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تحضير بعض أكاسيد الفلزات الانتقالية وتفريقها على اسطح الكرافيت النانوي المعدل  
ودراسة خصائصها

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وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

إعداد

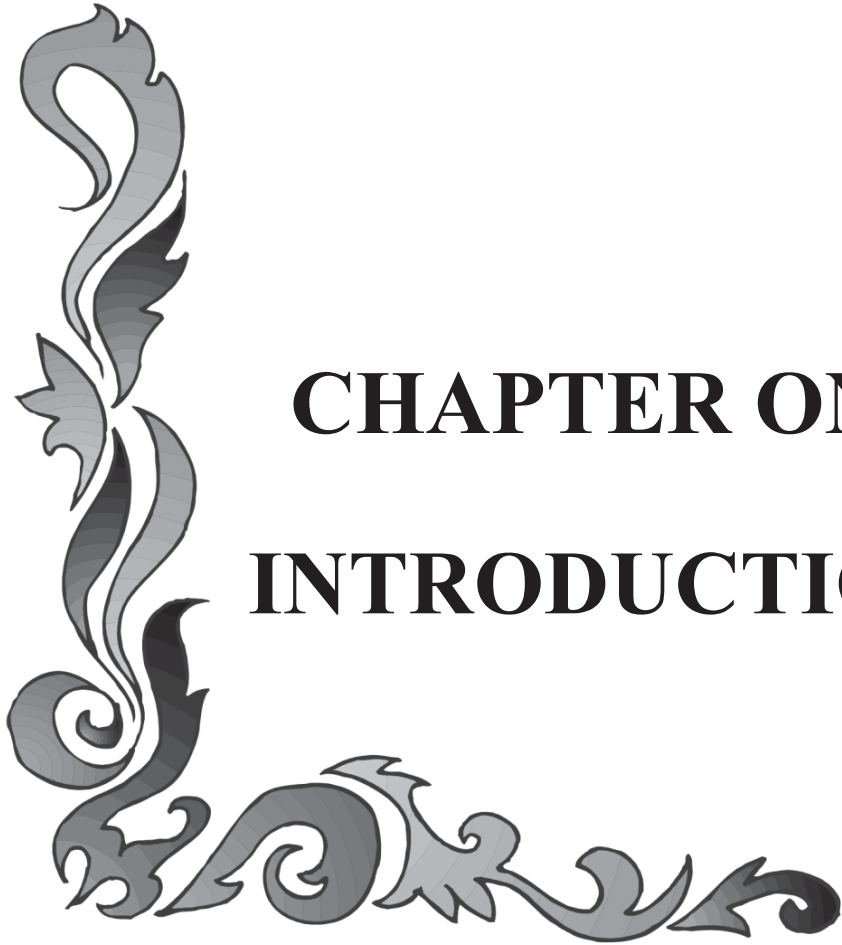
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إشراف

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**CHAPTER ONE**  
**INTRODUCTION**

## 1. General Introduction

One of the very basic results of the physics and chemistry of solids is the insight that most properties of solids depend on the microstructure, i.e. the chemical composition, the arrangement of the atoms (the atomic structure) and the size of a solid in one, two or three dimensions. In other words, if one changes one or several of these parameters, the properties of a solid vary. The most well-known example of the correlation between the atomic structure and the properties of a bulk material is probably the spectacular variation in the hardness of carbon when it transforms from diamond to graphite<sup>[1]</sup>. Comparable variations have been noted if the atomic structure of a solid deviates far from equilibrium or if its size is reduced to a few interatomic spacings in one, two or three dimensions such as Nano-materials<sup>[2]</sup>. The nanomaterial defined as the materials that has a least one dimension in the Nano-scale range of 1–100 nm and Depending on the overall shape these materials can be 0D,1D, 2D or 3D<sup>[3]</sup>. Nanoparticles are not simple molecules itself and therefore composed of three layers, (a) The surface layer, which may be functionalized with a variety of small molecules, metal ions, surfactants and polymers, (b) The shell layer, which is chemically different material from the core in all aspects, and (c) The core, which is essentially the central portion of the NP and usually refers the NP itself <sup>[4]</sup>. Nano-materials have numerous applications in areas ranging from catalysis, photonics, molecular computing, energy storage, fuel cells, tunable resonant devices, sensing to Nano-medicine<sup>[5]</sup>. This is due to an increase in reactivity when compared to their micro-sized counterparts since Nano-scaled materials exhibit larger surface to- volume ratio which provides unsaturated and, thus, more reactive surface atoms<sup>[6]</sup>. To consider nanoparticles for biological applications, such as drug delivery,

bio-sensing, imaging and antibacterial therapeutics, several key requirements have to be fulfilled, the first is to deal with the engineered nanoparticles of well characterized composition, size, crystallinity and morphology, the second implies manipulation of stabilized, non-agglomerated Nano-materials in order to control dosing and finally, the most crucial requirement is their biocompatibility<sup>[5] [7]</sup>. Despite very fast expansion of the bio-nanotechnology in the last 30 years, there are many challenges facing these three requirements<sup>[8]</sup>. Nanostructured materials offer promising opportunities for improved applications in different area of modern life due to their unique physicochemical properties <sup>[9]</sup>.

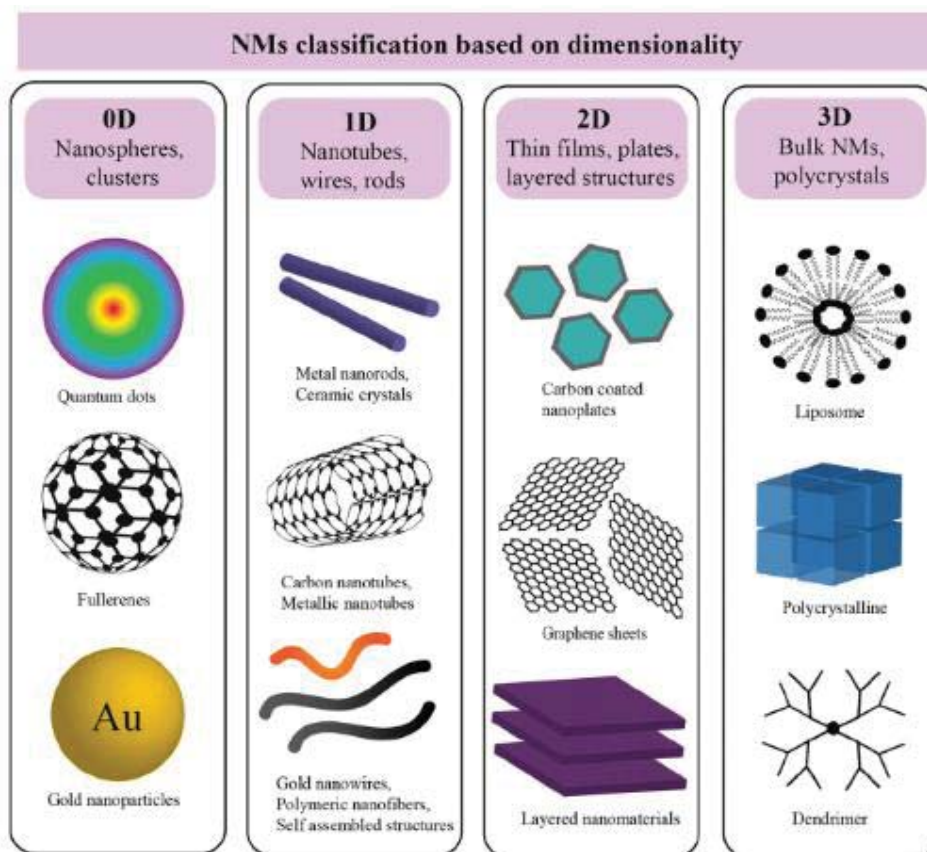
### 1.1. Classification of Nano-materials

Nano-materials (NMs) can be classified into different groups based on various criteria. Generally, NMs are categorized according to their dimensionality, morphology, state, and chemical composition<sup>[10]</sup>. This classification also depends on their size, which ranges from 1–100 nm in at least one dimension (Figure. 1.1). Based on their dimensionality and the overall shape of these materials (NMs) can be further divided into four classes<sup>[11]</sup>:

1. **Zero-dimensional (0D)** nanomaterials possess all dimensions at the nanoscale, i.e. the size is less than 100 nm. 0D includes spherical, cube, polygonal nanometer, hollow sphere, metallic.
2. **One-dimensional (1D)** nanomaterials are materials with one dimension not at the nanoscale while the other is two dimensions at the nanoscale. 1D includes metallic, polymeric, ceramic, nanotube, ,nanorod filament, nanowires and nanofibers.
3. **Two-dimensional (2D)** nanomaterials only one of the dimensions is located on the nanoscale while the other two are not. 2D includes

thin films, nanosheets, and monolayer (crystalline or amorphous nanolayers).

**4-Three-dimensional (3D)** nanomaterials have various dimensions exceeding 100 nm. (3D) NMs combine multiple nanocrystals in different directions. Examples include foams, fibres, carbon nanotubes, fullerenes, pillars, polycrystalline, honeycombs, and layered structures<sup>[12] [13]</sup>.



Figure(1-1).Schematic illustratinon of the relative dimensions of nanoparticles with examples of each category<sup>[14]</sup>.

## 1.2. Metal Oxides Nanoparticles

To date, as many as 60 bio-minerals have been identified as being necessary for the correct function of organisms, and more than 60% of these are reported to be coordinated to either hydroxyl moieties or water molecules, enabling the rapid release of ions in solution<sup>[15]</sup>. Metal oxides, in particular, provide a fundamental stepping-stone for the development of functional nanomaterial. In an oxidative environment, such as the atmosphere of the Earth, oxides are the lowest free energy states for most metals in the Periodic Table and demonstrate applications ranging from semiconductors to insulators. As insulators, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are the two most commonly used supports for catalysis, as they are non reducible oxides. Semiconductors, such as ZnO and SnO<sub>2</sub>, have high electrical resistivity that provide alternative templates for gas sensors<sup>[16]</sup>. Surprisingly, the properties associated with metal oxides in technology are not so far removed from what is observed in natural systems. Through precisely tuned processes, Nature is able to synthesize a variety of metal oxide nanomaterial under ambient conditions; the magnetic navigation device found in magnetoactive bacteria (MTB) is one such example. Here, magnetite (Fe<sub>3</sub>O<sub>4</sub>) nano crystals are aligned with the Earth's geomagnetic field and contained within specific organelles known as magnetosomes<sup>[17]</sup>. Fresh water salmon, for example, utilizes these magnetic nanoparticles in the nasal cavities of their forehead as a bio-magnetic compass during migration<sup>[18]</sup>.

### 1.2.1. Zinc Oxide Nanoparticles

ZnO is one of the most significant nano-materials that has been widely studied for many decades, generally, ZnO crystallizes in three forms hexagonal Wurtzite, cubic zinc blende and cubic rock salt as in Figure (1-2)<sup>[19]</sup>. It is obtained only at optimum pressure and temperature. The crystal structure is composed of two interpenetrating hexagonal-close-pack (hcp) sublattices<sup>[20]</sup>. ZnO is present in the earth's crust and has been extensively used as an additive in different products such as rubber, ceramics, pigments, cement, sealants, plastic and paint. Also, it is an attractive material for biomedical applications, because it is a bio-safe material. With the passage of time ZnO proved to be a versatile material because of its direct/wide band gap (3.37 eV) and high exciton binding energy (60 meV). ZnO nanoparticles can remove both anionic and cationic dyes (malachite green) and anionic dyes (acid-fuchsin and Congo red, called AF and CR) from aqueous solution. The adsorption process is dependent on pH and temperature<sup>[21]</sup>.

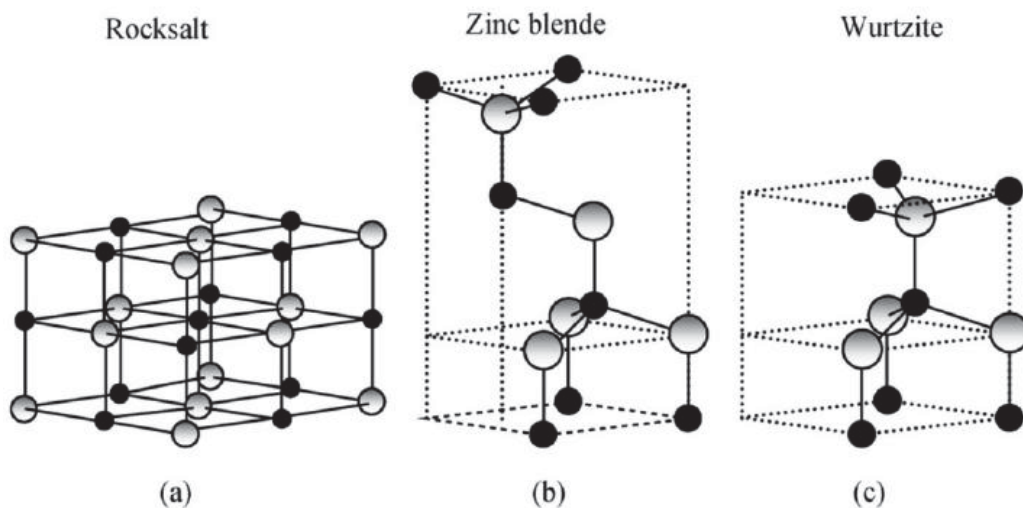


Figure 1-2. Stick and ball representation of ZnO crystal structures: (a) cubic rocksalt, (b) cubic zinc blende, and (c) hexagonal wurtzite.<sup>[22]</sup>

### 1.2.2. Copper Oxide Nanoparticles

Copper oxide is a semiconductor metal with unique optical, electrical and magnetic properties and it has been used for various applications, such as the development of super capacitors, near-infrared filters, in magnetic storage media, sensors, catalysis, semiconductors<sup>[23]</sup>. CuO have attracted attention mostly because of their antimicrobial and biocide properties and they may be used in many biomedical applications<sup>[24]</sup>. One of the most important parameters in the synthesis of these nanoparticles is the control of particle size, morphology and crystallinity and in order to achieve this goal, different synthesis methods were developed; some of the most investigated approaches include the sonochemical method, the sol-gel method, laser ablation, the electrochemical method, chemical precipitation and surfactant-based techniques<sup>[25]</sup>. Even though CuO nanoparticles (CuO NPs) have proved their use in biomedical applications; The main toxicity process relies on the increased production of reactive oxygen species. These nanoparticles thus induce oxidative stress in human pulmonary epithelial cells, promote toxicity and can damage DNA and mitochondria<sup>[26]</sup>. CuO-NPs chemically synthesized copper oxide nanoparticles (CuO-NPs), were successfully employed for two processes: one is photo-catalytic degradation and second one adsorption for the sorption of safranin (SA) dye in an aqueous medium at pH = 12.01<sup>[27]</sup>.

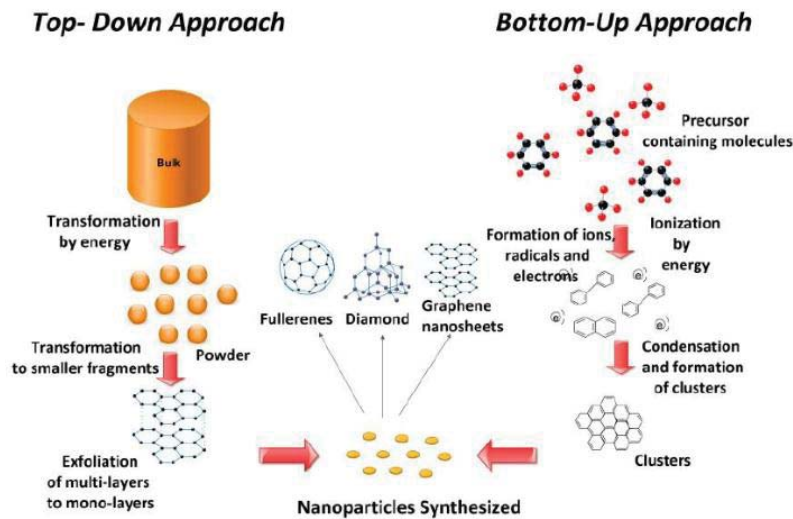


### 1.2.3. Cobalt Oxide Nanoparticles

Cobalt has two stable oxide states known as CoO and Co<sub>3</sub>O<sub>4</sub>. At room temperature both compounds are found to be kinetically stable. It have been captured a lot of interest among research community because of their potential applications In different fields of science and technology. Cobalt (II, III)oxide is an inorganic compound and as a mixed valence compound, its formula is written as CoIICoIII<sub>2</sub>O<sub>4</sub> or CoO.Co<sub>2</sub>O<sub>3</sub> or Co<sub>3</sub>O<sub>4</sub><sup>[28]</sup>. It is believed that transition metal oxides are good candidates as electrode materials, because they have variation in oxide states which is suitable for effective redox charge transfer. That is why as the most active transition metals, Co<sub>3</sub>O<sub>4</sub> has been used extensively as heterogeneous catalysts, solid-state sensors and in pigment, magnet as well. Co<sub>3</sub>O<sub>4</sub> is an important magnetic p-type semiconductor having direct optical band gaps as 1.48 and 2.19 eV , but 1.6 eV<sup>[29]</sup> is also reported in the literature. In last decade researchers have spent a lot of time on Co<sub>3</sub>O<sub>4</sub> nanostructures due to their high electro- chemical performance; because the features like high surface area, short path length for ion transport and easily tunable surface have made Co<sub>3</sub>O<sub>4</sub> a promising material for electrochemical device. Therefore in order to get maximum advantage of these properties an economical, stable, fast and sensitive H<sub>2</sub>O<sub>2</sub> sensor has been prepared in the presented work<sup>[30]</sup>. Uddina and co- worker described the synthesis of cobalt-oxide nanoparticles by simple precipitation technique and their environmental application. The prepared Co<sub>3</sub>O<sub>4</sub> nanoparticles were adsorbent displayed its efficiency in methyl orange adsorption from aqueous solution<sup>[31]</sup>.

### 1.3. Synthesis Method of Nano-materials

There are physical, chemical, photochemical and biological methods of nanoparticle preparation<sup>[32]</sup>. Further, methods of preparation of colloidal nanoparticle solutions can be divided into dispersing and condensing figure (1.3). Dispersion methods are based on destruction of the crystal lattice of the material laser ablation, cathode sputtering and electric arc dispersion), it belongs to the type “top-down.” Condensation methods are based on the chemical reaction (reduction in solution, followed by the nanoparticle precipitation, formation and stabilization). Each method has its advantages and disadvantages. The modified Turkevich method<sup>[33]</sup> results in mono disperse nanoparticles, the size of which varies depends on the reducing agent concentration and also the size of the ligand which it stabilizes. By other methods, stabilization of the nanoparticles is accomplished by forming an organic monolayer on the growth surface, controlling the size and shape by the concentration of the reducing agent and the stabilizer. Also, the reducing agent may be a stabilizer.<sup>[34]</sup>



Figure(1.3). Bottom-up and the top-down approaches in synthesis of carbon-based Nano-materials.<sup>[35] [36-35]</sup>

### 1.3.1. Chemical Precipitation and Co-precipitation

Chemical precipitation is generally not a controlled process in terms of reaction kinetics and the solid phase nucleation and growth processes. It consists of three main steps chemical reaction, nucleation and crystal growth. Therefore, solids obtained by chemical precipitation have a wide particle size distribution plus uncontrolled particle morphology, along with agglomeration<sup>[37]</sup>. To obtain nanoparticles with a narrow size distribution, the necessary requirements are (i) a high degree of supersaturation, (ii) a uniform spatial concentration distribution inside a reactor and (iii) a uniform growth time for all particles or crystals. co-precipitation is the other commonly method used solution for the synthesis of multi component oxide, that is produces a “mixed” precipitate comprising two or more insoluble species that are simultaneously removed from solution <sup>[38]</sup>. The precursors used in this method are mostly inorganic salts (nitrate, chloride, sulfate, etc.) that are dissolved in water or any other suitable medium to form a homogeneous solution with clusters of ions. The solution is then subjected to pH adjustment or evaporation to force those salts to precipitate as hydroxides, hydrous oxides or oxalates. The crystal growth and their aggregation are influenced by the concentration of salt, temperature, the actual pH and the rate of pH change. Generally, a calcination step is necessary to transform the hydroxide into crystalline oxides. In most of the binary, ternary and quaternary systems, a crystallization step is necessary, which is generally achieved by calcinations or, more elegantly, by a hydrothermal procedure in high-pressure autoclaves<sup>[39]</sup>.

### 1.3.2. Sol-gel Method

This method is applied often as it ensures the rigorous control of the nanoparticle size. The method was optimized in order to obtain nanoparticles with dimensions ranging between 10 and 40 nm. sol-gel technique is a simple and relatively fast method and therefore it is widely used in the design of nanoparticles<sup>[40]</sup>. Karthik et al.<sup>[41]</sup> synthesized CuO NPs with dimensions of 25 nm by a sol-gel method. The physical properties of CuO NPs also depend on the applied sol-gel method and the calcination time. Moreover, in the case of sol-gel method, the size of nanoparticles is proportionally related with the temperature, physical conditions are very important for the design of functional nanoparticles using this approach. Also by a sol-gel method, Jayaprakash et al. synthesized uncapped and capped CuO NPs by using ethylene di aminetetra acetic acid (EDTA)<sup>[42]</sup>. The capping agent was used to control the dimensions of CuO NPs. Uncapped CuO NPs were synthesized with  $\text{Cu}(\text{CH}_3\text{COO})_2\text{H}_2\text{O}$  and urea. It was reported that this method allows the fine control of morphology and shape of the nanoparticles<sup>[43]</sup>.

### 1.3.3. Chemical Vapour Deposition (CVD)

CVD is a process which a solid is deposited on a heated surface via a chemical reaction from the vapour or gas phase. In thermal CVD the reaction is activated by a high temperature above 900 °C. A typical apparatus comprises of a gas supply system, a deposition chamber and an exhaust system<sup>[44]</sup>. In plasma CVD, the reaction is activated by plasma at temperatures between 300 and 700 °C. In laser CVD, pyrolysis occurs when laser thermal energy heats an absorbing substrate<sup>[45]</sup>. In photo-laser CVD, the chemical reaction is induced by ultra violet radiation which has sufficient photon energy to break the chemical bond in the reactant

molecules. In this process, the reaction is photon activated and deposition occurs at room temperature. Nano composite powders are also prepared by CVD method<sup>[46]</sup>. For example, SiC/Si<sub>3</sub>N composite powder was prepared using SiH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and NH<sub>3</sub> as a source of gas at 1400 °C (Hong and Lai 1999). Chemical Vapour Condensation (CVC) process was developed in Germany in 1994. A metal organic precursor is introduced in the hot zone of the reactor using mass flow controller. The reactor allows synthesis of mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of reactor and coated nanoparticles by supplying a second precursor in a second stage of reactor. The process yields quantities in excess of 20 g/hr<sup>[47]</sup>. The yield can be further improved by enlarging the diameter of hot wall reactor and mass of fluid through the reactor.

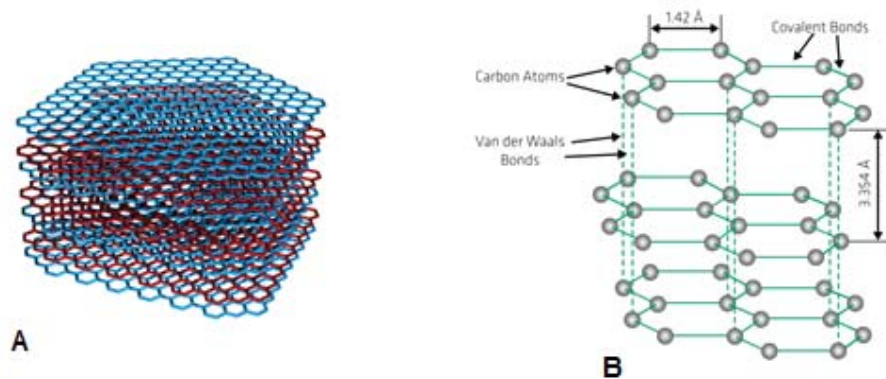
## **1.4. Carbon**

Carbon is special because of its ability to bond to many elements in many different ways. It is the sixth most abundant element in the universe. The most known types of carbon materials: diamond; graphite; fullerenes; and carbon nanotubes.

### **1.4.1. Graphite**

graphite, also called plumbago or black lead, mineral consisting of carbon. Graphite has a layered structure that consists of rings of six carbon atoms arranged in widely spaced horizontal sheets. Graphite thus crystallizes in the hexagonal system, in contrast to the same element crystallizing in the octahedral or tetrahedral system as diamond. Such dimorphous pairs usually are rather similar in their physical properties, but not so in this case. Graphite is dark gray to black, opaque, and very soft (with a hardness of 1 1/2 on the Mohs scale), while diamond may be

colourless and transparent and is the hardest naturally occurring substance. Graphite has a greasy feel and leaves a black mark, thus the name from the Greek verb graphein, “to write.” Graphite is formed by the metamorphosis of sediments containing carbonaceous material, by the reaction of carbon compounds with hydrothermal solutions or magmatic fluids, or possibly by the crystallization of magmatic carbon. It occurs as isolated scales, large masses, or veins in older crystalline rocks, gneiss, schist, quartzite, and marble and also in granites, pegmatites, and carbonaceous clay slates. Small isometric crystals of graphitic carbon (possibly pseudomorphs after diamond) found in meteoritic iron are called cliftonite<sup>[48] [49]</sup>.



**Figure(1.4).** Show A) Multiple sheets of graphite. B) Graphite structure.<sup>[50]</sup>

### 1.4.2. Nano-graphite

elemental carbon comes in a couple of crystalline forms called allotropes based on the chemical bindings. Diamond and graphite are the most known forms of carbon allotropes with buckminsterfullerene as the least common form<sup>[51]</sup>. The chemical bonds in graphite are  $sp^2$  hybridization with the atoms forming a planar pattern where each carbon atom binds to 3 neighboring atoms of carbon located at  $120^\circ$  degrees apart. If graphite is exfoliated to individual layers, graphene can be

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obtained. Carbon atoms on graphite align in honeycomb lattice 0.142 nm apart with the planar distance of 0.335 nm. The carbon atoms in the planes are bound covalently with three electrons involving in binding and one free electron to migrate in the plane giving graphite electrical conductivity. The graphite layers are bound through weak Van Der Waals forces making it easier for the layers to be separated easily or slide on each other to serve as a lubricating agent. Based on its morphology, graphite could be categorized as hexagonal alpha graphite and rhombohedral beta graphite with nearly<sup>[52]</sup>. Graphite is among the materials with a higher thermal conductivity and low density and can easily be dispersed into fluids because of its flake shape. Graphite nanoparticles appear to have a higher heat-transfer coefficient as well as cheap price among oxide nanoparticles and metalloids<sup>[53]</sup>. The lubrication quality of graphite is an important property that many mechanical devices can benefit from. In addition, they can easily be recycled without causing any pollution. Graphite nanoparticles are basically conjugated  $\pi$ -electron systems. When a crystal of graphite falls into Nano-scales, there appears edges surrounding the particles. A single graphite nanoparticle consists of Nano-sized graphene sheets stacked on each other in which the peripheries that are technically made of dangling bonds are exposed to species likes hydrogen and oxygen for any probable reaction leading to a complete bound structure. Particularly in this case, nanoparticles are determined by finite flat graphene layers with open edges, while in carbon nanotubes the surface is closed. The existence of unbounded open edges around the peripheral region in graphite nanoparticles gives them a specific property compared to other close surface systems like fullerene and carbon nanotubes <sup>[54]</sup>.

## 1.5. Application of Oxide-Nano- materials

Several metal oxides in form of nanoparticles have been reported to exhibit marked antibacterial activity allowing efficient eradication of various bacterial strains<sup>[55]</sup>. This fact has attracted significant interest of environmental, agricultural and health care industries that are searching for newer and better agents to control or prevent bacterial infections. Many studies have been undertaken to explain the efficacy and mechanisms of antibacterial action of metal oxide nanoparticles but the existent literature is still controversial and incomplete<sup>[56]</sup>. A device which has the capability to detect the existence or concentration of a particular toxic and explosive gases is called as a gas sensor. Metal oxide semiconductors show good sensing activity. The change in electrical conductivity arises from the chemical reaction between the adsorbed oxygen onto the metal oxide surface and the gas molecules<sup>[57]</sup>. The adsorbed oxygen molecule on the surface of metal oxides like ZnO nanoparticles is ionized to  $O^{+2}$ ,  $O^-$  and  $O^{-2}$  by acquiring electrons from the conductance band (CB). So it exhibits resistivity towards air environment. The reducing gases such as carbon monoxide, ammonia, dihydrogen and ethanol at modest temperature, the oxygen species on the nanowire surface react with the investigated gas resulting in the decrease in oxide ion on the surface and rise of concentration in electrons. Hence, ZnO nanowire sensors exhibits enhanced conductivity in reducing gases.<sup>[58]</sup>



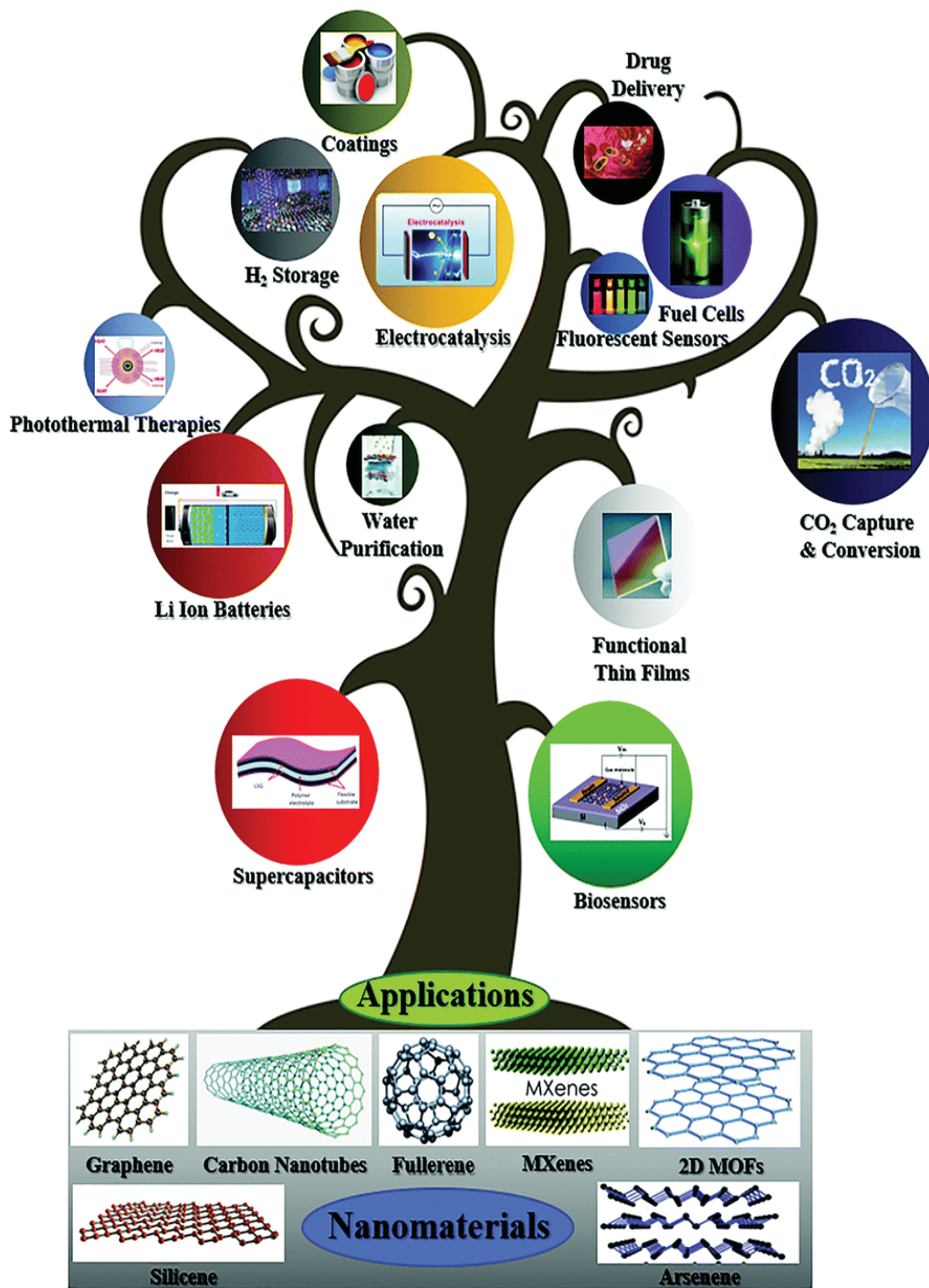
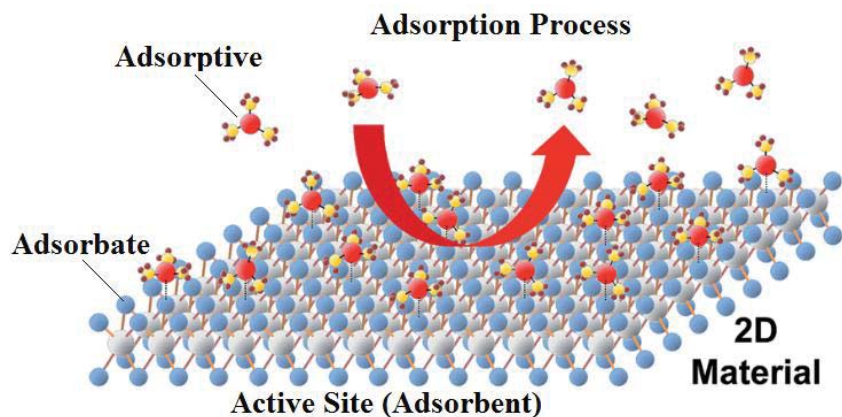


Figure (1-5): Types of Nano-materials and Their.<sup>[59]</sup>

## 1.6. Adsorption

Adsorption is an inexpensive, cheap and simple method. It is readily available to remove organic and inorganic pigments, such as removing organic pigments from many industries. Various, and Figure(1. 6) shows the adsorption process of these pigments that are produced as main files for industries Various. It has become of great importance in many modern industries through the many studies that conducted to used in theory and practice in many chemical and petrochemical industries as a major tool in developing Modern technology. surface chemistry is an important source of adsorption. The direction of the light and the oxidizing agents, which has a negative effect on human health and the environment, so adsorption was used to evade of these by using low-cost materials <sup>[60]</sup>. Adsorption is defined as the forces arising from the bonding between molecules, atoms or ions of certain substances called matter (adsorbate) and a solid surface called an adsorbent, the relationship arising between the area The surface of the adsorbent material and the nature and size of the adsorbent material depend on the degree of adsorption, and adsorption is accompanied by a change in energy The free surface ( $\Delta G$ ) as well as the decrease in entropy ( $\Delta S$ ) due to the molecules that bind to the diesel surface, which are bound Therefore, it loses its freedom before it was before adsorption, so it decreases when it limits the free energy and entropy at the same time A decrease in enthalpy also (happens)  $\Delta H$  as in the following equation <sup>[61]</sup> <sup>[62]</sup>.

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



The figure( 1.6). Shows the adsorption process

### 1.6.1. Type of Adsorption

#### 1.6.1.1. Physisorption

Physical adsorption is formed on the surfaces of hydrated materials because their atoms are saturated and also as a result of bonding bonds. Its atoms with atoms of neighboring materials, and here the forces of attraction are weak<sup>[63]</sup>. Physical adsorption consists of several layers and does not need The energy of activation and heat of adsorption is less than (40 KJ/ mol) and it is derived through its dependence on the surface chemistry in several ways. Known methods for determining the surface area of a solid material that is not characterized by purity, and the temperature of physical adsorption is lower From the boiling point of the adsorbent<sup>[64]</sup>.

### 1.14.2. Chemical Adsorption

In chemical adsorption, the surfaces in it work to form chemical bonds with the molecules or atoms of the substance that be adsorbed on a surface, and this adsorption is of a special type, as it forms under certain conditions on a specific surface and may It does not form in the same conditions on another surface<sup>[65]</sup>. Heat (chemical adsorption is 80 KJ/mol) and needs energy Activation, a type of adsorption that is localized because it depends on the adsorption sites that are characterized by the minimum potential energy and temperature Chemical adsorption is higher than the boiling point of the adsorbent<sup>[66]</sup>.

## 1.7.Factors Influencing Adsorption Processes

### 1.7.1.Effect of Temperature

The temperature of the solution mainly affects the enlargement nature of adsorbents, mobility of Lithium ions and solid/liquid interface<sup>[67]</sup>. temperature, thermodynamic parameters were used to determine the nature of adsorption process viz exothermic or endothermic, spontaneity and randomness and also to determine whether the temperature is favorable for the process or not. The important thermodynamic parameters are  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  representing the change in Gibbs free energy, enthalpy and entropy. The negative values of  $\Delta G^0$  are associated with the adsorption process being spontaneous. Similarly, the positive values of  $\Delta H^0$  indicate that the process is endothermic. Moreover, the positive values of  $\Delta S^0$  could be explained as that increase in entropy occurred due to the exchange of metal ions by more mobile ions during adsorption process.

### 1.7.2. Effect of Contact Time

The contact time significantly affects the adsorption process. Also, contact time can influence the economic efficiency of the process as well as the adsorption kinetics<sup>[68]</sup>. Therefore, contact time is another performance governing factor in adsorption process. Adsorption of Lithium (La) on Fe<sub>3</sub>O<sub>4</sub>/chitosan Nano-composite was investigated by , they achieved 86% La removal after a contact time of 60 min. Notably, La removal reduced by increasing the contact time from 60 to 150 min<sup>[69]</sup>.

### 1.7.3. Effect of Adsorbent quantity

In general, the extent of adsorption of a solute increases with the increase in the concentration of an adsorbent because the increase in adsorbent concentration translates into increased active exchangeable adsorption sites. However, the overall solute adsorption per unit weight of an adsorbent can decrease following the increase in adsorbent concentration due to interference caused by the interaction of active sites of an adsorbent<sup>[70]</sup>.

## 1.8. Theory of 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 and Freundlich<sup>[71]</sup> [72] figure( 1-7 ).

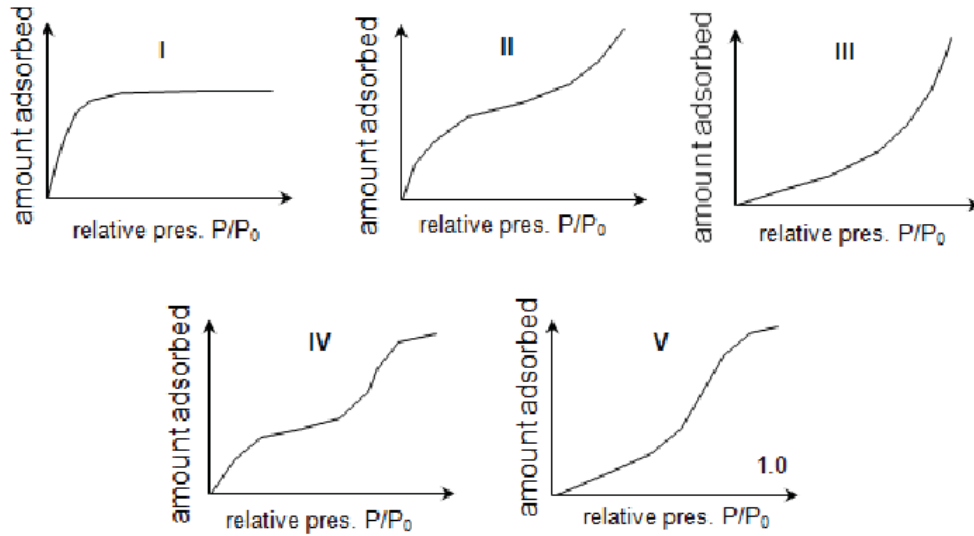


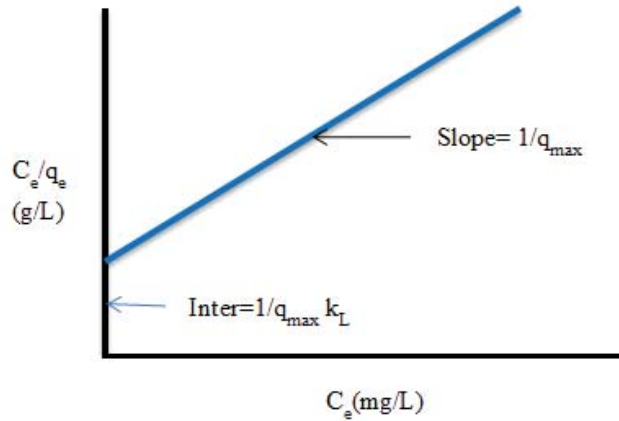
Figure (1.7) isotherm models.

### 1.8.1. Langmuir Isotherm

It is describe monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies with no transmigration of adsorbate in the plane surface<sup>[73]</sup>. Once a site is filled, no further sorption can take place at that site. This indicates that the surface reaches a saturation point where the maximum adsorption of the surface will be achieved. The isotherm is represented by:

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

The linear plot of specific adsorption ( $C_e/q_e$ ) against the equilibrium concentration ( $C_e$ ) adsorption obeys the Langmuir model. The constants  $b$  and  $q_{max}$  relate to the energy of adsorption and maximum adsorption capacity.



**Figure (1-8) The linear form of Langmuir isotherm**

This form can be used as a linearization of experimental data by plotting  $(C_e / q_e)$  against  $(C_e)$  as shown in Figure (1-8). The Langmuir's constants (a) and (b) can be evaluated from the slope  $(1/a)$  and intercept  $(1/ab)$  of the linear equation.<sup>[74]</sup>

### 1.8.2. Temkin Isotherm

It can be used in evaluating characteristic energies of an adsorption process. The adsorption is characterized by a uniform distribution of binding energies, which is up to some maximum binding energy. The Temkin isotherm is expressed as<sup>[75]</sup>:

$$q_e = \frac{RT}{b} \ln(A_T C_E) = B \ln(A_T C_E) \text{-----(1-3)}$$

Equation ( 1-4) can be also rewritten as;

$$q_e = B \ln(A_t) + B \ln(C_e) \text{-----(1-4)}$$

It is linear relationship between  $\ln(C_e)$  and  $(q_e)$  as shown in Figure (1-9). The intercept is  $B \ln(A_T)$  and the slope is  $B$ . Where:  $A_t$  is Temkin isotherm equilibrium binding constant (L/g),  $b$  is Temkin isotherm constant,  $R$  is universal gas constant ( $8.314 \text{ mol}^{-1} \text{ K}^{-1}$ ),  $T$  (K),

$B$  is constant related to heat of sorption (J/mol),  $b$  is heat of sorption<sup>[76]</sup>. The Temkin constants (AT) and (BT) were obtained from the slope and intercept of the plot between the  $q_e$  and  $\ln C_e$ .

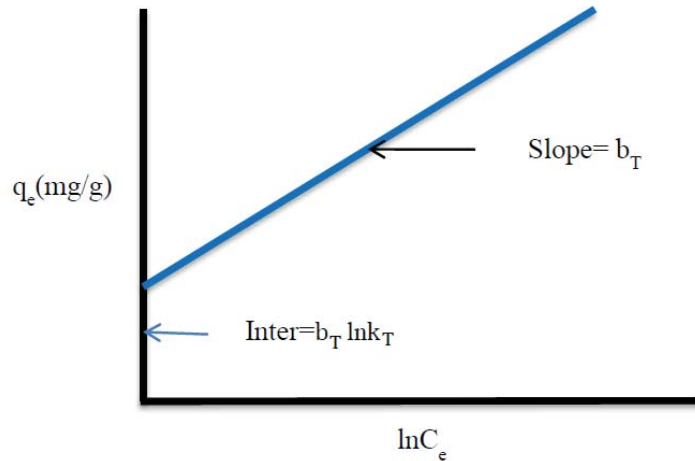


Figure (1-9) The linear form of Temkin isotherm

### 1.8.3. Dubinin–Radushkevich Isotherm

Dubinin–Radushkevich isotherm (DR) is one of the important methods to determine the adsorption type and expressed. 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<sup>[77]</sup>. the equation are expressed, respectively by:

$$q_e = q_{max} \exp^{-(K_D)\epsilon^2} \text{----(1-5)}$$

where

$q_e$  is the amount of ions adsorbed per unit weight of adsorbent at equilibrium ( $\text{mg g}^{-1}$ ).  $K_D$  is The constant  $KD$  ( $\text{mol}^2 \text{kJ}^{-2}$ ) gives the mean free energy  $E$  ( $\text{kJ mol}^{-1}$ ) of adsorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution.



E is 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. The linear plot of specific adsorption  $\ln q_e$  against the equilibrium concentration ( $\epsilon^2$ ) (Fig 1.10) 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<sup>[78]</sup>. The linear form of the isothermal D-R model can be expressed by the following equation:-

$$\ln q_e = \ln q_s - B \epsilon^2 \quad \dots (1-6)$$

$q_e$ : the amount of material adsorbed at equilibrium (mg/g)

$q_s$ : is the theoretical adsorption saturation capacity

B: is the Dubnin-Redochkvig constant ( $\text{mol}^2 \cdot \text{KJ}^2$ )

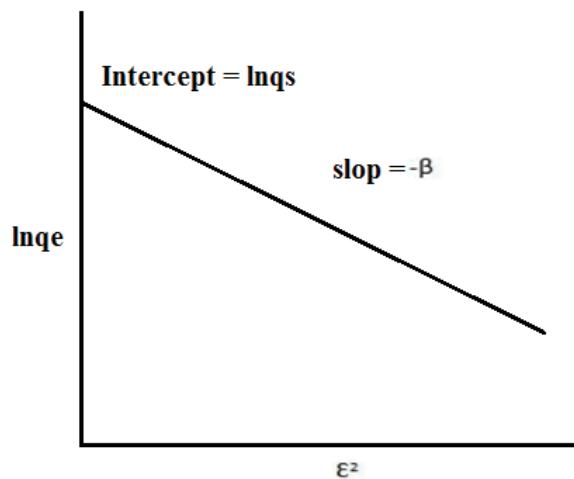


Figure (1-10) The linear form of Dubinin–Radushkevich isotherm (DR)

## 1.9. Adsorption Kinetics

various studies have reported the kinetics of the adsorption system through conducting time interval experiments. These experiments are

based on withdrawing a sample at specified time intervals and measuring the concentration<sup>[79]</sup>. The obtained data are used to build a profile and fit a suitable kinetics model that can describe the adsorption system. Based on the model, the adsorption mechanism can be identified. From the many different kinetics models, the most common models in PW adsorption were observed to be: pseudo-first order, pseudo-second order, intra-particle diffusion model<sup>[80]</sup>.

### 1.9.1. Pseudo-First Order Adsorption

In terms of the pseudo-first order adsorption is taking place through physical forces. most commonly used to describe the adsorption of solute from a liquid solution. The pseudo-first order equation is given by:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \dots\dots\dots(1-7)$$

Where  $q_t$  and  $q_e$  are the amounts of pigment adsorbed at time  $t$  and equilibrium (mg/g) respectively, and  $k_1$  is the pseudo-first order rate constant for the adsorption process (1/min). as shown in Figure (1-11)

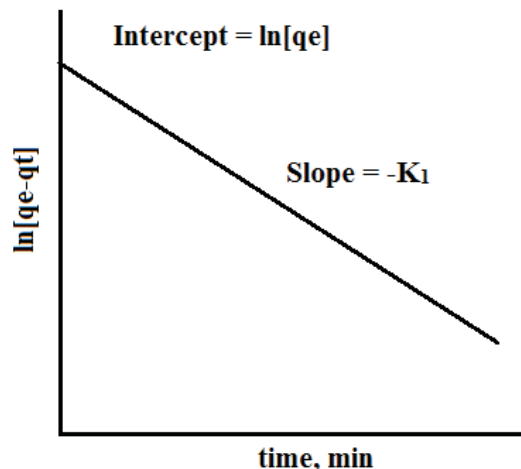


Figure (1-11) The linear form of pseudo-first order

### 1.9.2. Pseudo-Second Order Adsorption

This model assumes that the uptake rate is second order with respect to the available surface sites. When the adsorbate removal from a solution is due to physicochemical interactions between the two phases; the kinetics rate equation is expressed as<sup>[81]</sup>:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \text{-----(1-8)}$$

where  $k_2$  is the pseudo-second-order (PSO) rate constant. Other symbols have the same meanings as in the PFO model. Integrating Eq (1-8) with initial conditions of  $q = 0$  when  $t = 0$  and subsequent rearrangement obtains the linearized form:

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \text{-----(1-9)}$$

The initial rate of adsorption ( $q$ ) at ( $t \rightarrow 0$ ) is  $k_2 q^2 e$ . A plot of  $t/q$  vs  $t$  gives a straight line for PSO-compliant kinetics as shown in figure (1-12). The slope is  $1/q_e$ , and the intercept is  $1/k_2 q_e^2$ . Other linearized forms are available but less frequently used.

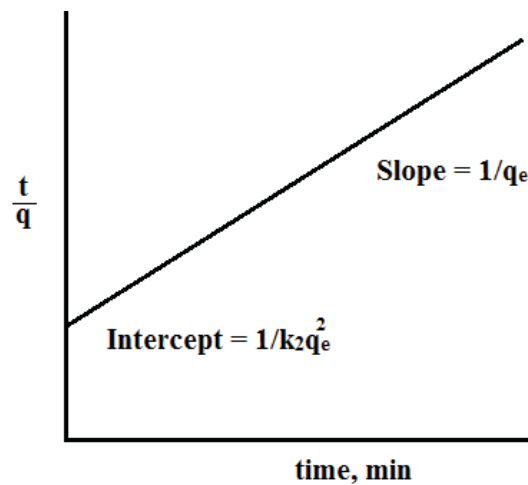


Figure (1-12) The linear form of pseudo-second order

### 1.9.3. Intra-Partical Diffusion Model

The equation of the implicit particle diffusion concerns the adsorption flow in terms of the velocity of the implied diffusion or the mass transfer of the liquid phase. The equation is expressed in the following linear form<sup>[82]</sup>:

$$q_t = k_J \cdot t_{1/2} + C \dots (1-10)$$

Whereas:

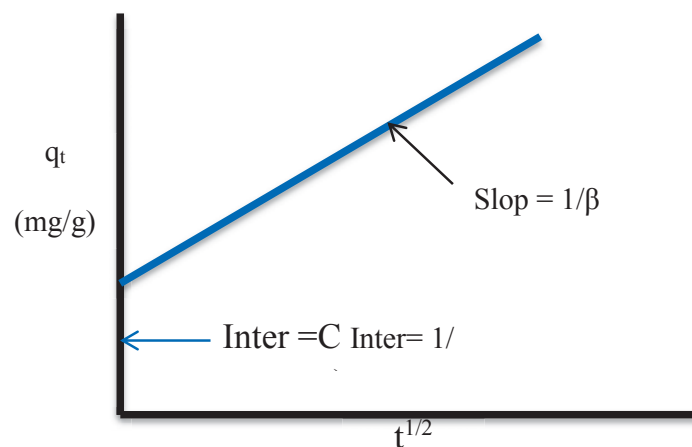
$k_J$ : implied minute diffusion rate (mg. g<sup>-1</sup>. min<sup>-1</sup>)

$C$ : represents the intersection of a straight line (intersection)

$q_t$ : the amount adsorbed at time  $t$  (mg/g)

$t_{1/2}$ : square root of time (1/2 minute)

And by plotting between  $q_t$  vs. ( $t_{1/2}$ ).

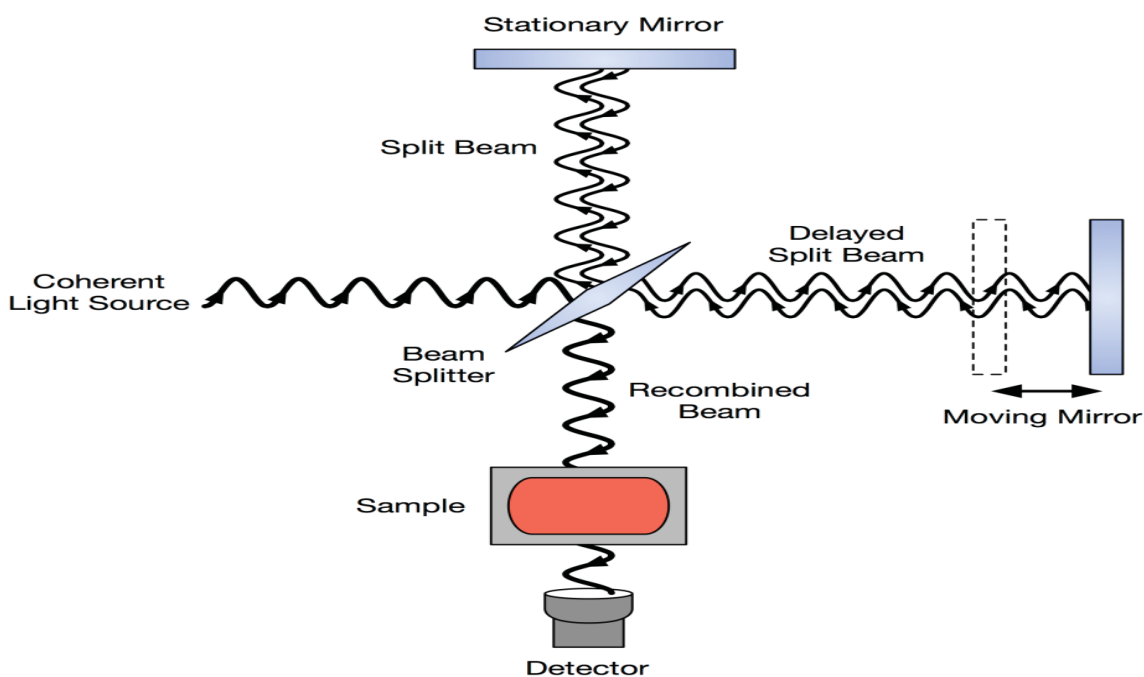


**Figure (1.13) Shows the graphic representation of the adsorption kinetics equation for the implicit fine diffusion.**

## 1.10. Characterization of Metal Oxide Nanoparticles and their Composites

### 1.10.1. FT-IR Spectrometry (FTIR) Technique

It is a physicochemical method based on the vibration of a molecule with infrared rays. According to a specific wavelength, a technique used to obtain an absorption or emission spectrum Matter, whether solid, liquid or gaseous, the spectrometer collects data and information High-resolution on the extent of strengthening over the extent of the body's



absorption of families exposed to standing in the sun rays path In infrared spectroscopy in Figure 14.

Figure (1.14): Schematic diagram of a Michelson interferometer, configured for FTIR.<sup>[83]</sup>

### 1.10.2. X-Ray Diffraction

X-ray diffraction is now a common technique for studying crystal structure and atomic spacing. Principle of X-ray diffraction It relies on the constructive interference of monochromatic X-rays and sample crystal

structures. These X-rays are created by A monochromatic cathode ray tube is filtered to produce a focused radiation to be directed towards the sample<sup>[84]</sup> when the conditions of Bragg's law are met:

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

Since (n) is an integer, ( $\lambda$ ) is the wavelength of the X-rays, (d) is the spacing between two successive planes in a crystal and it is born Diffraction and ( $\theta$ ) is the diffraction angle, and the angle of incidence. X-ray powder diffraction is widely used to identify unknown crystalline materials (such as metals and compounds Recognition of unknown solids is critical for studies in geology, environmental sciences, materials science, and engineering X-ray diffraction is a high-tech, non-destructive technique for analyzing a wide range of materials including Liquids, metals, polymers, catalysts, plastics, pharmaceuticals, thin films, ceramics, solar panels and the like<sup>[85]</sup>.

### 1.10.3. Field Emission Scanning Electron Microscope (FESEM)

It is used to show very small to pographical details over an entire surface or objects. Implementation It was as small as 1 nanometer (= billion millimeter). Figure 15 FESEM works by releasing two fields of electrons from an emission source. These ignited elementary electrons are accelerated by a high electric field gradient inside the high vacuum column And directing it with electronic lenses to produce a narrow scanning beam of the body that bombards the electrons and emits them Spot on the body, varieties, classes of these electrons secondary to the structure of the body's surface to receive Electrons as the secondary cache capture a video signal that includes a signal and convert it into a video scan image It can be seen on a screen or in a digital image that can be stored and processed.<sup>[86]</sup>

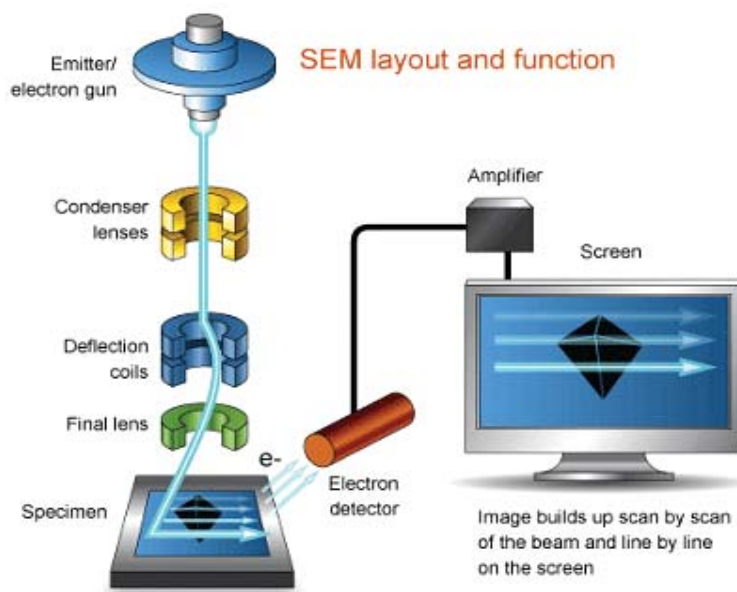


Figure (1.15) Show all Scanning Electron Microscope (SEM) components.<sup>[86]</sup>

#### 1.10.4. The Brunauer–Emmett–Teller (BET) Theory

Surface area is best described as the external surface area of a solid object including surface attributable to pores. Gas adsorption provides a distinct advantage as many classical models for particle measurement and characterization fail to consider porosity<sup>[87]</sup>. As mentioned earlier, physisorption is generally weak and reversible, the solid must be cooled and a method used to estimate the monolayer coverage from which surface area can be calculated. The area covered may be calculated by considering the amount of gas/vapour used to form the monolayer as well as the dimensions and the number of molecules. Though there are a number of methods in use, which take into account the full range or part of the isotherm, by far the most prevalent and successful methods are based on the BET method for gas adsorption onto a solid surface. The

BET equation, as shown below, is the most commonly used method to determine the monolayer and specific area values in various physicochemical areas.

$$\frac{x}{v(1-x)} = \frac{1}{v_m c_{bet}} + \frac{x(c_{bet}-1)}{v_m \cdot c_{bet}} \text{-----(1-11)}$$

where V is the volume of adsorbed molecules,  $V_m$  is the monolayer volume,  $C_{BET}$  is the BET constant, and x is the relative pressure (P/P0)<sup>[88]</sup>.

### 1.10.5. Dynamic Light Scattering (DLS)

DLS (dynamic light scattering) – also known as photon correlation spectroscopy or quasi-elastic light scattering - and ZP (zeta potential)<sup>[89]</sup> have emerged as simple table-top techniques executable under ordinary lab environments to investigate the (hydrodynamic( size and surface charge of NPs, respectively<sup>[90]</sup>. From techniques that were exclusively available to colloid chemists, both DLS and ZP have evolved into popular tools within pharmacy community. The integrated, compact and affordable instruments offer user-friendly digital interfaces along with possibility for comprehensive data analysis. Additionally, the techniques are non-invasive, require minimal sample preparation and no pre-experimental calibration. The modern instruments are able to guide the users on the quality of the generated data with possibility for time-dependent measurements and ability to export the data traces as files compatible with various plotting soft-wares.

## 1.11. Literature Review

The literature has referred to many studies that include treating the problem of water pollution with dyes, including methy orange dye, by using Maze surfaces. The most important of these surfaces used in this study is nano oxides (CuO,Co3O4,ZnONps) its and compounds. We review a number of these studies, including:



(In 2016, Slavica Stankic ,et.al) were published a report about Pure and multi metal oxide nanoparticles: synthesis, antibacterial and cytotoxic properties. The importance of their application as antibacterial agents is evident keeping in mind the limited range and effectiveness of antibiotics, on one hand, and the plethora of metal oxides, on the other, along with the propensity of nanoparticles to induce resistance being much lower than that of antibiotics. Effective inhibition against a wide range of bacteria is well known for several nano oxides consisting of one metal ( $\text{Fe}_3\text{O}_4$ ,  $\text{TiO}_2$ ,  $\text{CuO}$ ,  $\text{ZnO}$ ), whereas, research in the field of multi-metal oxides still demands extensive exploration<sup>[55]</sup>.

(SINGH, et.al) were synthesized cupric oxide ( $\text{CuO}$ ) nanoparticles by electrochemical discharge process using strong base electrolytes. The experiments were carried out separately using  $\text{NaOH}$  and  $\text{KOH}$  electrolytes. The mass output rate and the crystal size were obtained with variation of the rotation speed of magnetic stirrer for both types of electrolytes. The mass output rate of  $\text{CuO}$  nanoparticles increased with the increase in the speed of rotation, and, after an optimum speed, it started decreasing. However, the size of the particles reduced with the increase of the rotation speed. The crystal plane of the obtained  $\text{CuO}$  nanoparticles was similar for both the electrolytes whereas the yield of nanoparticles was higher in  $\text{KOH}$  as compared with  $\text{NaOH}$  under the same experiment conditions. In this set of experiments, the maximum output rates obtained were  $21.66 \text{ mg h}^{-1}$  for  $\text{NaOH}$  and  $24.66 \text{ mg h}^{-1}$  for  $\text{KOH}$  at 200 rpm for a single discharge arrangement<sup>[91]</sup>.

(In 2017 Thirumamagal R<sup>1</sup>,et.al)  $\text{Ni}$ ,  $\text{Fe}$  and  $\text{Co}$  nanoparticles are synthesized by chemical route using leaf extraction. Structural, biological morphological and magnetic properties were investigated. X ray pattern shows a polycrystalline structure of samples. Diffraction planes of (200),

(122) and (200)-oriented crystal structures were revealed by X-ray pattern for NiO, Fe<sub>2</sub>O<sub>3</sub> and CoO respectively. Hexagonal, orthorhombic and cubic crystal structures have been revealed respectively for NiO Fe<sub>2</sub>O<sub>3</sub> and CoO nanoparticles. Microscopic structure has been detected by using of Scanning Electron Microscopy<sup>[92]</sup>.

(Mansour Faraj and Mohamed Erhayem in 2018), were study Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm of equilibrium sorption of Methylene Blue from Aqueous Solution onto Mulberry tree (*Morus nigra* L) roots powder. The effects of different parameters on adsorption processes were investigated. The maximum adsorption capacity,  $q_{\max}$ , was found to be 32.63 mg/g at 45°C. Among the all isotherms tested in this study, Langmuir isotherm model gave the best fit with  $R^2$  and Chi square The adsorption process was found to be physisorption process due to the calculated mean energy of adsorption calculated form Dubunin- Radushkevich (D-R) isotherm model ranged from 1.24 to 1.71 KJ/mol. This study demonstrates that MNLRP could be used to remove MB dyes from aqueous solutions<sup>[93]</sup>.

In 2019, S. Dey and G.C. Dhal ware used cobalt nanoparticles for low-temperature oxidation of carbon monoxide. Cobalt oxide catalysts has shown a great potential for CO oxidation catalyst in a catalytic converter for their high thermal stability and tailoring flexibility. Supported cobalt oxide nanoparticles have been synthesized over different supports at subsequent heat treatment. The cobalt oxides (Co<sub>3</sub>O<sub>4</sub> and Co O) can be well dispersed over supporting materials such as gamma-alumina and other covalent frameworks with average particle sizes below 5 nm. The cobalt oxide catalysts usually refer to particles of cobalt (2 and 3) oxide in nanometer size, with various shapes and crystal structures. In cobalt oxide catalyst presence of Co<sub>3</sub>/Co<sub>2</sub> redox couple with

oxygen vacancy formation. Under steady-state conditions, the  $\text{Co}_3\text{O}_4$  surface appeared with oxidized  $\text{Co}_2$  species. Activity order of CO oxidation over various cobalt nanoparticles was observed as follows: nanoplates > nanorods > nanocubes > nanosphere.<sup>[94]</sup>

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 ( $\text{C}_2\text{H}_2$ ) 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 thermo-gravimetric analysis.<sup>[95]</sup>

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.<sup>[96] [97]</sup>

Co-precipitation method was used to synthesize deoxyribonucleic acid (DNA) capped CuO-NiO bimetallic Nano-composite by Sona G. Krishnan and co-workers<sup>[98]</sup>. The morphology and structure related properties of the samples were analyzed using Energy Dispersive X-Ray Analysis, X-Ray Diffraction, Transmission Electron Microscopy and Scanning Electron Microscopy. Widely used Agar well diffusion method evaluated the antimicrobial activity of the sample. DPPH and FRAP assays were applied to test the antioxidant activity of the sample. Average crystallite size of 16.218 nm NiO and 15.871 nm CuO were confirmed

within CuO- NiO bimetallic oxide nanoparticles by means of XRD technique. EDAX studies confirmed the purity of the sample. The grain size obtained from TEM studies matches with the XRD results.

### **1.11. Aim of Study**

1. Preparation and characterization of ZnO,Co<sub>3</sub>O<sub>4</sub> and CuO nanoparticles using chemical precipitation method and their binary composite with graphite, nanographite and oxidized nanographite.
2. Preparation of oxidized nanographite by acidic oxidation method.
3. Determining the ideal condition for the adsorption of methyl orange dye (contact time, quantity of adsorbent, temperature).
4. Thermodynamic studies of adsorption processes of methyl orange dye on these adsorbents.
5. Investigate the kinetic studies of adsorption process.