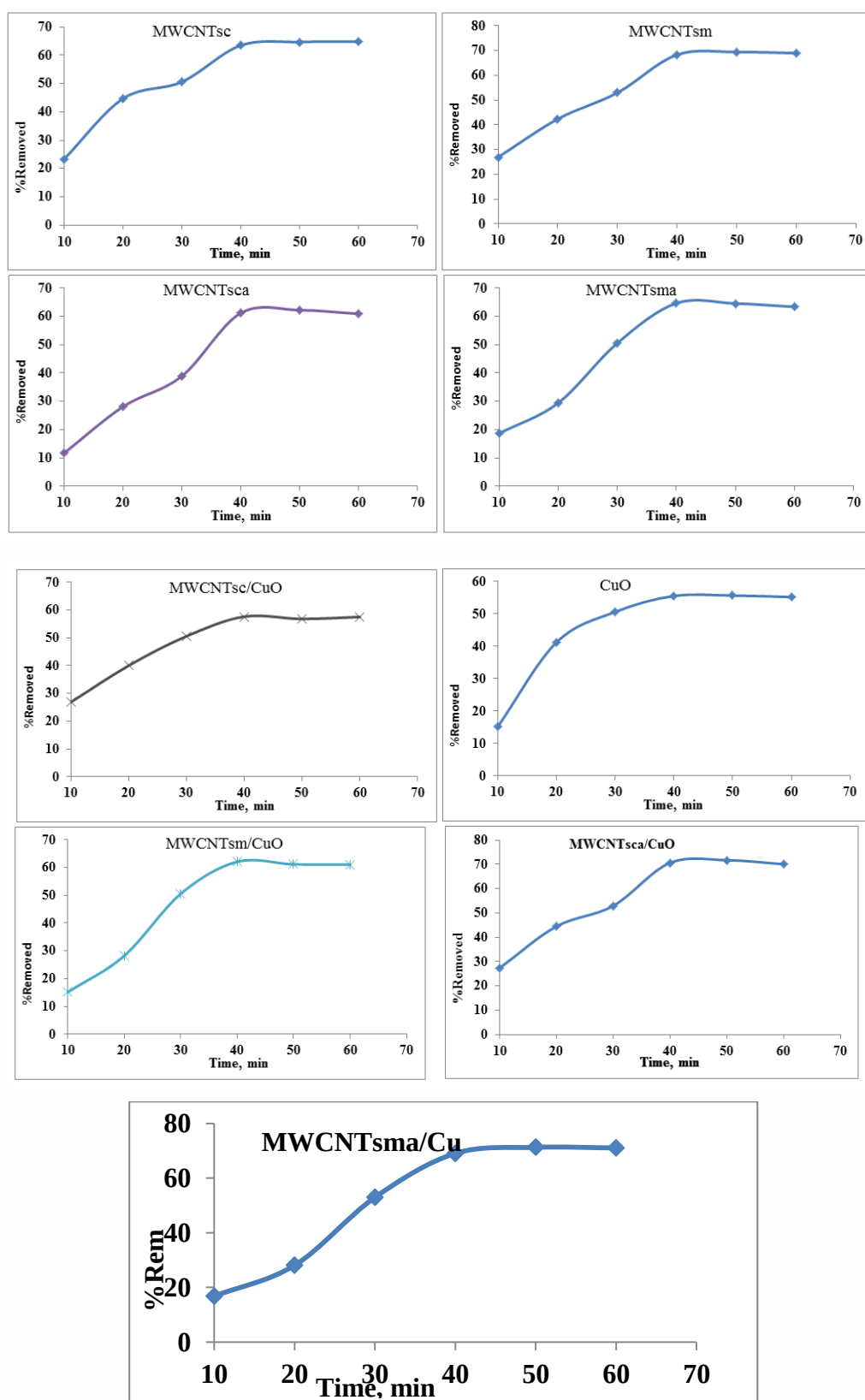


Fig4. 22 The effect of contact time on the % removed of Pb^{+2} by (a) MWCNTsc, (b) MWCNTsm, (c) MWCNTsca, (d) MWCNTsma, (e) CuO, (F) MWCNTsc/CuO, (g) MWCNTsm/CuO, (h) MWCNTsca/CuO and (i)MWCNTsma/CuO.

4.2.2. Effect of Adsorbent Quantity on Adsorption

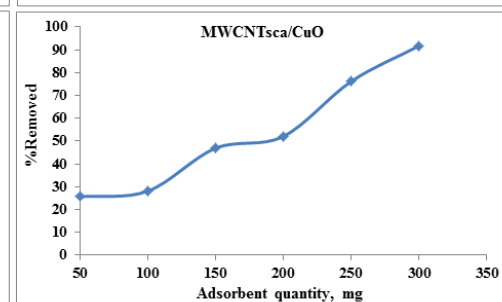
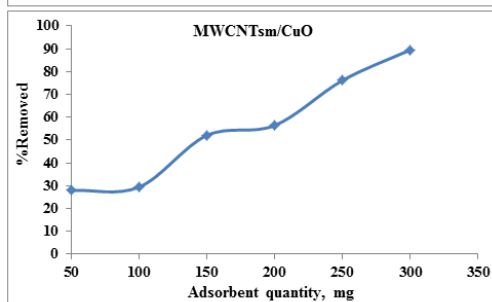
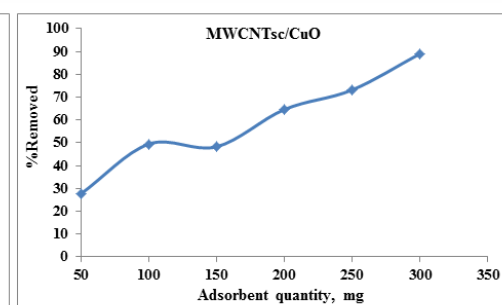
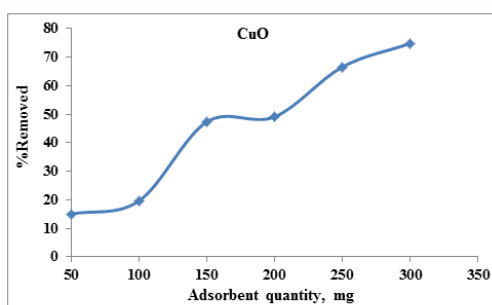
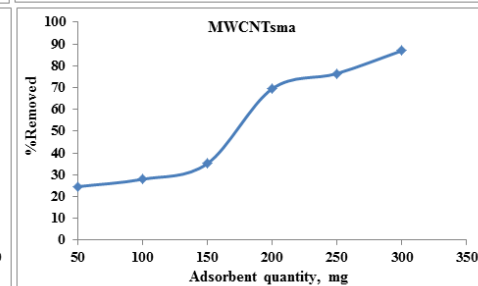
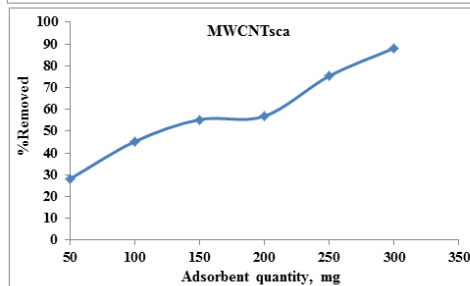
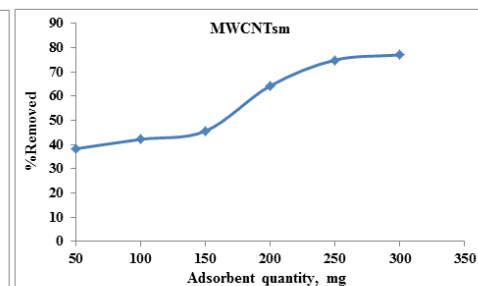
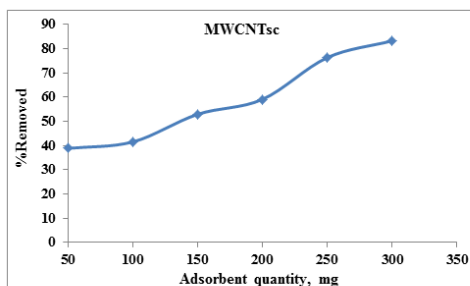
The adsorbent quantity is one of the important factors to determine the ratio of adsorption rate capacity adsorption on the concentration of lead ion, as well as the economics of process, through this study it was found that the capacity of adsorption of metal ions was highest when using the amount of 300 mg of nanomaterials. The effect of the adsorbent quantity of Pb^{+2} ion removal on the all prepared samples surfaces, was studied using different amount of the adsorbent (50, 100, 150, 200, 250 and 300) mg at (298) K, fixed concentration of Pb^{+2} ion (0.8523) mg/L, contact time for each samples are (60) min. The influence of adsorbent quantity on the uptake of the Pb^{+2} ion are shown in tables (4.2), and in figures (4.23) with increasing the quantity of each samples, the lead ion Pb^{+2} removal will increases too, this means that the increase the amount of nanomaterials (MWCNT, CuO and binary composite MWCNT/CuO) increases the concentration removal of Pb^{+2} from polluted water. The increase in the concentration removal can be explained by the increasing surface area to adsorbent nanomaterials^[143].

The Effect of adsorbent quantity on adsorption the lead ion for all samples were evaluated and found to follow order: MWCNTsma/CuO > MWCNTsca/CuO > MWCNTsm/CuO > MWCNTsc/CuO > MWCNTsca > MWCNTsma > MWCNTsc > MWCNTsm > CuO

Tables (4.2): Effect of adsorbent quantity on the adsorption of Pb^{+2} ion at 298 K with contact time 60 min by all samples were prepared

MWCNT _{sc}				MWCNT _{sm}			
Adsorbent quantity (mg)	C ₀ mg/L	C _t mg/L	R%	Adsorbent quantity (mg)	C ₀ mg/L	C _t mg/L	R%
50	0.8523	0.521	38.87129	50	0.8523	0.526	38.28464
100		0.4983	41.53467	100		0.493	42.15652
150		0.4012	52.92737	150		0.464	45.55908
200		0.3487	59.08718	200		0.395	64.21448
250		0.2019	76.31116	250		0.254	74.89147
300		0.1429	83.2336	300		0.186	77.0034
MWCNT _{sca}				MWCNT _{sma}			
Adsorbent quantity (mg)	C ₀ mg/L	C _t mg/L	R%	Adsorbent quantity (mg)	C ₀ mg/L	C _t mg/L	R%
50	0.8523	0.613	28.07697	50	0.8523	0.643	24.55708
100		0.467	45.20709	100		0.473	27.92444
150		0.403	55.29743	150		0.353	35.11674
200		0.348	56.82272	200		0.261	69.37698
250		0.211	75.24346	250		0.201	76.41675
300		0.102	88.03238	300		0.112	86.85909
CuO				MWCNT _{sc} /CuO			
Adsorbent quantity (mg)	C ₀ mg/L	C _t mg/L	R%	Adsorbent quantity (mg)	C ₀ mg/L	C _t mg/L	R%
50	0.8523	0.724	15.05338	50	0.8523	0.617	27.60765
100		0.585	19.62924	100		0.511	49.43095
150		0.449	47.31902	150		0.401	48.25766
200		0.334	49.07896	200		0.322	64.56647
250		0.285	66.56107	250		0.229	73.13153
300		0.215	74.77414	300		0.094	88.97102
MWCNT _{sm} /CuO				MWCNT _{sca} /CuO			
Adsorbent quantity (mg)	C ₀ mg/L	C _t mg/L	R%	Adsorbent quantity (mg)	C ₀ mg/L	C _t mg/L	R%
50	0.8523	0.614	27.95964	50	0.8523	0.634	25.61305
100		0.522	29.36759	100		0.501	28.07697
150		0.409	52.0122	150		0.353	46.8497
200		0.312	56.3534	200		0.219	52.0122
250		0.204	76.06477	250		0.104	76.06477
300		0.0901	89.4286	300		0.0712	91.64613
MWCNT _{sma} /CuO							
Adsorbent quantity (mg)	C ₀ mg/L	C _t mg/L	R%				
50	0.8523	0.614	27.95964				
100		0.507	40.5139				
150		0.437	48.72697				

200		0.209	75.47812
250		0.123	85.56846
300		0.0643	92.45571



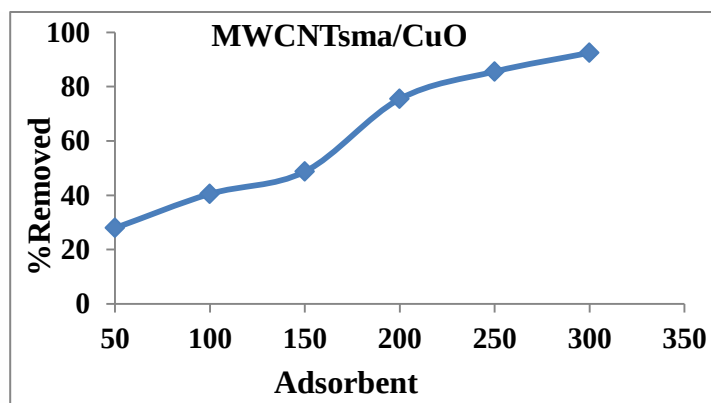


Fig 4.23 The effect of adsorbent quantity on the percent removed of Pb^{+2} ion by (a) MWCNTsc, (b) MWCNTsm, (c) MWCNTsca, (d) MWCNTsma, (e) CuO, (F) MWCNTsc/CuO, (g) MWCNTsm/CuO, (h) MWCNTsca/CuO and (i)MWCNTsma/CuO.

4.2.3. Effect of temperature on Pb^{+2} Adsorption

The temperature had an obvious effect on the extent of lead ion adsorption onto all synthesized samples. To investigate the effect of temperature on the removal percentage of Pb^{+2} , experiments were carried out at different temperatures, 298, 308, 318, 328, 338 and 343K, using optimum adsorbent quantity 300 mg with initial concentration of 0.8523 mg L^{-1} and pH equal to 7.0. The effect of temperature on Pb^{+2} removals can be concluded from Figure 4.25. The removal percentage of Pb^{+2} from polluted water was 24.55% at 298 °C which increased to 95.29% at 348 °C. The increase of removal efficiency with increasing temperature shows that the Pb^{+2} adsorption process is exothermic in nature^[144]

Tables (4.3): Effect of temperature on the adsorption of Pb^{+2} ion at 0.03 g for each sample and contact time 60 min.

MWCNT _{sc}				MWCNT _{sm}			
T, K	C ₀ mg/L	C _t mg/L	R%	T, K	C ₀ mg/L	C _t mg/L	R%
298	0.8523	0.142	83.33919981	298	0.8523	0.132	84.5125
308		0.232	72.77953772	308		0.241	71.72357
318		0.301	64.68379679	318		0.322	62.21988
328		0.458	46.26305292	328		0.488	42.74317
338		0.532	37.58066409	338		0.617	27.60765
348		0.643	24.55708084	348		0.723	15.17071
MWCNT _{sca}				MWCNT _{sma}			
T, K	C ₀ mg/L	C _t mg/L	R%	T, K	C ₀ mg/L	C _t mg/L	R%
298	0.8523	0.121	85.80312097	298	0.8523	0.103	87.91505
308		0.262	69.25965036	308		0.251	70.55028
318		0.402	52.83350933	318		0.437	48.72697
328		0.518	39.22327819	328		0.604	29.13293
338		0.663	22.21048926	338		0.683	19.8639
348		0.694	18.57327232	348		0.704	17.39998
CuO				MWCNT _{sc} /CuO			
T, K	C ₀ mg/L	C _t mg/L	R%	T, K	C ₀ mg/L	C _t mg/L	R%
298	0.8523	0.105	87.68039	298	0.8523	0.151	82.28323
308		0.239	71.95823	308		0.214	74.89147
318		0.398	53.30283	318		0.311	63.5105
328		0.522	38.75396	328		0.437	48.72697
338		0.663	22.21049	338		0.599	29.71958
348		0.694	18.57327	348		0.675	20.80253
MWCNT _{sm} /CuO				MWCNT _{sca} /CuO			
T, K	C ₀ mg/L	C _t mg/L	R%	T, K	C ₀ mg/L	C _t mg/L	R%
298	0.8523	0.139	83.69119	298	0.8523	0.125	85.3338
308		0.262	69.25965	308		0.272	68.08635
318		0.311	63.5105	318		0.331	61.16391
328		0.484	43.21248	328		0.553	35.11674
338		0.577	32.30083	338		0.677	20.56788
348		0.693	18.6906	348		0.779	8.600258
MWCNT _{sma} /CuO							
T, K	C ₀ mg/L	C _t mg/L	R%				
298	0.8523	0.117	86.27244				
308		0.202	76.29943				
318		0.311	63.5105				
328		0.503	40.98322				
338		0.689	19.15992				
348		0.718	15.75736				

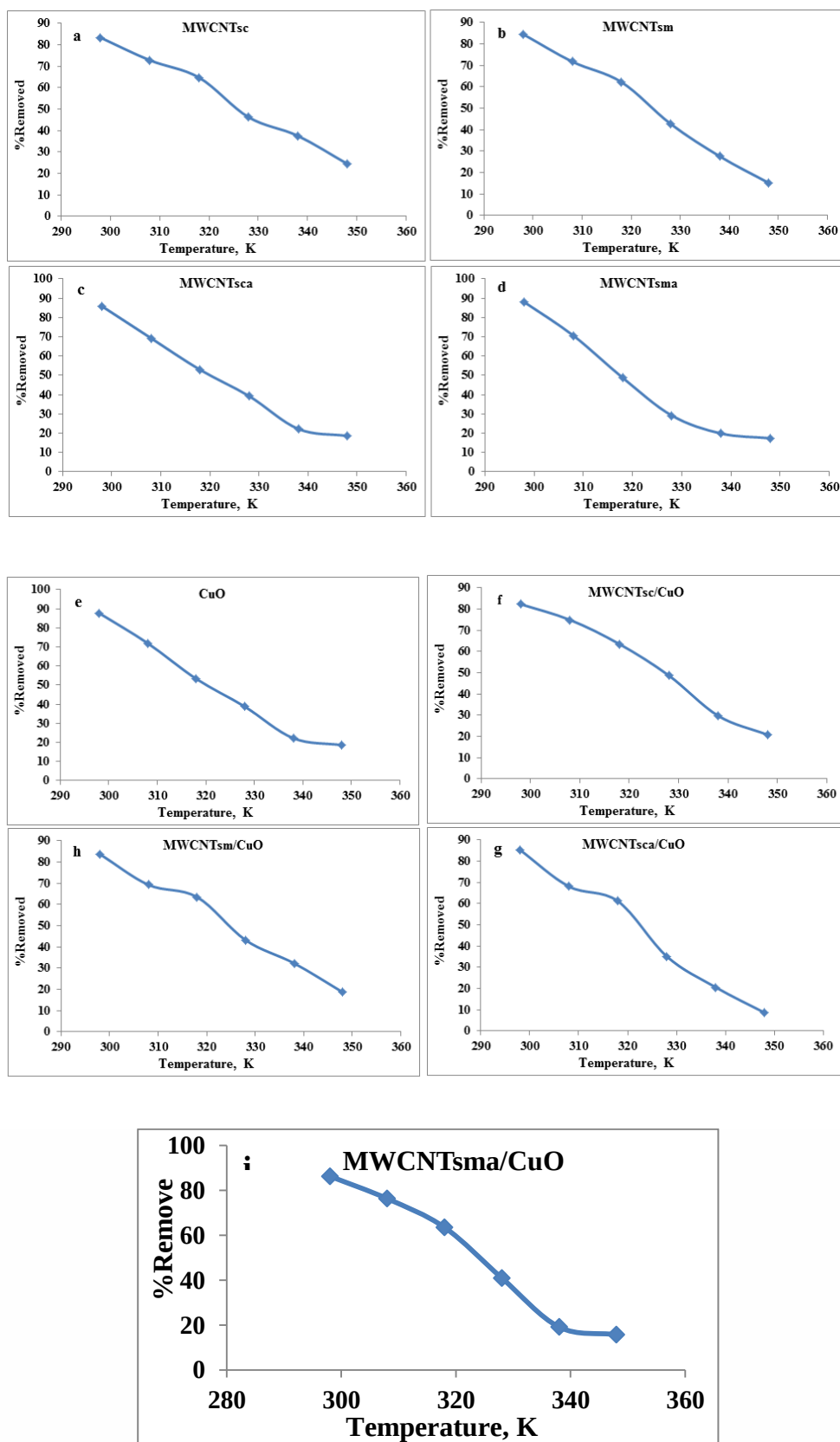


Fig 4.24. The effect of temperature on the % removed of Pb^{+2} ion by (a) MWCNTsc, (b) MWCNTsm, (c) MWCNTsca, (d) MWCNTsma, (e) CuO, (F) MWCNTsc/CuO, (g) MWCNTsm/CuO, (h) MWCNTsca/CuO and (i)MWCNTsma/CuO.

4.3. Kinetics Studies of Adsorption Process for Pb^{+2} ions

4.3.1. Adsorption Kinetics

To investigate the adsorption process of lead ions (Pb^{+2}) onto all synthesized samples, the pseudo-first-order kinetic (1st)^[142], pseudo-second-order kinetic (2nd)^[34], and intraparticle diffusion models ((IPD)^[144] were applied to the experimental data.

The pseudo-first-order kinetic model equation is shown as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \dots (4 - 1)$$

where q_e and q_t are the amounts of lead (Pb^{+2}) ions (mg g^{-1}) that absorbed at equilibrium and at time t , respectively, and k_1 is the first-order rate constant (min^{-1}).

The pseudo-second-order kinetic model is shown as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \dots (4 - 2)$$

Where q_2 is the maximum adsorption capacity (mg g^{-1}) for the pseudo-second-order adsorption and k_2 is the equilibrium rate constant for the pseudo-second-order adsorption ($\text{gmg}^{-1} \text{min}^{-1}$).

The intraparticle diffusion can be presented by the following equation:

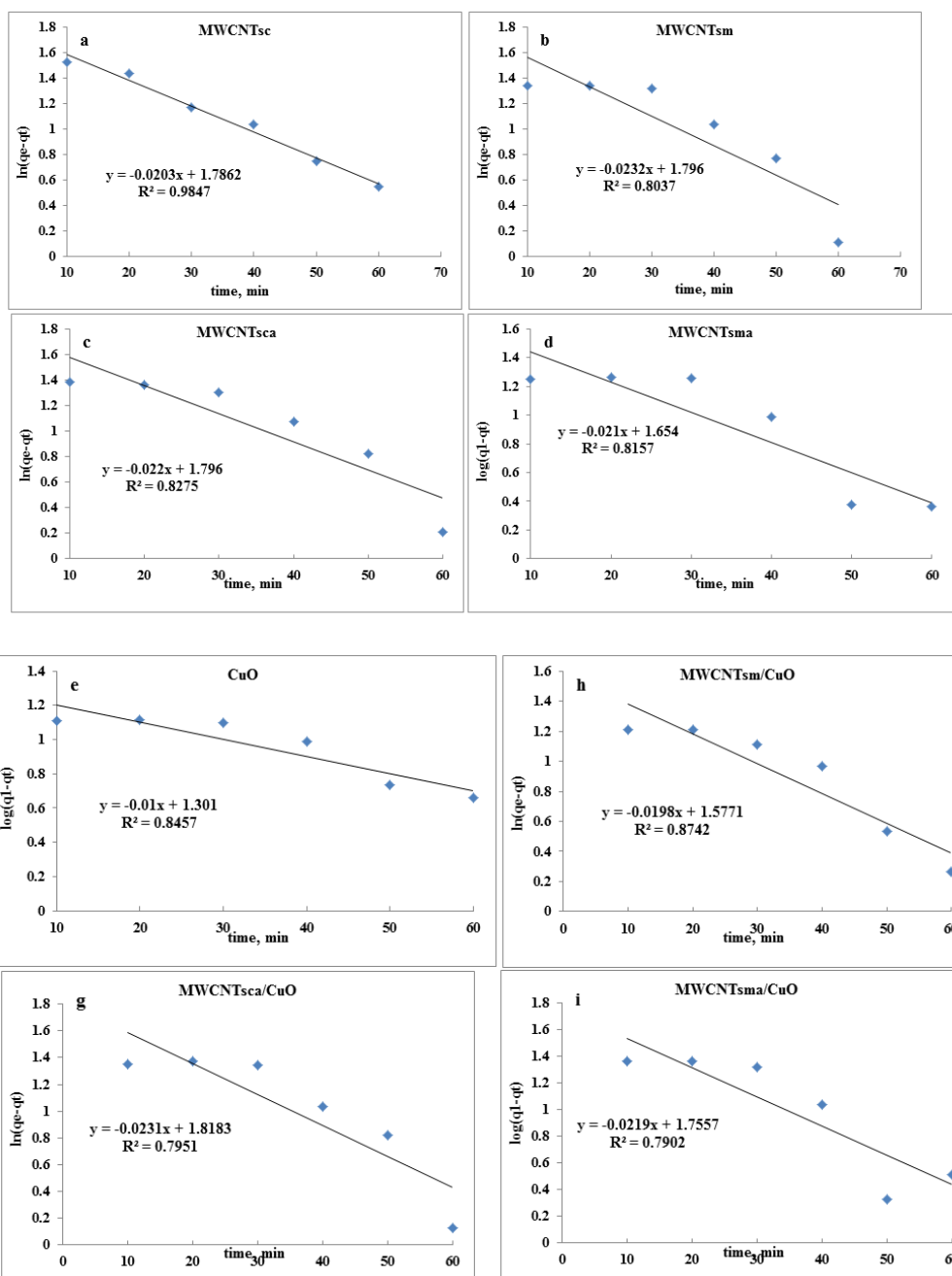
$$q_t = K_p t^{1/2} + C \dots (4 - 3)$$

where C is the intercept and k_p is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1/2}$).

4.3.1.1. The pseudo-first-order

Plotting $\ln(q_e - q_t)$ versus t for the lead ion at the all different samples under investigation did not converge well and did not give straight lines (Fig4. 26), which indicates that the pseudo-first-order.

Lagergren equation was inappropriate to describe the adsorption of the Pb^{+2} on all samples were synthesized.



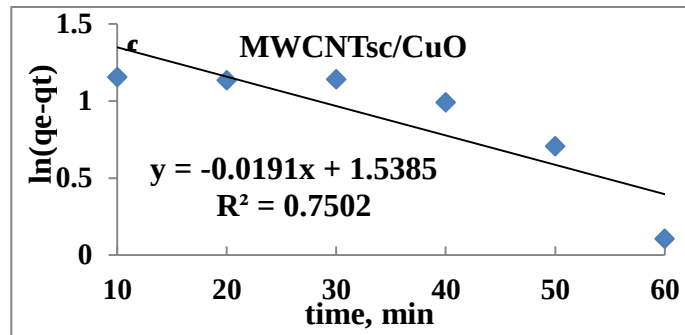


Fig4. 25 Pseudo-first order plots for lead ion adsorbed on (a)MWCNTsc (b) MWCNTsm, (c) MWCNTsca, (d) MWCNTsma, (e) CuO, (f) MWCNTsc/CuO, (h) MWCNTsm/CuO, (g) MWCNTsca/CuO and MWCNTsc/CuO.

4.3.1.2. The pseudo- second order

The pseudo-second-order model assumed that the adsorption; in general, might be second order, the rate limiting step may be chemical adsorption involving sharing or exchange of electrons between the solid adsorbent and divalent lead ion.

The plot of t/q_t and t from equation (4-2) .

$$h = k_2 q_e^2 \dots (4-5)$$

Where h represent the initial adsorption rate ($\text{mg g}^{-1}\text{min}^{-1}$), when t/q_t approaches to 0, must give a linear relationship from which q_e and k_2 can be estimated from the slope and intercept of the plot, respectively.

Applying the pseudo-second-order rate equation to the adsorption of Pb^{+2} experimental data converged very well for the lead ion with excellent regression coefficients ($R^2 = 0.99$) and straight lines (Fig 4. 27).

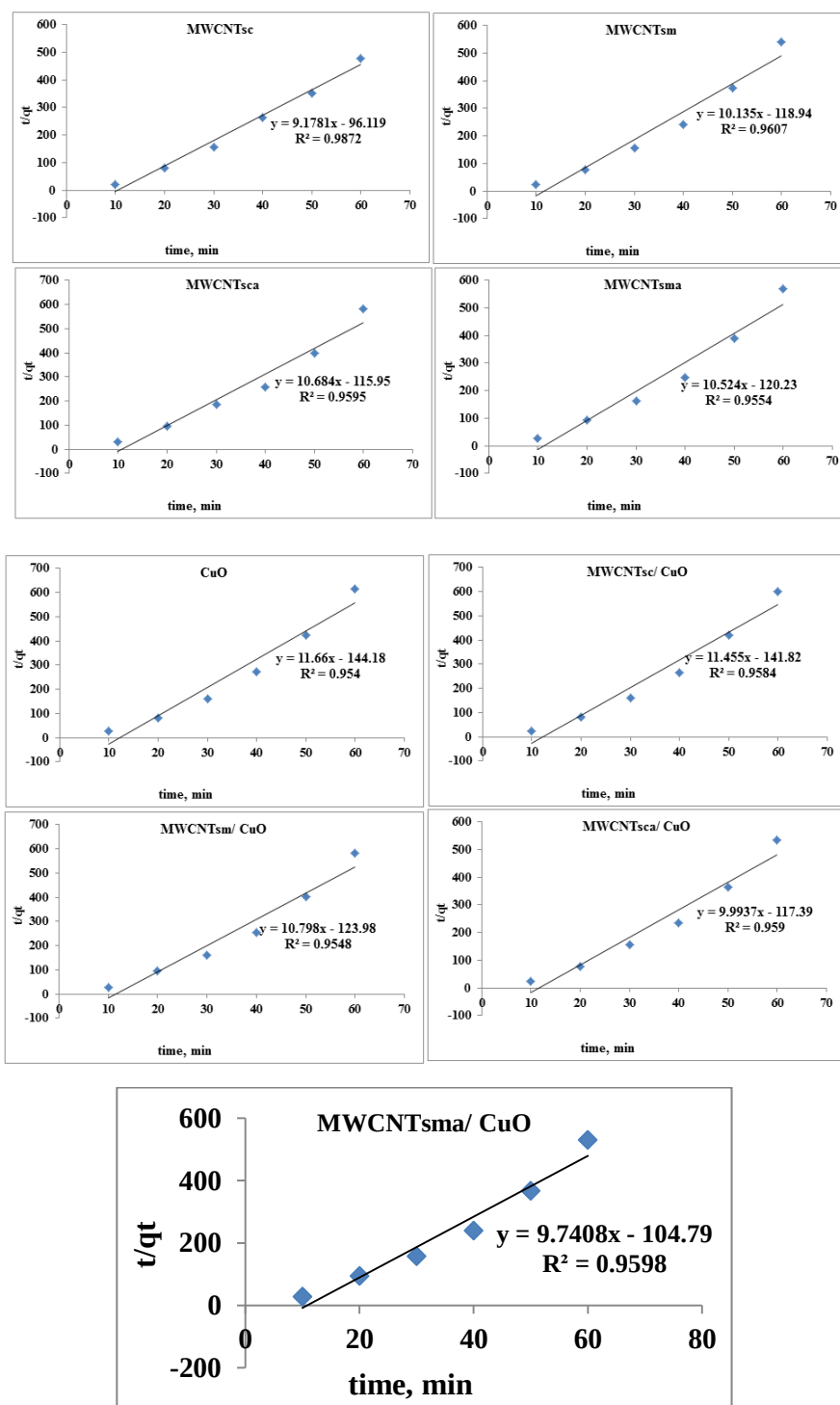


Fig4. 26 Pseudo-second order plots for lead ion adsorbed on (a)MWCNTsc (b) MWCNTsm, (c) MWCNTsca, (d) MWCNTsma, (e) CuO, (f) MWCNTsc/CuO, (h) MWCNTsm/CuO, (g) MWCNTsca/CuO and MWCNTsc/CuO.

4.3.1.3. The intra-particle diffusion model by Weber and Morris

Weber-Morris intra-particle kinetic model gives useful information about the diffusion of Pb^{+2} ion for all samples in the liquid-solid adsorption systems. The mathematical expression for the intra-particle kinetic model is given in Equation (4-3).

Fig 4.28 show the intra-particle curve obtained for the removal of Pb^{+2} ion from polluted water by all synthesized samples. From the graph it can be seen that the plots are not linear throughout the whole range, which indicate more than one process involved in the adsorption process. The first linear portion of the plots indicates the rapid removal of selected lead ion due to boundary-layer diffusion, while curved portion ascribed the intra-particle diffusion as a time-consuming process^{[145] [145b]}

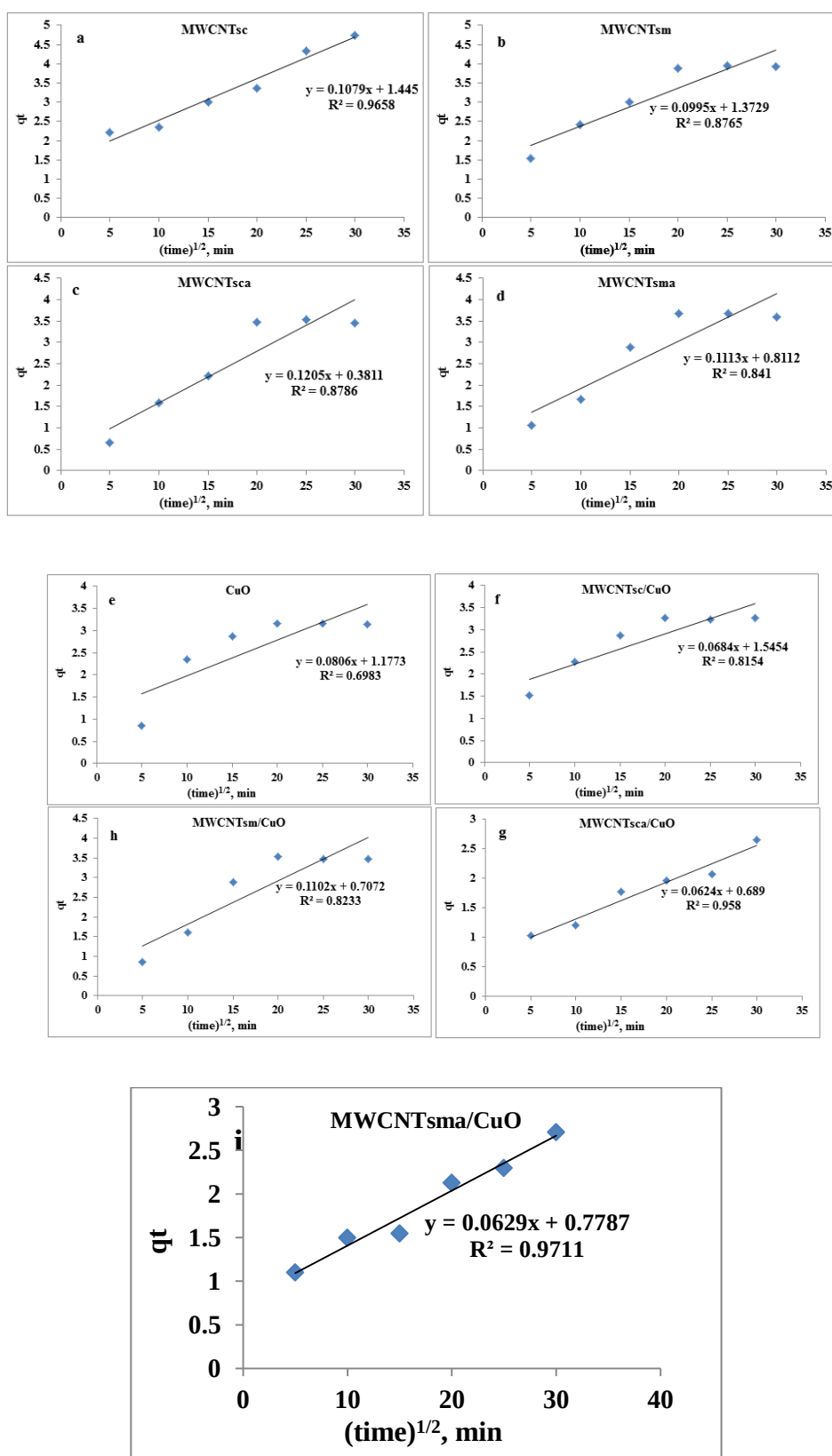


Fig 4.27. Diffusion model intra-particle in the removal of Pb^{2+} on to (a)MWCNTsc (b) MWCNTsm, (c) MWCNTsca, (d) MWCNTsma, (e) CuO, (f) MWCNTsc/CuO, (h) MWCNTsm/CuO, (g) MWCNTsca/CuO and MWCNTsc/CuO.

Table (4.4) : Kinetic parameters for the adsorption of lead (Pb^{+2}) ions onto all samples were prepared at 298 k. (k_1 (min^{-1}), q_1 (mg g^{-1}), k_2 ($\text{gmg}^{-1} \text{min}^{-1}$), q_2 (mg g^{-1}), k_p ($\text{mg g min}^{-1/2}$)

Sample	Pseudo-first order			Pseudo-second order			the intra particle diffusion		
	K_1	q_e	R_1^2	K_2	q_e	R_2^2	K_p	C	R_p^2
MWCNTsc	0.0203	4.953	0.98	0.8763	0.1089	0.987	0.1079	2.0	0.96
MWCNTsm	0.0232	4.572	0.80	0.8636	0.0986	0.960	0.0994	1.75	0.87
MWCNTsca	0.0220	4.854	0.82	0.9844	0.0936	0.959	0.1205	0.97	0.87
MWCNTsma	0.0210	4.137	0.81	0.9211	0.0950	0.955	0.1113	1.4	0.84
CuO	0.00996	3.320	0.84	0.9429	0.0857	0.954	0.0806	1.6	0.69
MWCNTsc/CuO	0.0190	3.743	0.75	0.9522	0.0857	0.958	0.0683	1.9	0.81
MWCNTsm/CuO	0.0198	4.481	0.87	0.9404	0.0872	0.954	0.1102	1.3	0.82
MWCNTsca/ CuO	0.0231	6.049	0.79	0.9054	0.0926	0.959	0.0624	1.0	0.95
MWCNTsma/ CuO	0.0219	5.473	0.79	0.8784	0.1026	0.958	0.06292	1.1	0.97

The results of kinetic parameters are shown in Tables (4.4). The values of the correlation coefficients of the pseudo-second-order kinetic model R_2^2 were higher than those of the pseudo-first-order kinetic model and intra-particle diffusion model r_1^2 and r_p^2 . This indicates that the adsorption of lead (Pb^{+2}) ions followed the pseudo-second-order kinetic with the correlation coefficients of is higher than 0.95 for all tested temperatures.

By comparing the results that obtained from the application of different chemical reaction models; fractional power function model, the Lagergren pseudo-first-order model, the pseudo-second-order model, and the intra-particle diffusion model by Weber and Morris, to fit the experimental data, it can conclude that the adsorption of Pb^{+2} from a polluted water by all samples could be expressed well by the intra-particle diffusion model. Fitting the experimental data with the intra-particle diffusion model gave straight lines with excellent regression coefficients ($R^2 = 0.96$ to 0.99) and good agreement between

experimental and calculated amount of adsorbed lead ion per unit mass of sample at equilibrium. The finding agrees with previous results for the adsorption of heavy metals on different adsorbents.^{[146] [147]}

4.3.1.4 The calculation of activation energy

Based on the rate constant the best kinetic equation for the suitable lead Pb^{+2} ion adsorption data on the surface of the samples were studied, the equation was of the pseudo-second order (k_2). The activation energy was calculated using Arrhenius equation to determine the type of adsorption.

$$\ln K_2 = \ln A - \frac{E_a}{RT} \dots (4-7)$$

The values of activation energy E_a can be obtained from the slope of a plot of $\ln K_2$ against $1/T$, figure (4.29). The obtained values for E_a are listed in Table (4.5). The E_a values indicates that the adsorption of lead (Pb^{+2}) ions followed the Physical Adsorption for all tested temperatures.

Table (4.5) the values of activation energy E_a (KJ/mole) for the lead (Pb^{+2}) ion adsorption for the prepared samples

samples	Activation energy (E_a) kJ/mol
MWCNTsc	-18.33924
MWCNTsm	-28.3514
MWCNTsca	-26.2218
MWCNTsma	-19.9719
CuO	-22.5975
MWCNTsc/CuO	-18.0521
MWCNTsm/ CuO	-22.108
MWCNTsca/ CuO	-23.2849
MWCNTsma/ CuO	-21.339

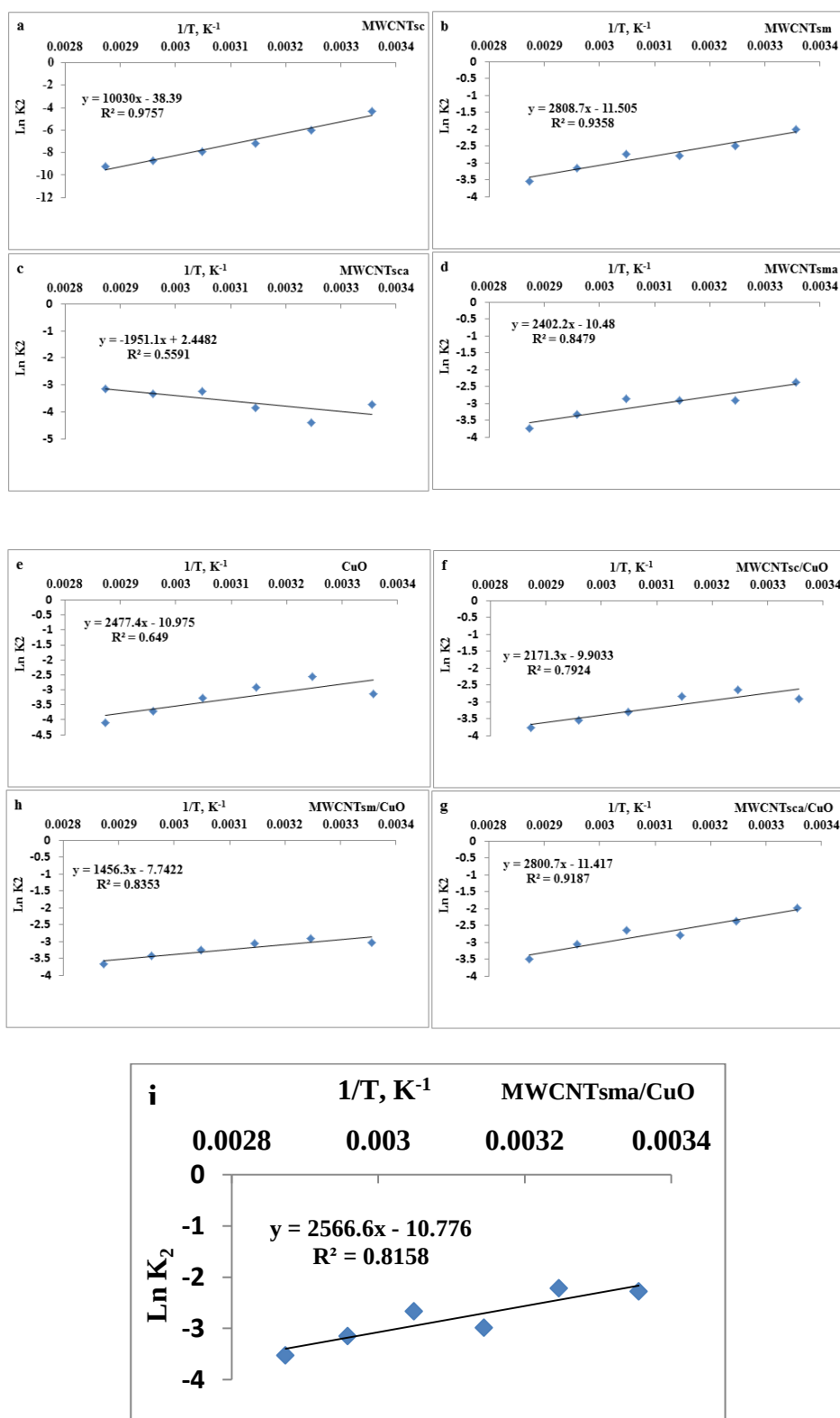


figure .4.28. The graphic represent the Arrhenius equation for the adsorption of lead ion (Pb^{+2}) on the surfaces for the prepared samples: (a)MWCNTsc (b) MWCNTsm, (c) MWCNTsca, (d) MWCNTsma, (e) CuO, (f) MWCNTsc/CuO, (h) MWCNTsm/CuO, (g) MWCNTsca/CuO and MWCNTsc/CuO.

4.4. Thermodynamic Study of Pb⁺² Adsorption

The effect of temperature on removal of Pb⁺² ions from polluted water by each prepared samples at different temperature (298, 308, 318, 328, 338 and 348) K was investigated. In this study, the values of thermodynamic parameters such as free energy change (ΔG), standard enthalpy change (ΔH) and standard entropy change (ΔS) can be determined from the following Equations:

$$K_{eq} = q_{max} \cdot \frac{m}{C_e} \cdot V \dots (4 - 8)$$

$$\Delta G = -RT \ln K_{eq} \dots (4 - 9)$$

$$\ln K_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \dots (4 - 10)$$

$$\Delta G = \Delta H - T\Delta S \dots (4-11)$$

Where K_{eq} is the sorption distribution coefficient, ΔG is the free energy change of sorption (kJ mol^{-1}), T is the temperature in K, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), ΔH is the enthalpy change (kJ mol^{-1}) and ΔS is entropy change ($\text{kJ mol}^{-1} \text{ K}^{-1}$). The values of ΔH and ΔS can be obtained from the slope and intercept of a plot of $\ln K$ against $1/T$, figure (4.30) . The obtained values for ΔG , ΔH and ΔS are listed in Table (4.7).

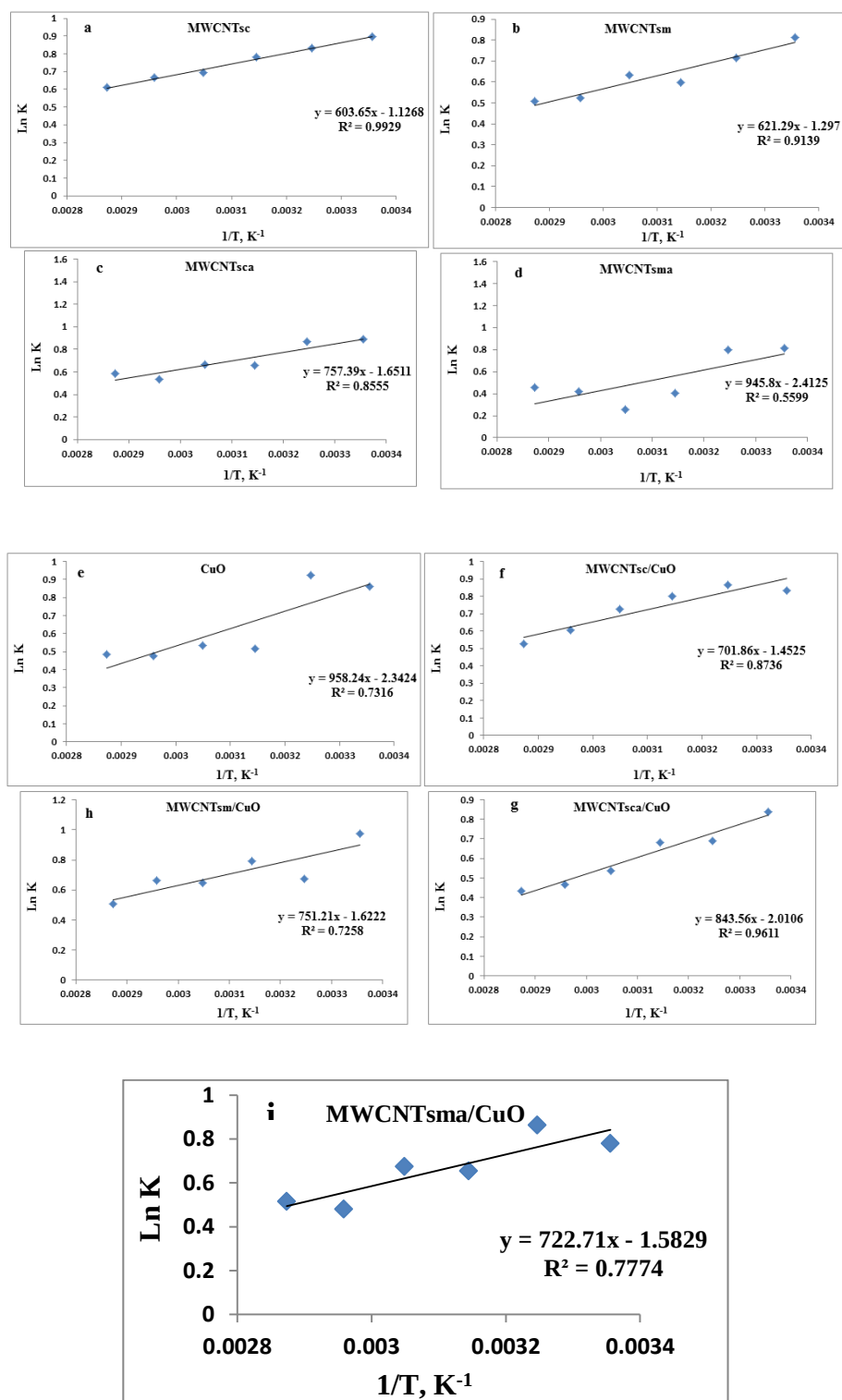


Fig 4.29. Plot of $\ln K_{eq}$ versus $1/T$ to estimate the thermodynamic parameters for the adsorption of Pb^{+2} on (a) MWCNTsc, (b) MWCNTsm, (c) MWCNTsca, (d) MWCNTsma, (e) CuO, (f) MWCNTsc/CuO, (g) MWCNTsm/CuO, (h) MWCNTsca/CuO and (i) MWCNTsma/CuO.

Table (4.6)-Thermodynamic parameters of Pb^{+2} ion adsorption onto MWCNTsc.

T	ΔG , KJ/mol	ΔH , KJ/mol	ΔS , J mol ⁻¹ k ⁻¹
298	-14.996	-13.018	4.9884
308	-15.494		
318	-15.993		
328	-16.492		
338	-16.991		
348	-17.489		

Table (4.7)-Thermodynamic parameters of Pb^{+2} ion adsorption onto MWCNTsm.

T	ΔG , KJ/mol	ΔH , KJ/mol	ΔS , J mol ⁻¹ k ⁻¹
298	-12.061	-17.165	3.99072
308	-12.460		
318	-12.859		
328	-13.258		
338	-13.657		
348	-14.056		

Table (4.8)-Thermodynamic parameters of Pb^{+2} ion adsorption onto MWCNTsca.

T	ΔG , KJ/mol	ΔH , KJ/mol	ΔS , J mol ⁻¹ k ⁻¹
298	-12.053	-16.296	4.157
308	-12.452		
318	-12.851		
328	-13.250		
338	-13.649		
348	-14.048		

Table (4.9)-Thermodynamic parameters of Pb^{+2} ion adsorption onto MWCNTscm.

T	ΔG , KJ/mol	ΔH , KJ/mol	ΔS , J mol ⁻¹ k ⁻¹
298	-18.9043	-17.863	3.4942
308	-18.9392		
318	-18.9742		
328	-19.0091		
338	-19.044		
348	-19.079		

Table (4.10) -Thermodynamic parameters of Pb^{+2} ion adsorption onto CuO.

T	ΔG , KJ/mol	ΔH , KJ/mol	ΔS , J mol ⁻¹ k ⁻¹
298	-18.8871	-17.966	3.0909
308	-18.918		
318	-18.9489		
328	-18.9798		
338	-19.0107		
348	-19.0416		

Table (4.11)-Thermodynamic parameters of Pb^{+2} ion adsorption onto MWCNTsc/CuO.

T	ΔG , KJ/mol	ΔH , KJ/mol	ΔS , J mol ⁻¹ k ⁻¹
298	-17.1977	-15.835	4.5727
308	-17.2434		
318	-17.2891		
328	-17.3348		
338	-17.3806		
348	-17.4263		

Table (4.12)-Thermodynamic parameters of Pb^{+2} ion adsorption onto MWCNTsm/CuO.

T	ΔG , KJ/mol	ΔH , KJ/mol	ΔS , $\text{J mol}^{-1}\text{k}^{-1}$
298	-17.5829	-16.245	4.48956
308	-17.6278		
318	-17.6727		
328	-17.7176		
338	-17.7625		
348	-17.8074		

Table (4.13)-Thermodynamic parameters of Pb^{+2} ion adsorption onto MWCNTsca/CuO.

T	ΔG , KJ/mol	ΔH , KJ/mol	ΔS , $\text{J mol}^{-1}\text{k}^{-1}$
298	-18.004	-17.013	3.3256
308	-18.0373		
318	-18.0705		
328	-18.1038		
338	-18.1371		
348	-18.1703		

Table (4.14)-Thermodynamic parameters of Pb^{+2} ion adsorption onto MWCNTscm/CuO.

T	ΔG , KJ/mol	ΔH , KJ/mol	ΔS , $\text{J mol}^{-1}\text{k}^{-1}$
298	-17.1725	-16.008	3.90758
308	-17.2115		
318	-17.2506		
328	-17.2897		
338	-17.3288		
348	-17.3678		

The negative values of ΔG indicates that the removal of Pb^{+2} ion using prepared samples are a spontaneous process. The negative value of ΔH confirmed the exothermic nature of the sorption process due to the adsorption leads to a reduction in the residual forces on the outside of the adsorbent. While, the negative values of ΔS indicates the lead (Pb^{+2}) ion adsorption process from polluted water on all surfaces was regular. Adsorption is an exothermic process since surface particles of the adsorbent are unstable and when the adsorbate is adsorbed on the surface the energy of adsorbent decreases and these results in the increase of heat, therefore, adsorption is always exothermic. It has also been stated that the value of ΔH provides useful information about the type of adsorption process. The typical range of ΔH value for physisorption is between 2.1-20.9 kJ/mol and for chemisorption involving complexation is between 20.9-418.4 kJ/mol^[148]. At point, when liquid is adsorbed on a solid surface, its movement is confined leading to a reduction in the entropy of the liquid.

4.5. Adsorption Isotherm

Adsorption isotherms were used to investigate the relationship between the amount of lead ions adsorbed onto the samples (MWCNTsc, MWCNTsm, MWCNTsca, MWCNTsma, CuO and binary composite) surface which synthesized and the concentration of lead ions in the aqueous phase at equilibrium state. In addition, adsorption isotherm plays major role in the design of adsorption system and it provides the maximum sorption capacity for all samples for the removal of Pb^{+2} ion from polluted water. Many isotherm models have been used to describe the adsorption process. However, among the numerous isotherm models the Langmuir and Dubinin–Radushkevich isotherm model, isotherm have been widely employed to describe the adsorption equilibrium process^[149].

4.5.1. Langmuir isotherm

The most popular linear form of the Langmuir isotherm is represented by Equation follow:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} \cdot b + \left(\frac{1}{q_{max}} \right) C_e \dots (4-12)$$

Where C_e is the equilibrium concentration of lead ion in solution (mg/L), q_e is the amount of lead ion adsorbed per unit weight of the sorbent (mg/g), q_{max} (mg/g) is maximum monolayer adsorption capacity, b (L/mg) is Langmuir isotherm constant that relates to the energy of adsorption. The linear plot was derived between C_e/q_e versus C_e to calculate adsorption parameters. To identify the feasibility of the adsorption process, the essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor or equilibrium parameter, R_L .

$$R_L = 1/(1 + bC_0) \dots (4-13)$$

Where C_0 (mg L⁻¹) is initial concentration of lead (Pb⁺²) ion. R_L value indicates the adsorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$. The values of q_{max} and b were computed from the slope and intercept of the Langmuir plot of C_e/q_e versus C_e . The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L , which is a dimensionless constant referred to as separation factor or equilibrium parameter. Table (4-15)

sample	C_0 , mg/L	b , L/mg	R_L
MWCNTsc	0.8523	0.33	0.780482
MWCNTsm		0.321	0.785183
MWCNTsca		0.512	0.696196
MWCNTsma		0.011	0.990712
CuO		0.05	0.959127
MWCNTsc/CuO		0.09	0.928758
MWCNTsm/ CuO		0.431	0.731346
MWCNTsca/ CuO		0.254	0.822041

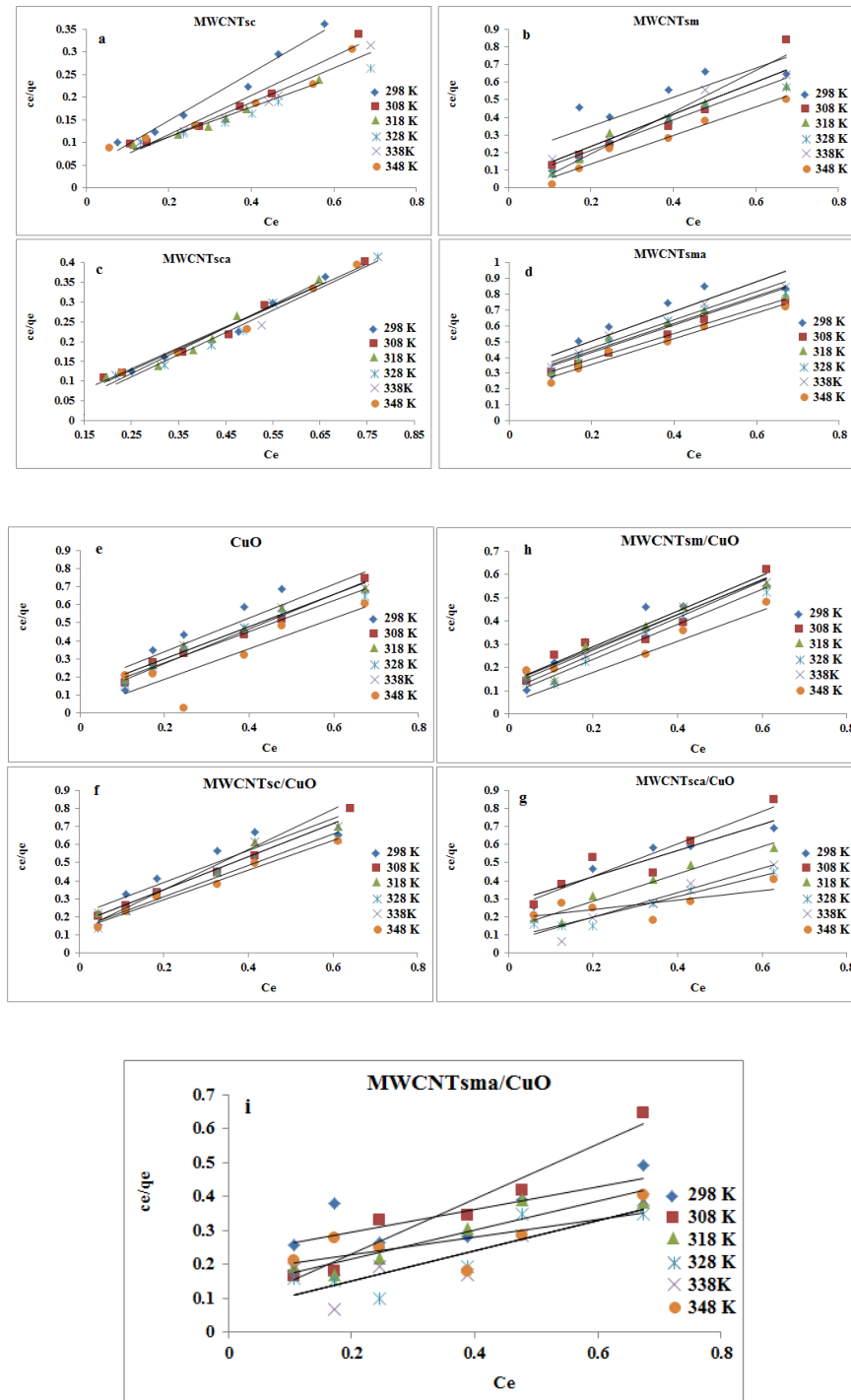


Fig4.30. Langmuir isotherm model of Pb^{+2} removal (a)MWCNTsc (b) MWCNTsm, (c) MWCNTsca, (d) MWCNTsma, (e) CuO, (f) MWCNTsc/CuO, (h) MWCNTsm/CuO, (g) MWCNTsca/CuO and MWCNTsc/CuO surface at different temperature.

Table (4.16): Langmuir Isotherm constants for the adsorption of Pb^{+2} ion on samples (Citrus aurantium as sources) at different temperature.

T(K)	Surface														
	MWCNTsc			MWCNTsca			CuO			MWCNTsc/CuO			MWCNTsca/CuO		
	q _{max} mg/g	b L/mg	R ²	q _{max} mg/g	b	R ²	q _{max} mg/g	KL	R ²	q _{max} mg/g	b	R ²	q _{max} mg/g	b	R ²
298	0.45	0.285	0.985	0.37	0.177	0.931	0.42	0.124	0.891	0.71	0.107	0.965	0.73	0.232	0.975
308	0.52	0.236	0.946	0.51	0.143	0.914	0.48	0.136	0.922	0.73	0.119	0.958	0.74	0.294	0.974
318	0.67	0.112	0.936	0.58	0.128	0.916	0.57	0.128	0.856	0.75	0.115	0.956	0.74	0.197	0.986
328	0.69	0.164	0.975	0.63	0.197	0.927	0.59	0.145	0.865	0.78	0.175	0.965	0.79	0.155	0.995
338	0.78	0.192	0.965	0.68	0.141	0.973	0.61	0.163	0.911	0.81	0.263	0.961	0.81	0.273	0.981
348	0.93	0.198	0.912	0.76	0.185	0.945	0.74	0.135	0.895	0.82	0.156	0.952	0.84	0.156	0.992

Table (4.17): Langmuir Isotherm constants for the adsorption of Pb^{+2} ion on samples (morus as sources) at different temperature.

T(K)	Surface														
	MWCNTsm			MWCNTsma			CuO			MWCNTsm/CuO			MWCNTsma/CuO		
	q _{max} mg/g	b L/mg	R ²	q _{max} mg/g	b L/mg	R ²	q _{max} mg/g	KL L/mg	R ²	q _{max} mg/g	b L/mg	R ²	q _{max} mg/g	b L/mg	R ²
298	0.38	0.231	0.942	0.43	0.201	0.972	0.47	0.124	0.812	0.74	0.237	0.975	0.656	0.242	0.995
308	0.42	0.242	0.916	0.48	0.234	0.967	0.49	0.136	0.852	0.75	0.242	0.978	0.694	0.254	0.994
318	0.55	0.134	0.913	0.55	0.178	0.926	0.53	0.128	0.764	0.77	0.198	0.986	0.734	0.216	0.996
328	0.63	0.174	0.922	0.67	0.108	0.947	0.57	0.145	0.875	0.79	0.275	0.995	0.785	0.162	0.987
338	0.67	0.131	0.937	0.71	0.208	0.982	0.67	0.163	0.923	0.82	0.266	0.991	0.798	0.234	0.983
348	0.82	0.153	0.915	0.74	0.145	0.958	0.72	0.135	0.835	0.84	0.196	0.992	0.824	0.184	0.985

It is clear from table (4.16) and Fig (4.30) that the adsorption process was enhanced by the activated composite, and table (4.18) showed the average of Langmuir constants (K_L), which confirm binary activated composite which is better than other samples. This tells that the best surface to which the Langmuir isotherm is applied are MWCNTsca/CuO and MWCNTsma/CuO . On the other

hand, it was observed that the values of Langmuir constants (K_L) fluctuated on all surfaces of the samples used with increasing temperature.

Table (4.18): Average langmuir constants for the adsorption of Pb^{+2} ion on samples prepared at different temperature.

sample	Average of K_L (L/mg)
MWCNTsc	0.197833
MWCNTsm	0.1775
MWCNTsca	0.161833
MWCNTsma	0.179
CuO	0.1385
MWCNTsc/CuO	0.155833
MWCNTsm/CuO	0.235667
MWCNTsca/ CuO	0.217833
MWCNTsma/ CuO	0.215333

4.5.2. Dubinin–Radushkevich isotherm model

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [92]. The model has often successfully fitted high solute activities and the intermediate range of concentrations data well.

$$\ln q_e = \ln q_{max} - (K_D \varepsilon^2) \dots (4 - 14)$$

$$\varepsilon = RT \ln[1 + 1/C_e] \dots (4 - 15)$$

where K_{ad} is Dubinin–Radushkevich isotherm constant (mol^2/kJ^2), ε is Dubinin–Radushkevich isotherm constant, R , T and C_e represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively. The value of k_{ad} is used to calculate the mean of free energy E (kJ/mol) of the sorption, E ;

$$E = -(2k)^{-0.5} \dots (4-16)$$

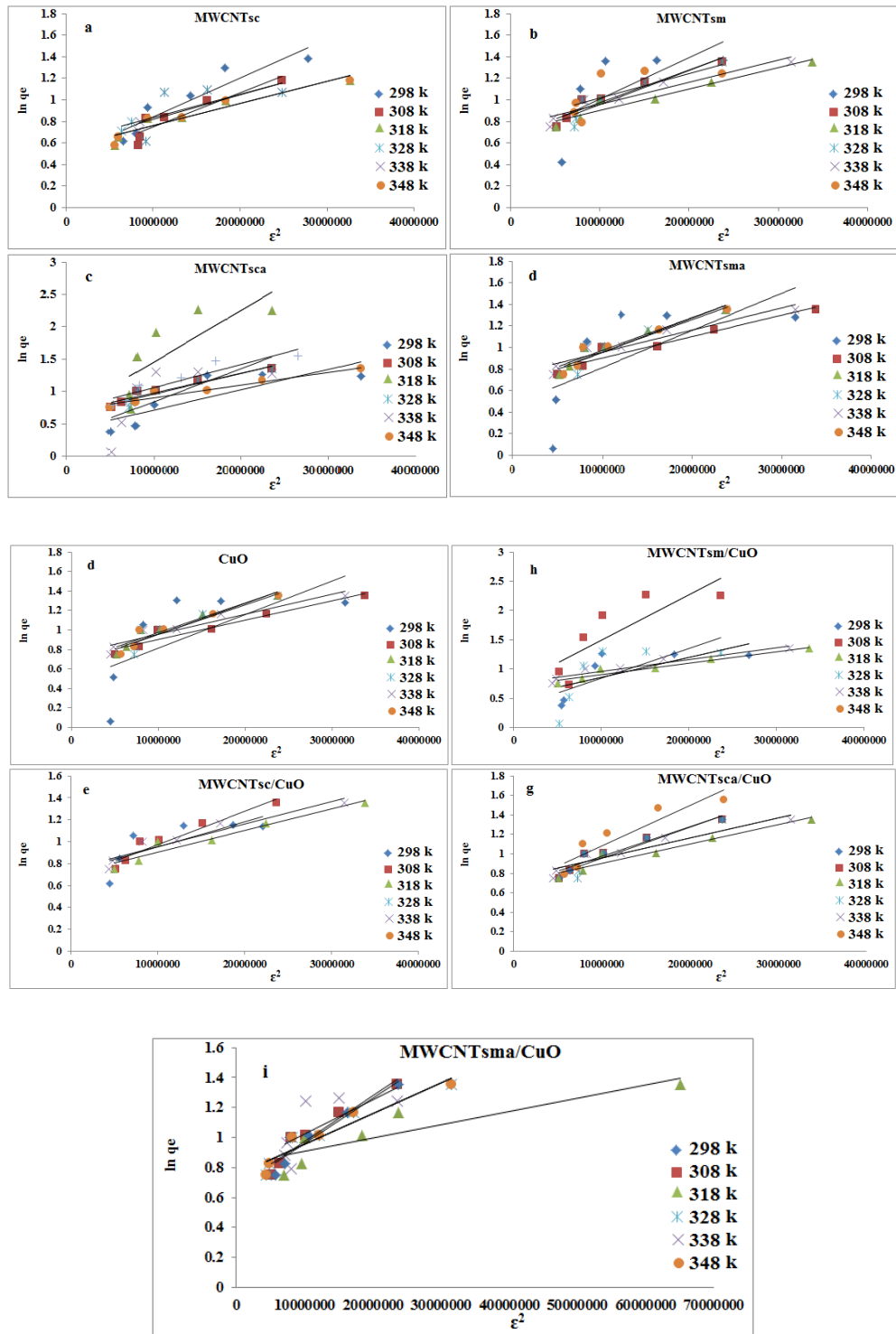


Fig4.31. Dubinin–Radushkevich isotherm model of Pb^{2+} On removal (a)MWCNTsc (b) MWCNTsm, (c) MWCNTsca, (d) MWCNTsma, (e) CuO, (f) MWCNTsc/CuO, (h) MWCNTsm/CuO, (g) MWCNTsca/CuO and MWCNTsc/CuO surface at different temperature.

Table (4.19): Dubinin–Radushkevich constants for the adsorption of Pb^{+2} ion on samples at different temperature. $\ln q_e = \ln (q_s) - (K_{ad} \epsilon^2) \dots (4.17)$

T(K)	Surface							
	MWCNTsc				MWCNTsm			
	K_{ad}	q_s	E, kJ/mol	R^2	K_{ad}	q_s	E, kJ/mol	R^2
298	-3.59×10^{-8}	0.4596	3.72	0.86	-3.84×10^{-8}	0.4596	3.60	0.49
308	-3.16×10^{-8}	0.4918	3.97	0.69	-1.60×10^{-8}	0.3672	5.57	0.61
318	-3.44×10^{-8}	0.6487	3.81	0.45	-1.20×10^{-8}	0.6742	6.43	0.63
328	-2.27×10^{-8}	0.0137	4.68	0.59	-1.60×10^{-8}	0.6672	5.57	0.61
338	-2.13×10^{-8}	0.8221	4.84	0.47	-1.20×10^{-8}	0.5742	6.43	0.63
348	-3.44×10^{-8}	0.5999	3.80	0.49	-1.60×10^{-8}	0.5672	5.57	0.61
T(K)	Surface							
	MWCNTsca				MWCNTsma			
	K_{ad}	q_s	E, kJ/mol	R^2	K_{ad}	q_s	E, kJ/mol	R^2
298	-3.17×10^{-8}	0.7341	3.39	0.88	-3.55×10^{-8}	0.3167	3.53	0.94
308	-3.15×10^{-8}	0.7842	3.44	0.86	-1.13×10^{-8}	0.1023	5.54	0.94
318	-3.43×10^{-8}	0.5388	3.93	0.92	-1.34×10^{-8}	0.5912	5.63	0.92
328	-2.33×10^{-8}	0.1163	3.75	0.91	-1.41×10^{-8}	0.5845	5.67	0.91
338	-2.24×10^{-8}	0.9796	4.95	0.92	-1.73×10^{-8}	0.4866	6.87	0.92
348	-3.45×10^{-8}	0.6712	3.70	0.95	-1.65×10^{-8}	0.6713	5.32	0.88
T(K)	Surface							
	CuO				MWCNTsa/CuO			
	K_{ad}	q_s	E, kJ/mol	R^2	K_{ad}	q_s	E, kJ/mol	R^2
298	-3.33×10^{-8}	0.8146	3.44	0.73	-3.91×10^{-8}	0.5612	3.44	0.85
308	-3.16×10^{-8}	0.3956	3.56	0.68	-1.43×10^{-8}	0.4634	5.41	0.91
318	-3.44×10^{-8}	0.5734	3.75	0.75	-1.59×10^{-8}	0.6924	5.62	0.92
328	-2.27×10^{-8}	0.1492	4.91	0.73	-1.48×10^{-8}	0.5744	5.09	0.88
338	-2.13×10^{-8}	0.6311	4.88	0.49	-1.40×10^{-8}	0.6855	5.23	0.87
348	-3.44×10^{-8}	0.6778	3.84	0.51	-1.55×10^{-8}	0.6671	5.07	0.91
T(K)	Surface							
	MWCNTsm/CuO				MWCNTsca/CuO			
	K_{ad}	q_s	E, kJ/mol	R^2	K_{ad}	q_s	E, kJ/mol	R^2
298	-3.87×10^{-8}	0.3561	3.55	0.91	-3.54×10^{-8}	0.3457	3.13	0.56

308	-3.55×10^{-8}	0.3477	3.84	0.82	-1.43×10^{-8}	0.3612	4.91	0.65
318	-3.87×10^{-8}	0.5945	3.82	0.56	-1.70×10^{-8}	0.5320	5.66	0.82
328	-2.43×10^{-8}	0.5253	4.98	0.68	-1.21×10^{-8}	0.6743	5.48	0.84
338	-2.91×10^{-8}	0.7931	4.33	0.72	-1.13×10^{-8}	0.7655	5.88	0.67
348	-3.62×10^{-8}	0.6443	3.76	0.61	-1.18×10^{-8}	0.4532	5.73	0.81
T(K)	Surface							
	MWCNTsam/CuO							
	K_{ad}	q_s	E,kJ/mol	R^2				
298	-3.33×10^{-8}	0.4723	3.35	0.80				
308	-3.45×10^{-8}	0.4784	3.72	0.81				
318	-3.42×10^{-8}	0.5871	3.34	0.51				
328	-2.34×10^{-8}	0.3945	4.56	0.48				
338	-2.18×10^{-8}	0.7543	4.38	0.46				
348	-3.51×10^{-8}	0.5129	3.74	0.51				

The constant such as q_s , and K_{ad} were obtained from the appropriate plot using equation (4.17). From the linear plot of DRK model, q_s , K_{ad} and E were determined, the mean free energy to samples less than 20 kJ/mol indicating a physisorption process. Finally, from the value of R^2 it can conclude that the Langmuir isotherm model is better than Dubinin–Radushkevich isotherm model.

Table (4.20): the Langmuir and Dubinin–Radushkevich constants and the correlation coefficients.

Samples	Langmuir isotherm				Dubinin–Radushkevich isotherm			
	q_e	K_L	R_L	R^2	K_{ad}	q_s	$E, \text{kJ/mol}$	R^2
MWCNTsc	0.93	0.285	0.780482	0.985	-3.59×10^{-8}	2.4596	3.72	0.86
MWCNTsm	0.82	0.242	0.785183	0.942	-3.84×10^{-8}	2.4596	3.60	0.49
MWCNTsca	0.76	0.197	0.696196	0.973	-3.16×10^{-8}	1.4918	3.97	0.69
MWCNTsma	0.74	0.234	0.990712	0.982	-3.44×10^{-8}	1.6487	3.81	0.45
CuO	0.72	0.163	0.959127	0.923	-2.27×10^{-8}	2.0137	4.68	0.59
MWCNTsc/CuO	0.82	0.263	0.928758	0.965	-2.13×10^{-8}	1.8221	4.84	0.47
MWCNTsm/ CuO	0.84	0.275	0.731346	0.995	-3.44×10^{-8}	1.5999	3.80	0.49
MWCNTsca/ CuO	0.84	0.294	0.822041	0.995	-1.60×10^{-8}	0.0672	5.57	0.61
MWCNTsma/ CuO	0.824	0.254		0.996	-1.20×10^{-8}	0.0742	6.43	0.63

Conclusions

1. Plant stems of a Citrus aurantium and morus were successfully used as a source of charcoal, activated carbon and carbon nanotubes production
2. The charcoal and activated carbons are good raw materials for the production of multi-walled carbon nanotubes
3. Chemical Flame Deposition methods (CFDM) is a suitable method to prepare the multi-walled carbon nanotubes.
4. CuO nanoparticles were prepared by well, simple and quick synthesis via Lemon Leaves Extract methods.
5. FTIR spectroscopy revealed CuO nanoparticles synthesis.
6. The measuring of the particle size using X-ray diffraction were (37.8) nm for CuO nanoparticles.
7. The FESEM image of the normal MWCNTs was a bit smaller than the activated MWCNTs.
8. Raman spectroscopy revealed D and G bands present as evidence for the formation of MWCNTs, with the ratio of ID/IG of the normal MWCNTs (0.85) is less than activated MWCNTs (0.91).
9. The removal percentage of Pb^{+2} ion reaches equilibrium in contact time (40) min for all prepared samples with removal efficiency reached 71% revealed to samples based on SWCNTs and MWCNTs.
10. The kinetics results conforms the best correlation of the experimental data of adsorption of all samples by pseudo – second order equation.
11. The negative values of free energy ΔG , the negative values of enthalpy ΔH and negative values of entropy ΔS for the adsorption of Pb^{+2} ion on samples

indicates that the adsorption processes is spontaneous, exothermic and non randomness at solid– solution interface.

12. Finally, carbon nanotubes and their composite demonstrated that they are a promising adsorbent for the removal of lead ion from polluted water.

Future works

1. Using the MWCNTs and their composite that prepared by Chemical Flame Deposition method (CFDM) in removal of other various heavy metals such as; Co, Zn, Cu etc.
2. Preparation of MWCNTs and CuO nanoparticles using other methods.
3. Experimenting adsorption of other heavy metals such as Co, Zn, Cu ,Cd, Mo, Hg.....etc) by MWCNTs / multi metal oxide nanoparticles .
4. Using other models in adsorption isotherm such as Freundlich and Temkin models.

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الخلاصة

في هذه الدراسة ، تم تحضير أنابيب الكربون النانوية متعددة الجدران باستخدام طريقة الترسيب الكيميائي للهب (CFDM) من ساق نباتات النارج والتوت ، وتم تحضير اوكسيد النحاس النانوي (CuO nanoparticles) بطريقة بسيطة باستخدام مستخلص أوراق الليمون وسداسي هيدرات كلوريد النحاس ($\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$) كمصدر للنحاس مع التكليس عند درجة حرارة 550°C يتبع ذلك تحضير متراكب ثنائي من أنابيب الكربون النانوية متعددة الجدران (MWCNTs) اوكسيد النحاس النانوي (CuO nanoparticles) معلقة في الايثانول عن طريق خلط نسب مختلفة من MWCNTs وأكسيد النحاس النانوي CuO بواسطة جهاز الموجات فوق الصوتية.

تم استخدام تقنيات التحليل الطيفي كمتيافية الأشعة تحت الحمراء FTIR ، مطيافية Raman ، حيود الأشعة السينية والمجهر الالكتروني الماسح (FESEM) لتشخيص المركبات المحضرة.

أكدت أطياف رامان تحضير أنابيب الكربون النانوية من خلال ظهور قمم تعود للنطاقين D و G في جميع العينات المحضرة (MWCNTs) حيث وجد ظهور قمم عند 1359cm^{-1} و 1436cm^{-1} تنتمي إلى النطاق D وقم عند 1444cm^{-1} و 1582cm^{-1} تعود للنطاق G كذلك أكدت أطياف XRD ذلك. باستخدام معادلة ديبيي - شيرر تم حساب معدل حجم الجسيمات لجسيمات النحاس النانوية CuO وكانت حوالي 37.8 nm والتي تتفق مع نتائج المجهر الالكتروني الماسح FESEM.

يسبب تلوث الماء بأيون الرصاص (Pb^{+2}) كمعدن ثقيل ضررًا كبيرًا للبيئة ، لذلك فإن العينات MWCNTs و nano CuO و MWCNTs / CuO أعدت لإزالته من المياه الملوثة وفي هذا المجال تمت دراسة عدد من العوامل التي تؤثر على النسبة المئوية لإزالة أيون الرصاص مثل وقت التماس وكمية المادة المازة ودرجة الحرارة ووجد ان الوقت اللازم لإزالة أيون (Pb^{+2}) للوصول إلى حالة التوازن هو 40 min ، بالمقابل أن إزالة أيون الرصاص كانت جيدة وتزداد مع زيادة وقت التماس وكمية المادة المازة بينما تقل مع زيادة درجة الحرارة مما يعني أن العملية باعثة للحرارة وهذا متوافق جيدًا مع قيم الدوال الترموديناميكية المحسوبة.

تم دراسة البيانات التجريبية على النماذج الحركية التالية: المرتبة الاولى الكاذبة ، المرتبة الثانية الكاذبة ونموذج الانتشار الحركي داخل الجسيمات وتبين من الدراسة الحركية ان النموذج الحركي للمرتبة الثانية الكاذبة هو الاكثر ملائمة من النماذج الحركية الاخرى في امتزاز ايون الرصاص (Pb^{+2}) من المياه الملوثة.

بينت القيم المحسوبة للدوال الترموديناميكية (ΔS ، ΔH ، ΔG) ان امتزاز ايون الرصاص (Pb^{+2}) تلقائي حسب قيم ΔG السالبة ، باعث للحرارة حسب قيم ΔH السالبة وزيادة في العشوائية وعدم الانتظام حسب قيم ΔS الموجبة على جميع العينات المحضرة.

أخيرًا ، تم تطبيق ايزوثيرم Langmuir وايزوثيرم Dubinin–Radushkevich على النتائج المستحصلة للدراسة ووجد ان امتزاز ايون الرصاص (Pb^{+2}) على جميع العينات يتبع ايزوثيرم Langmuir .



جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة ديالى- كلية التربية للعلوم الصرفة- قسم الكيمياء



تحضير ومقارنة الأنابيب النانوية الكربونية المنتجة بطريقة ترسيب الذهب من مصادر نباتية
وامتزاز Pb^{+2}

رسالة مقدمة الى

مجلس كلية التربية للعلوم الصرفة / جامعة ديالى

وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

إعداد

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