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تحضير الاكاسيد الفلزية النانوية بأستخدام طرق مختلفة و مقارنة خواصها في أزالة الكبريت من النفط الخام

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Chapter One

Introduction

1.1 Introduction**Nanotechnology and Nano Science**

The term "nanotechnology" describes the synthesis or use of particles with dimension that fall under the nanometer range, or one billionth of a meter ^[1]. Due to its enormous potential and significant economic impact, it is currently one of the most important study areas in many countries ^[2]. A nanoparticle is a very small particle having a size between 1 and 100 nm that enable materials to exhibit particular photonic, electrical, catalytic, and medicinal properties ^[3].

The application potential of nanomaterials (NMs), which have at least one structural dimension at the nanoscale (one nanometer is one billionth of a meter), has attracted study interest. It should be noted that the typical nanomaterial structures should fall between single atoms and bulk materials. Consequently, NMs typically display distinctive and greatly improved, though occasionally surprising, features such as chemical, physical, and biological ones that differ from those of their bulk materials. Today's researchers can fabricate a wide range of materials at the nanoscale ^[3]. Therefore, the simplest definition of nanotechnology is "technology on the Nano scale," which is a scale comprising 1-100 nm ^[4].

Nanotechnology is the ability to use matter at the nanoscale for observation, control, manipulation, measurement, and manufacturing purposes. The National Nanotechnology Initiative in the United States defines nanotechnology as “a engineering, science, and technology conducted at the nanoscale, where unique phenomena enable novel applications in a wide range of fields, from chemistry, biology and physics to medicine, engineering and electronics.” According to this definition, nanotechnology needs to meet two requirements. The first problem has to do with novelty: because it operates at the nanoscale. Using a single atom or

molecule to product a functioning structure The second is a scale issue: Nanotechnology is concerned with using structures by regulating their size and shape at the nanoscale ^[5].

1.2 Methods for Metal Oxides Nanoparticles Synthesis

Nanotechnology should be widely accepted since nanoscience includes the development of safe, environmentally acceptable nanoparticles. Shape, size, physicochemical qualities, and morphology all have a significant impact on the morphology of integrated particles when solvents are used to reduce nanoparticles (NPs) ^[6].

There are generally two different approaches for synthesis nanomaterials :

1-A bottom-up approach that includes miniaturization of materials components up to atomic level with further self-assembly process (physical forces operating at the nanoscale are used to combine basic units into larger stable structures) leading to the formation of nanostructures. This approach organizes atomic or molecular components in hierarchical nanocomplexes. Such examples is nanoparticles formed from colloidal dispersion.

2-Top-down approach rather initiate with macroscopic structures, controlling externally the process of formation of nanostructures. The top-down approach adds or removes thin layers of bulk materials as do ball milling, mask etching, etc ^[7].

1.2.1 Green Synthesis of Metal Oxide Nanoparticles

Green synthesis is a method that uses organisms like Plants, Bacteria, Fungi, and Yeast to synthesize nanoparticles. This approach limits the use of expensive and harmful chemicals and has applications in the biomedical field. It is also more economical, more catalytic, and environmentally benign. Natural strains and plant

extracts both release certain phytochemicals that function as stabilizing or capping agents and reducing agents ^[8]. By enabling the synthesis of NPs at low pressure, temperature, and pH at a substantially cheaper cost, the biological synthesis of NPs avoids many of the negative characteristics. Eco-friendly bio-organisms found in plant extract include protein treating as a capping agent and reducing agent. Plant extract can be employed for the manufacture of shape-controlled and stable nanoparticles. Plants' blossoms and leaves, which are examples of plant components, can be used to synthesize nanoparticles ^[9].

1.2.1.1 Green Synthesis of Metal Oxide NPs by Plant Extracts

One of the most significant environmentally friendly techniques for synthesis various types of nanoparticles is the use of plant extracts. Through the use of plant extracts can be convert metal ions into nanoparticles in a single step. The extract is simply combined with a solution of the metal salt in this method at room temperature. Within minutes, at normal temperature and pressure, this biogenic transition from a metal ion to a metal nanoparticle can be easily carried out, very quickly, and on a large scale, so it is environmentally safe. Plant metabolites that are water soluble such as terpenoids, phenolic compounds and alkaloids are among the reducing agents of metal ions. (Mittal ,et.al.2013), Succeeded to synthesize nanoparticles using extracts from a wide variety of plant species ^[10]. Using aqueous extracts of various plant parts, several publications have been produced on the biosynthesis of nanoparticles (Au, Ag, ZnO, Fe, etc.) ^[11] ,^[12]. The FeNPs were synthesized via a single step green route using aqueous leaves extract of *Plumeria obtusa* as a capping/reducing and stabilizing agents ^[13]. (Shekhawat, et.al, 2013), reported a synthesis silver nanoparticles Ag NPs from the aqueous extracts of leaves, flower petals and fruit pulp of *Couroupita guianensis* Aubl. Because it is a one-step process, nonpathogenic, economical, produces a significant quantity of

metabolites, non-cost, effective and an environmentally benign method, using plant extracts of NPs synthesis offers more advantages than utilizing microbes^[14].figure 1.1

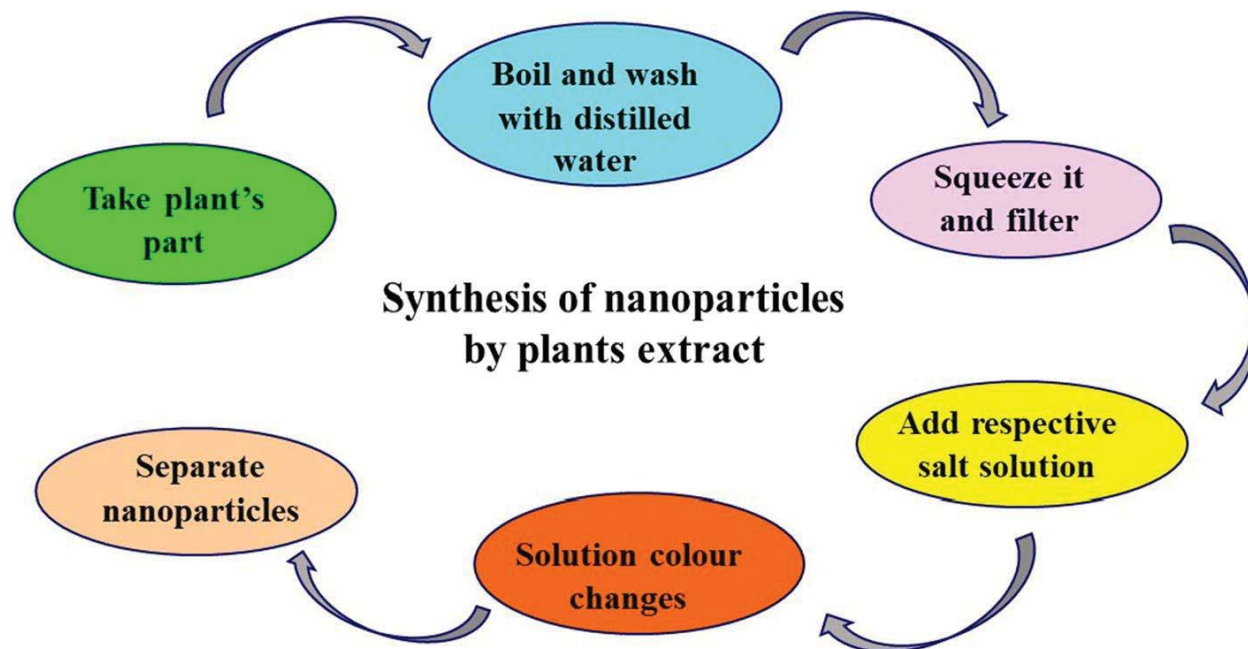


Fig.1.1 Synthesis of nanoparticles via biological and physicochemical approach^[15].

1.2.1.2 Green Synthesis of Metal Oxide NPs by Bacteria Source

NPs synthesis using bacteria is a green approach. When compared to other environmentally friendly methods, it has a number of defects, including the lengthy process of microbe examination, the lack of control over NP size and shape, the need for careful monitoring of culture broth throughout the entire process, and the high cost of the media used to cultivate bacteria. (B. licheniformis et.al.2014) reported a novel, simple and cost effective approach to prepare nanosized ZnO flowers at ambient laboratory temperature, and ZnO nanoflowers has been developed by incubating bacterial biomass of B. licheniformis with Zinc precursors^[8].

Ag nanoparticles were synthesized using bacterial exopolysaccharide as a reducing and stabilizing agent ^[16]. Also, Iron oxide nanoparticles were synthesized by the *Proteus vulgaris* ATCC-29905, which it showed good antibacterial activity and also showed good activity against methicillin resistant staphylococcus aureus ^[17].

1.2.1.3 Green Synthesis of Metal Oxide NPs by Fungus Source

It frequently serves as a sustainable and green precursor for the green producing of metal oxide nanoparticles. The fungus's extracellular synthesis of NPs is extremely beneficial because to its large-scale production, commercial viability, and simple downstream processing. Because of their superior tolerance and ability to bioaccumulate metals, fungi are preferred to bacteria. *Aspergillus fumigatus* mycelia were used to make ZnO NPs. DLS analysis showed that NPs ranged in size from 1.2 to 6.8, with an average size of 3.8. After 90 days, the particles formed an agglomerate with an average size of 100 nm, suggesting that the formed NPs were stable for 90 days even though their size was greater than 100 nm during that time. NPs produced from Trichocomaceae family member *Aspergillus terreus*. Primary alcohol, primary or secondary amine, amide, and aromatic nitro compounds were found in the NPs formed, according to FTIR studies. The synthesis of NPs from fungal strains has frequently used *Aspergillus* species, which in the majority of cases produced spherical-shaped NPs ^[8]. Iron oxide nanoparticles were synthesized using manglicolous fungi isolated from soil sample of Indian Sundarbans ^[18].

1.2.2 Chemical Methods

1.2.2.1 Chemical Precipitation is the process of turning a liquid into a solid by adding chemical agents, supersaturating the liquid, and then separating the precipitates from the liquid. ZnO and ZnS nanoparticles can be made using this

technique. Since it only requires one step and the production of pure nanoparticles on a large scale. It is a very helpful technique that even aids in water purification and offers a long-term solution or results that produces permanent results ^[19]. This method uses an arrested precipitation mechanism to control the size of the nanoparticles. The fundamental difficulty was to synthesize and study the nanomaterial in the same liquid medium without allowing any physical alterations or the accumulation of minute crystallites. The synthesis required a reaction between the component parts in an appropriate solvent. The parent solution is first mixed with the dopant before the precipitation reaction. To keep the generated particles apart by surfactant. The nanocrystals separated by centrifugation then cleaned with deionized water and dried ^[20].

1.2.2.2 Sol-gel Method is the most straightforward method that enables systematic monitoring of reaction parameters to regulate the morphology particle size ^[21]. It is a wet-chemical process containing a chemical solution acting as a precursor for an integrated system of discrete particles. It includes from two solutions as sol – a colloidal solution of solids suspended in a liquid phase and the gel – a solid macromolecule submerged in a solvent. Sol-gel is the most preferred bottom-up method due to its simplicity and as most of the nanoparticles can be synthesized from this method. Metal oxides and chlorides are the typically used precursors in sol-gel process. The precursor is then dispersed in a host liquid either by shaking, stirring or sonication and the resultant system contains a liquid and a solid phase. A phase separation is carried out to recover the nanoparticles by various methods such as sedimentation, filtration and centrifugation and the moisture is further removed by drying ^[22].

1.2.2.3 Thermal decomposition A chemical process in which metal precursor when heated above its decomposition temperature in high boiling solvent is known as thermal decomposition. Usually, use of an aqueous and volatile solvent for metal oxide preparation suffers from agglomeration and poor crystallinity. Metal oxide nanoparticles obtained by thermal decomposition do not need post-synthesis thermal treatment and these nanoparticles are high monocrystalline. Along with monocrystalline nature, particles are monodisperse in size and shape. Nucleation and growth rate of metal oxide formation by thermal decomposition is very well understood and has shown a good control over particle size and shape by slight changes in the reaction parameters. Most of the metal oxide nanoparticles synthesized by this method uses organometallic precursors dissolved in an organic solvent and a surface stabilizing agent at a high temperature in an inert environment as MnO and NiO [23].

1.3 Iron Oxide Nanoparticle (Fe₂O₃ NPs)

The element iron is one that can exist in a variety of forms, from zero to three valence. Additionally, every iron compound has a unique set of properties, ranging from magnetic to ferromagnetic. Iron oxides classified as magnetic NPs include Magnetite (Fe₃O₄), Maghemite (γ -Fe₂O₃), Hematite (α -Fe₂O₃), and Goethite (FeO(OH)) [24].

Nanoparticles synthesized from α -Fe₂O₃ can be produced in an environmentally friendly and cost-effective manner. Simple, quick, affordable, and environmentally friendly are just a few benefits of NPs. Iron oxide nanoparticles come in three main varieties: FeO, Fe₂O₃, and Fe₃O₄. They are significant materials because of their catalytic abilities, biocompatibility, environmental friendliness, nontoxicity, and affordability. Hematite (α -Fe₂O₃), β -Fe₂O₃, maghemite (γ -Fe₂O₃) and ϵ -Fe₂O₃ are the four ferric oxide phases that make up the crystallographic structure of Fe₂O₃. In

nature, hematite is abundant and can be found in soils, sediments, and aquatic systems. The most stable iron oxide in an ambient environment is Fe_2O_3 , which has undergone extensive research due to its wide range of potential applications. Iron oxide nanoparticles in their firmly stable form, hematite ($\alpha\text{-Fe}_2\text{O}_3$), typically exist in rhombohedral crystal units with n-type semiconducting properties (the optical band gap is 2.1 eV) ^[25]. Hematite is anti-ferromagnetic and exhibits canting ferromagnetic responses at room temperature. Furthermore, it has a complicated defect structure that includes defect species like oxygen vacancies and iron (Fe^{2+}) interstitials ^[25]. ferrous oxide Nanoparticles can be production chemically using techniques like chemical precipitation, sol-gel, micro emulsion, hydrothermal technique, sonochemical technique, and electrochemical technique ^[26] .

1.4 Nickel Oxide Nanoparticles

A II-VI composite semiconductor called nickel oxide nanoparticles is built of nickel (group II) and oxygen (group VI) from the periodic table of naturally occurring elements. NiO is a P-type semiconductor transition metal oxide with straight band gaps of 3.5–3.8 eV and can exhibit super-paramagnetic and super-antiferromagnetic properties. NiO is extremely durable^[27]. Due to its homogeneous mixing, improved crystallinity, uniform particle distribution, and reduced particle size, sol-gel is an effective technique for synthesizing NiO nanoparticles. Particle size will be considerably influenced by different calcination temperatures. NiO nanoparticles have been calcined at a number of different temperatures, including 673 K, 723K, 773K, 823K, and 873K. The reaction rate and final phases are greatly influenced by the nickel nitrate/alcohol molar ratio^[28]. Numerous techniques, including chemical or physical ones like the co-precipitation, sol-gel, and solvothermal procedures, have been used to synthesize the NiO NPs ^[29].

1.5 Multi Metal Oxide Nanoparticles

One of the most recent developments in metal oxide nanotechnology is the development of nanostructured oxides that include two or more different metals. These nanoparticles are known as multi-oxide nanoparticles. It possesses special features including electrical, optical, magnetic and other physicochemical properties. Multi-metal oxide nanoparticles, such as Zn_xMg_xO and Ag/Fe_3O_4 nanocomposites, have demonstrated promising remedies for a number of issues that are present in pure metal oxide nanoparticles, such as excessive cytotoxicity or agglomeration. Three different synthesis techniques, such as chemical vapor synthesis, metal combustion, smoke $ZnMgO$, and irregular nanorods (sol-gel $ZnMgO$), were used to synthesize nano ($ZnMgO$) in these three different forms ^[30].

$NiCo_2O_4$, $NiMn_2O_4$, $ZnCo_2O_4$, and $ZnMn_2O_4$ are the four different types of spinel oxide nanocrystals that were synthesized using a straightforward and scalable procedure. This made it possible to conduct a thorough investigation into how transition metals affected how well electro catalysts for the oxygen reduction reaction (ORR) performed. The morphology and electro catalytic properties of the materials toward the ORR were examined in relation to the effects of the presence of various metals in the spinel oxide. Spinel-structured mixed-valence transition-metal oxides were discovered to be effective ORR catalysts under alkaline conditions. Spinel oxides based on cobalt have advantages such as high activity, low cost, easy preparation, and stability ^[31]. According to Shriram S. Sonawane and other researchers, combining Fe_2O_3 and NiO NP increases hydrogen recovery from complex distillery effluent by (1.2–4.5) orders of magnitude as compared to employing either one alone. The increase in hydrogen generation depends on ferredoxin, hydrogenase enzymes, oxidoreductase, and ferredoxin ^[32].

1.6 Applications of Iron, Nickel and Multi Metal Oxides Nanoparticles

1.6.1 Application of Iron Oxide Nanoparticles

Due to their disparate properties, iron oxide NPs were employed as covert carriers to deliver anti-retroviral medications to a latent form of HIV while documenting the localization of drugs [33]. α -Fe₂O₃ NPs have been used to synthesize virus-like particles in addition to bacteria antigens, demonstrating their exceptional utility as vaccines, gene-carrying nano containers, contrast agents for magnetic resonance imaging, and drug delivery vectors [34]. α -Fe₂O₃ hexagonal nanoparticles was synthesized via simple solution methods and applied as photocatalyst for the photocatalytic degradation of hazardous dye of Rhodamine B and as efficient electron mediator [35]. IONPs have many applications such as Biological activity , Electric activity because Hematite is an n-type semiconductor with an energy band gap in the range 2.1–2.3 eV where the conduction band is composed of empty d-orbitals of Fe³⁺ and the valence band consists of occupied 3d crystal field orbitals of Fe³⁺ with some mixture from the oxygen 2p non-bonding orbitals and Purification and aquatic environment treatment like Cu²⁺ , Pb²⁺ , Zn²⁺ , and Ni²⁺ [36]. The Anacardium occidentale leaf extract used to make the hematite nanoparticles. The biosynthesized nanoparticles could effectively degrade hazardous pollutants including methyl red and eosin yellowish within a short span [37]. The leaf extract contents in Bridelia retusa were employed as a reductant to fabricate α -Fe₂O₃NPs from FeSO₄.The catalytic activity of the nanoparticles was put to test by attempting to degrade crystal violet dye, which was completely achieved in 270 min [38].

1.6.2 Application of Nickel Oxide Nanoparticles

Nickel oxide nanoparticles are of great interest because they are a relatively inexpensive, non-toxic, and eco-friendly material. Many different applications,

including transparent conductive, chemical sensors, and resistive random access memory, make use of this material. Additionally, it is a well-researched material for use as a positive electrode in batteries and as a hole transport layer in quantum dot light emitting devices^[39]. NiO NPs were synthesized via solution combustion method using $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Additionally, to exhibiting excellent photo catalytic degradation activity against trypan blue-dye, the NiO NPs also demonstrated antibacterial properties against *P. aeruginosa*. Also, it has been demonstrated to be a good anode material and sensor^[40]. Nickel oxide has been extensively researched for super capacitors with excellent electrochemical performance as a competitive material of low cost and thus, economic benefit due to its attractive properties such as low cost and environment-friendly characteristics. Because pure NiO material has a relatively low electronic conductivity, which prevents electron transmission during electrochemical reactions and reduces the electroactive area, leading to inferior capacity characteristics, nickel oxide is the candidate material of choice for potential application in electrochemical capacitors^[41].

The biological properties of the biosynthesized nickel oxide nanoparticles from *E. heterophylla*, including blood compatibility assay, antibacterial activity, and cytotoxicity, were examined; as a result, the NiO nanoparticles are prepared to assist in the development of antibacterial activities and anticorrosive applications^[42]. Uses for the NiO NPs include transparent conducting layers, smart windows, gas sensors, optical fibers, and electrochromic devices^[43].

1.6.3 Applications of Multi Metal Oxides Nanoparticles

Wet-chemical methods have been used to prepare $\alpha\text{-Fe}_2\text{O}_3$ and NiO nanoparticles as well as nanocomposites of Fe/Ni oxide with various molar concentrations of nickel. The bacterial efficiency of the prepared Accepted samples were tested against pathogenic strains of *B. subtilis*, *S. aureus*, *E. coli* and *S. typhi* two distinct

methods. The Fe/Ni oxide nanocomposites have shown intensified antibacterial activity against all the exposed bacterial strains in comparison to the pure samples of α - Fe_2O_3 nanoparticles^[44]. (Raphael Neubauer, et al), studied the adsorption kinetics of a jet-A1 fuel enriched with benzothiophene, dibenzothiophene, and 4,6-dimethyldibenzothiophene was studied for Ag- Al_2O_3 . The adsorption of aromatic sulfur heterocycles on Ag- Al_2O_3 proceeds via three different adsorption mechanisms. Within these mechanisms the π -interaction (π -Ag) and the direct sulfur-silver interaction (S-Ag) are significantly stronger in comparison to the acid base interaction (S-H). The results showed that the π -Ag and S-Ag interactions are the major adsorption mechanisms in the first stage, where film-diffusion limits the adsorption rate. In the second stage, the S-H interaction plays only an important role for BT, where intraparticle diffusion is the rate controlling step. The S-H contribution was related to incorporation of silver into blank - alumina, which significantly increased the overall acidity of the adsorbent^[45].

A hydrothermal method was used to synthesize multi-metal co-doped MgFe_2O_4 nanoparticles from saprolite laterite ore that had a high specific surface area and medium netic property. When used as a heterogeneous photon-Fenton-like catalyst to break down rhodamine B, the coped MgFe_2O_4 catalyst demonstrated good recycling performance and stability^[46].

1.7 Sulfur Compounds in Crude Oil

Crude oil is a complex mixture of hydrocarbons that is found in nature^[47]. The largest and broadest source of energy in the world, crude oil is used to produce fuels for vehicles like gasoline, jet fuel, and diesel. Both organic and inorganic sulfur compounds are present. One of the most significant variables affecting the price of crude oil is the amount of sulfur. The various sulfur compounds found in

crude oil can be grouped into the following four broad groups: thiophenes, mercaptanes, sulfides, and disulfides. Because they can cause environmental pollution and the deactivation of the catalyst, sulfur compounds in the refining process are undesirable. The combustion of petroleum-derived fuels in an internal combustion engine of a motor vehicle releases significant amounts of sulfur oxides to the atmosphere. The air pollution due to SO_x causes ozone layer depletion, reduces soil fertility, and also acid rain. According to the survey of the World Health Organization (WHO), because air pollution, every year, around 3 million people die prematurely. Besides, the presence of sulfur compounds in petroleum products causes corrosion problems in petroleum refinery equipment and also poisons downstream catalysts. There is a tremendous incentive to minimize sulfur in fuels now because of strict environmental restrictions. Most nations have implemented new regulations requiring the use of low-sulfur petroleum fractions in order to reduce air pollution caused by the combustion of heavy petroleum fractions^{[48][49]}.

After carbon, hydrogen, and oxygen, sulfur is the element that is most plentiful in oil as a result of the biodegradation of the tissues of more seasoned organisms. (Orr et al), (2001) pointed out that two types of sulfur-based oil classifications sweet if the sulfur level is less than 0.5%wt and Sour (acid) if the sulfur content is greater than 0.5%wt —are used to determine whether an oil is sulfur-based. According to the results obtained, the sulfur content of midland oil company reservoir in BAGHDAD-Bob- Al-Sham- behind Al-Quds Electric Thermal Station is 4.8%wt, which is Sour(acidic)^[50].

1.8 Adsorption

Adsorption is the physical or chemical association of substance molecules on the active sites of a surface, either by the weak van der Waals force or by forming chemical bonds with the surface's active sites. Alternatively said, it is a phenomena that causes molecules, atoms, or ions of gas or liquid to accumulate on the surface of another solid substance^[51]. Adsorbate and adsorbent are two terms frequently used to describe the adsorption process. In the adsorption process, adsorbents are substances with a surface that may take in other compounds · Charcoal, Silica gel, and porous clays are examples of adsorbents, while an adsorbate is a substance that is absorbed on the surface of other substances during the adsorption process ^[52].

The basic steps that lead to adsorption from a solution by a porous surface are as follows: 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. 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 ^[53].

1.8.1 Types of Adsorption

Adsorption can be categorized into two types based on the type of force that exists between the molecules of the adsorbate and the adsorbent:

1.8.1.1 Chemical Adsorption is called chemisorption or chemical adsorption.

In this type, hydrogen bonds are formed between the surface and the molecules , atoms or ions that adsorb on the surface. The chemical adsorption consists of a single layer of adsorbent adsorption on the surface of the adsorbent which needs energizing energy (Activation Energy). The adsorption is quick , low and the

reaction is often irreversible and sometimes has strong chemical bonds. Since it is carried out on adsorption sites that are naturally low-energy, it also has a location (localized). The adsorbent requires chemical adsorption to a constant activation energy relative to the homogeneous surface and variable in relation to the heterogeneous surface ^[51].

1.8.1.2 Physical Adsorption is called natural adsorption or physical adsorption. This adsorption is also called Vander Waals adsorption. Physical adsorption is non-specific because the atom or molecule is interaction by force of Vander Waals with any atoms on the surface. The occupied area depends on the size of the atoms, molecules or evaporated ions, and the heat of physical adsorption is low. This type of adsorption also incorporates many layers on the surface. Since physical adsorption is an inverse process, it doesn't need activation energy. Because the atoms, molecules, and ions that adsorb on the surface can move within a particular surface area, this is not nonlocalized ^[51].

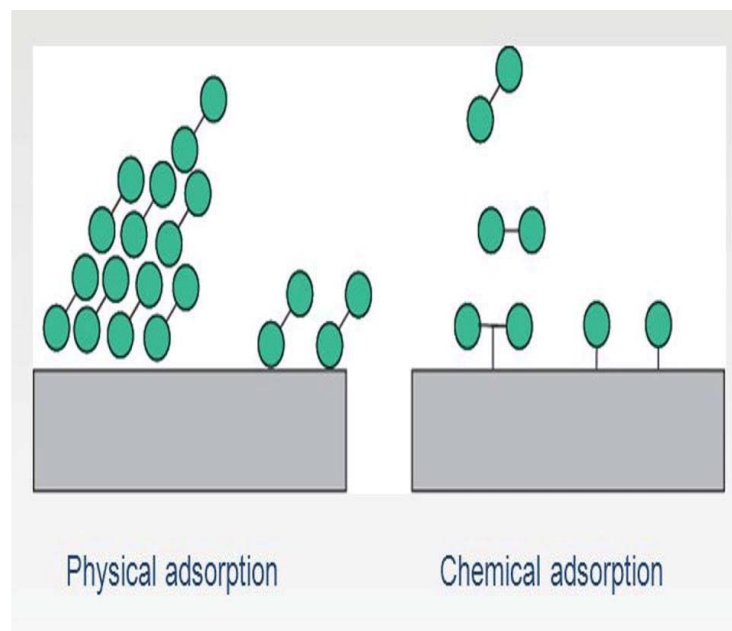


Figure 1.2 Illustration type of adsorption (a) Physical adsorption and (b) Chemical adsorption

1.8.2 Factors Influencing Adsorption Processes

The main factors that affect the percentage of adsorption are:

1.8.2.1 Contact Time

One of the most important variables in the batch adsorption process is contact time. It is the period of time during which the adsorption process is complete and reach equilibrium at 298 K. Adsorption of heavy metal (Cr (VI) from wastewater using magnetite NP_s. Time of adsorption is changed from 20 to 120 min, efficiency first decreased 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^[54].

1.8.2.2 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 . Because there is a lot of lead ion, it might sometimes be seen to be more intense than cadmium ion under certain conditions. The amount of the adsorbate is decreased by increasing its solubility in the solvent, which also affects the adsorption process ^[51].

1.9.2.3 Effect of temperature

The influence of temperature on adsorption is generally related to the thermodynamic nature of the adsorption process, and some parameters, such as enthalpy change (ΔH), free energy change (ΔG), and entropy (ΔS), which are evaluated from thermodynamic equations. ΔG and ΔH can be an auxiliary explanation of adsorption behavior by evaluating the isotherm data . Positive ΔH and negative ΔG in most adsorption of heavy metals by carbon materials, indicating that the adsorption process are spontaneous, and the adsorption capacity

would increase with increasing temperature in certain range . For instance, Mohan et al. confirmed the adsorption of Pb (II) by MgO-loaded graphene oxide at 293 is lower than the state at 303K . However, Hadavifar et al. found that Hg(II) adsorption onto MWCNTs-SH was more efficient at lower temperatures with the negative ΔG° and negative ΔH ; therefore, the adsorption process of one carbon-based material also could be exothermic reaction. Furthermore, Peng et al. believed that temperature can cause changes in solubility and intermolecular interactions, and it might be the reason of the temperature influencing the adsorption processes [55].

1.9 Adsorption Isotherm

Adsorption is usually described through isotherms, that is, functions which connect the amount of material absorbed on a surface and the equilibrium concentration of the substance absorbed in the solution at a constant temperature. It can also be defined as a description of the relationship between the amount of adsorbate on the surface of adsorbent and the initial concentration of the solution at a constant temperature [51]. Adsorption isotherms include the Langmuir, Freundlich, Redlich-Peterson, and Timken..etc. The adsorption data were analyzed using Freundlich (Freundlich 1906) and Langmuir models (Langmuir 1918) .

1.9.1 Langmuir Isotherm

It is the most widely used model in water treatment and one of the earliest empirical models to represent adsorption isotherms

The formulation is based on four premises: monolayer adsorption, adsorption only takes place at a finite number of sites, equal adsorption at all sites, and no interaction between adsorbed solutes. The Langmuir isotherm equation can be written as follows :

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

Where:

q_e (mg/g) refers to concentration of adsorbate at equilibrium. q_{max} (mg/g) is the maximum monolayer on the adsorbent. K_L (L/mg) is the Langmuir isotherm constant and C_e (mg/L) is the equilibrium concentration. The linear plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e). The constants K_L 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^[56].

1.9.2 Temkin Isotherm

Temkin isotherm model takes into account the effects of indirect adsorbate/adsorbate interactions on the adsorption process. It also assumes that as surface coverage increases, all molecules in the layer's layer experience a linear drop in the heat of adsorption (ΔH_{ads}). The Temkin isotherm is valid only for an intermediate range of ion concentrations. The linear form of Temkin isotherm model is given by the following :

$$q_e = B_t \ln K_T + B_t \ln C_e \dots(1-2)$$

where

$B_t = RT/b_T$ is Temkin constant which is related to the heat of sorption ($Jmol^{-1}$) and K_T is equilibrium binding constant .

Values of B_t and K_T are obtained from the slope and interception of the plot ^[57].

1.9.3 Freundlich Isotherm

The linear form of the Freundlich isotherm is as follows:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \dots (1-3)$$

Where K_F is adsorption capacity and $1/n$ is adsorption intensity; it also indicates the relative distribution of the energy and the heterogeneity of the adsorbate sites ^[58].

1.9.4. Redlich-Peterson Isotherm

Redlich-Peterson Isotherm is a mix of the Langmuir and Freundlich isotherms. The numerator is from the Langmuir isotherm and has the benefit of approaching the Henry region at infinite dilution. This isotherm model is an empirical isotherm incorporating three parameters. The process of adsorption is consequently a mix and does not adhere to perfect monolayer adsorption since it has components from both the Langmuir and Freundlich equations.

$$\ln C_e/q_e = \beta \ln C_e - \ln A \dots (1-4)$$

where A is Redlich-Peterson isotherm constant (Lg^{-1}), β is exponent that lies between 0 and 1, C_e is equilibrium liquid-phase concentration of the adsorbent (mgL^{-1}), and q_e is equilibrium adsorbate loading on the adsorbent ($mg g^{-1}$). A plot of $\ln(C_e/q_e)$ versus $\ln C_e$ enables the determination of Redlich-Peterson constants, where β is slope and A is intercept. Because of its adaptability, this isotherm model, which represents adsorption equilibrium over a wide range of adsorbate concentration in both homogeneous and heterogeneous systems, has a linear dependence on concentration in the numerator and an exponential function in the denominator ^[57].

1.10 Adsorption Kinetics

Adsorption kinetics describes the paths of reactions as well as the duration it takes to reach equilibrium. It also demonstrates a strong reliance on the adsorbent material's physical and chemical properties, which also affect the adsorption mechanism that can be either film or pore diffusion or due the combination of both depending on the system hydrodynamics ^[59].

The adsorption process has three parts. Adsorbate first undergoes external mass transfer from the bulk solution to the adsorbent's surface, then it diffuses internally to the sorption sites, and finally it actually sorbs. Some models assume that the rate-limiting stage in the adsorption process is sorption, whereas others assume that the rate-limiting step is diffusion. Determining the adsorption mechanism is thus made possible by fitting to the models. The ability to predict the adsorption rate for a given system is perhaps the most crucial factor in the design of an adsorption system. Adsorption mechanisms are best identified by having a thorough understanding of the system's kinetics. Pseudo-first order, pseudo-second order, first order model, and second order models were found to be the most prevalent adsorption kinetics models among the many others ^[60].

1.10.1 Pseudo-First Order Model

The most typical model for the solute adsorption from a liquid solution is the Lagergren pseudo-first order model. Physical forces are causing this adsorption to occur ^[64]. The kinetics rate equation is expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \dots (1 - 5)$$

The kinetic equation rests on five assumptions:

1. Sorption only occurs on localized sites and involves no interaction between the sorbed ions.
2. The energy of adsorption is not dependent on surface coverage.
3. Maximum adsorption corresponds to a saturated monolayer of adsorbates on the adsorbent surface.
4. The concentration of M is considered to be constant.
5. The metal ion uptake on the activated carbons is governed by a first-order rate equation ^[61].

1.10.2 Pseudo-Second Order Model

This model, which successfully approximates the experimental data, states that the adsorption mechanism involves chemical processes ^[62]. The kinetics rate equation is expressed as follows when the removal of an adsorbate from a solution is caused by physical interactions between the two phases.^[63]

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \dots (1 - 6)$$

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 1-8 becomes:

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

The integrated rate law for a pseudo-second order reaction. Equation (1-9) can be rearranged to obtain:

$$q_t = K_2 q_e^2 + \frac{t}{q_e} \dots (1 - 8)$$

Which has a linear form:

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

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

1.11 Characterization of Metal Oxide Nanoparticles

Pure and mixed α -Fe₂O₃, NiO nanoparticles differ from their bulk counterparts in terms of their physical and chemical characteristics because of the high surface-to-volume ratio that leads to an exponential rise in molecular reactivity. Electronic, optical, and chemical qualities are a few of these characteristics. There are different techniques to characterize these properties such as; FESEM, XRD, FTIR, BET, BJH, EDX and DLS [64]. FTIR was used to identify the presence of functional groups in (α -Fe₂O₃, NiO and Multi α -Fe₂O₃/NiO), XRD to analyze crystallinity and compute size, and FESEM to analyze surface shape. Hydrodynamic size is measured by DLS and EDX, agglomerates are detected, and the elemental-chemical composition of nanoparticles is represented [65].

1.11.1 Fourier-Transform Infrared Spectrometry (FTIR)

The infrared portion of the electromagnetic radiation spectrum is located between the visible and microwave ends. It is essentially separated into three primary regions: near IR (14000–4000 cm⁻¹), mid-IR (4000–400 cm⁻¹), and far IR (400–40 cm⁻¹). A method called Fourier transform infrared spectroscopy (FTIR) is based on the measurement of the absorption of electromagnetic radiation with wavelengths in the mid-infrared range. It is an advanced analytical tool and extensively used to investigate the structure of chemical compounds and identify the functional groups such as N-H, O-H, C=O, C-H, C-C, and C-O in the sample by irradiating with IR radiations. It is suitable for measuring all types of samples, including

gases, liquids, and solids. The molecule's radiation absorption and intensity were assessed by IR. If a molecule absorbs IR radiation, the dipole moment is altered in some way, and the molecule becomes IR active^[66,67].

1.11.2 X-Ray Diffraction (XRD)

A typical method for characterizing materials at the nanoscale is powder X-ray diffraction. Crystallite size, phase identification, sample purity, and morphology are just a few examples of the vital data that powder XRD analysis of samples can reveal. These data are complementary to various microscopic and spectroscopic methods. The XRD peaks widen as the size of the crystallite shrinks from bulk to nanoscale dimensions. The morphological and structural details of the investigated nanomaterial can be accessed through X-ray scattering and Bragg diffraction^[68].

The Scherrer equation, which connects the crystalline domain size (D) to the peak's width at half its height (β), quantitatively describes the broadening of a peak at a specific diffraction angle (θ). The Scherrer constant, κ , is typically considered to be 0.91 but can vary with the morphology of the crystalline domains. Depending on the kind of X-rays being used, the X-ray wavelength (λ) is a constant. As long as the sample can roughly be approximated as uniform, spherical particles, each peak can be evaluated independently and should result in a consistent crystalline domain size^[69]. Particle size can be determined, then, from the Scherrer equation;

$$D = \frac{\kappa \cdot \lambda}{\beta \cos \theta} \dots (1-10)$$

Consider a crystal that is composed of parallel ion planes that are separated by a distance d . The conditions for a sharp peak in the intensity of the scattered radiation are

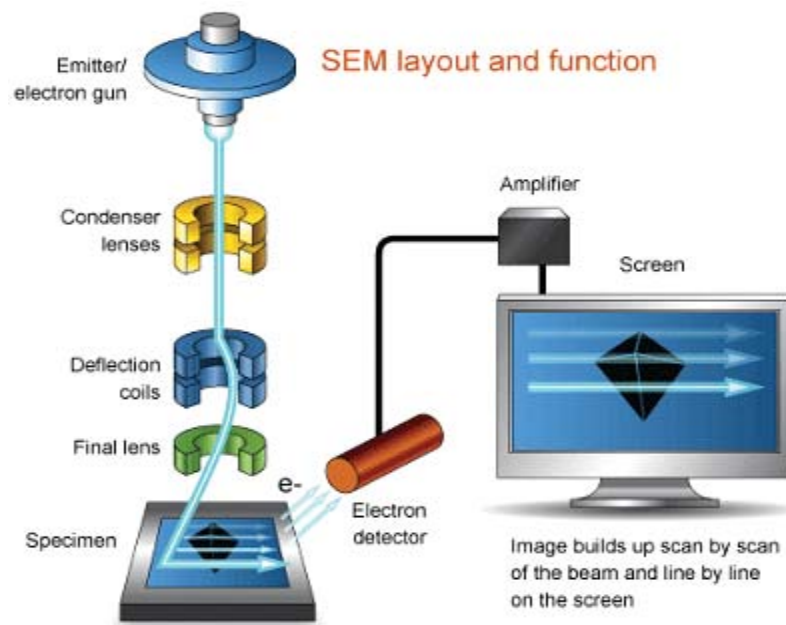
1. That the x-rays should be specularly reflected by the ions in any one plane.

2. That the reflected rays from successive planes should interfere constructively.

The Bragg's law is: $n\lambda = 2d \sin\theta \dots (1-11)$

1.11.3 Scanning Electron Microscope (SEM)

Scanning electron microscopy is a tool widely used for the high-resolution imaging of surfaces that can be employed to characterize nanoscale materials. It uses electrons for imaging. The SEM, which can image with resolutions as low as 1 nm using electrons. SEM is a tool that allows for the visualization of the micro- and nano-scale invisible worlds, and it may be used to perform extensive NPs analysis when in transmission mode. It is a frequently utilized technology for the high-resolution imaging of surfaces that can be used to describe nanoscale materials ^[66]. It can reveal the finer details and complexity that are hidden from view by light microscopy. The process shown below can be used to accomplish all of this (fig1-3) ^[68].



Fig(1- 3) Show all Scanning Electron Microscope (SEM)components^[70].

- A source to generate electrons of high energy between (100-30,000 electron volts) which 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 ^[71] .

1.11.4 Brunauer–Emmett–Teller (BET) Theroy

The Brunauer-Emmett-Teller method is used to characterize materials at the nanoscale. Its developers, Brunauer, Emmett, and Teller, contributed to its name, which is an acronym of their last names. It is based on the idea of a gas physically adhering to a solid surface. It is regarded as an effective, quick, and easy method for calculating the surface area of nanostructures ^[67] .

Despite the shortcomings of its theoretical underpinnings, the Brunauer-Emmett-Teller method is still the most popular method for determining the surface area of porous and finely divided materials. Indeed, under certain carefully controlled conditions, the BET-area of a nonporous, macroporous or a mesoporous solid (i.e., giving a well-defined Type II or a Type IV(a) isotherm) can be regarded as the ‘probe accessible area’ (i.e., the effective area available for the adsorption of the specified adsorptive). The BET method's application involves two steps. To

calculate the BET monolayer capacity, n_m , it is first essential to convert a physisorption isotherm into the "BET plot." The BET-area, a (BET), is determined from n_m in the second stage by using a suitable value for the molecular cross-sectional area, σ . The BET equation is typically applied in its linear form, where n represents the precise quantity adsorbed at the relative pressure p/p° and V_m represents the precise monolayer capacity. The energy of monolayer adsorption is exponentially proportional to the parameter C , per the BET theory. It is now widely acknowledged that the value of C really provides a helpful indication of the isotherm's form in the BET range. The surface area was found out using following equation:

$$\frac{P/P_0}{V(1 - P/P_0)} = \frac{1}{C V_m} + C - \left(\frac{1}{C V_m}\right) \left(\frac{P}{P_0}\right) \dots (1 - 12)$$

P - represents as the equilibrium pressure, P_0 - represents the equilibrium and saturation pressures of the adsorbed gas, P/P_0 - represents the relative pressure, V - denotes volume of adsorbed gas per kg adsorbent, V_m - denotes volume of monolayer adsorbed gas/kg adsorbent, and c - denotes the constant from the heat of adsorption. The BET (N_2 adsorption/desorption isotherm) ^[72], ^[73].

1.11.5 The Barrett, Joyner, and Halenda (BJH)

The Barrett, Joyner, and Halenda (BJH) technique enable the estimation of pore size distribution (PSD) based on physisorption equilibrium isotherms. Two key concepts of the BJH theory are put into practice: first, that pores have a cylindrical form; and second, that the amount of adsorbed material is a combination of physical adsorption on pore walls and capillary condensation in mesopores. The BJH, thus, considers the radius of pore as the sum of the multilayer thickness (t) and the cylindrical radius obtained from the Kelvin equation:

$$\ln P/p_0 = \frac{2\gamma V_M}{rRT} \dots (1 - 13)$$

where P/P_0 is the relative pressure in equilibrium with a cylindrical; γ is the surface tension of the adsorbate in the liquid form; V_M is the molar volume of the liquid; R is the universal gas constant; r is the radius of the meniscus formed in the mesopore ; and T is temperature. The drop in relative pressure in the desorption branch is used by BJH to determine the change in the thickness of the adsorbed film. Each diminution is thought to be caused by the removal of the biggest pores from the capillary condensate and a reduction in the thickness of the physically adsorbed layer. This theory results in a specific equation that, when solved through numerical iteration, correlates pore volume and radius. This technique fails to describe both the micropore diameter and the narrow mesopore due to the BJH's restricted hypothesis ^[73] .

1.11.6 Dynamic Light Scattering (DLS)

One orthogonal and complimentary technique for determining the size of the particles in a sample is DLS. It is a non-destructive, straightforward measurement that works well for detecting particles between 1 nm to 10 μ m. This technique is frequently used to determine the size distribution of samples in the nanometer to micron range, including nanoparticles (emulsions, liposomes) and macromolecules (protein). The Brownian motion theory, which holds that particles in solution move randomly yet continuously, forms the basis for sizing determinations. Smaller particles travel more quickly than larger ones, and the mobility of individual particles is dependent on their size. According to the Stokes-Einstein equation, the velocity due to Brownian motion of a spherical particle suspended in a liquid with a known viscosity at a fixed temperature is inversely proportional to the particle's

diameter. Algorithms can be used to ascertain the particle size distribution of a sample by resolving the equation using the data on particle velocities that have been gathered.

Stokes–Einstein equation:

$$D_h = \frac{k T}{3\pi\eta D_t} \dots (1 - 14)$$

where D_h =hydrodynamic diameter, k =Boltzmann's constant, T =temperature, η =solution viscosity, and D_t =translational diffusion coefficient (velocity of Brownian motion). k , T , and η are known and D_t is measured, solving for D_h .

A cuvette containing the sample is illuminated by a laser, and a detector collects the light that is dispersed by the solution's dissolved particles. Common detector positions are back angle (173°) and right angle (90°) relative to the incident laser [74].

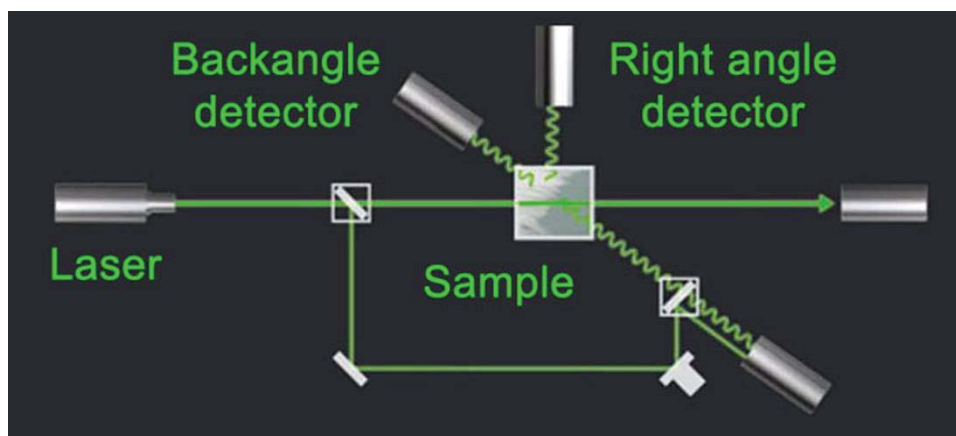


Fig 1.4 A top view of the optical setup for DLS is shown above.

1.11.7 Energy Dispersive X-Ray Spectroscopy (EDX)

Utilizing a scanning electron microscope, EDX spectroscopy is used to identify the elements that make up a sample. Elements with an atomic number higher than boron can be found using EDX and can be found at concentrations of at least 0.1 percent. The use of EDX comprises material assessment and identification, contaminant detection, spot detection analysis of areas up to 10 cm in diameter, quality control screening, and other applications ^[75] .

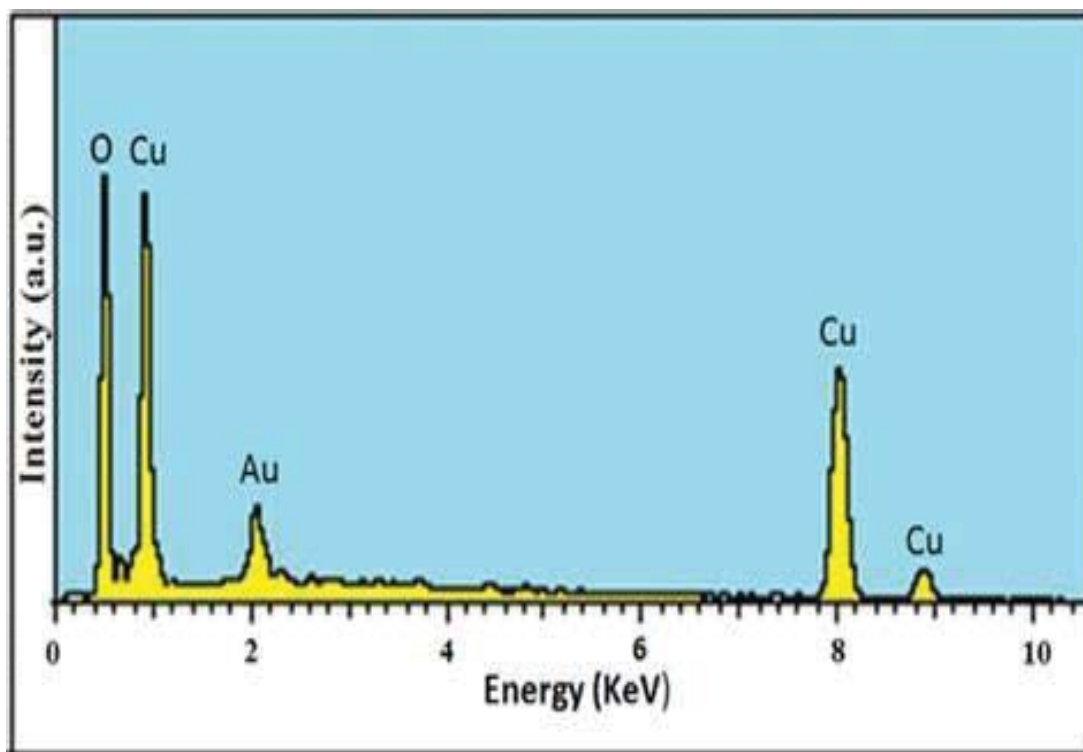


Fig 1. 5 EDX spectra of the CuO samples^[76] .

1.12 Literature Review

According to (Eri Fumoto, et al., 2015), the residual oil was hydrolyzed at atmospheric pressure by an iron oxide catalyst ($\alpha\text{-Fe}_2\text{O}_3$) after heavy oil was desulfurized using water vapor. Hydrogen sulfide was hardly produced during the decomposition without water vapor, but as the water vapor supply increased, more hydrogen sulfide was produced. The cyclic sulfur compound was demonstrated to be degraded by this reaction since this catalyst destroyed dibenzothiophene and produced carbon dioxide and hydrogen sulfide ^[77].

The preparation of iron-oxide nanoparticles in 2016 involved the precipitation method, which used ammonium hydroxide as a stabilizing agent and ferric chloride as a precursor (100,200,300). FTIR, FESEM, and X-ray diffraction were used to characterize it. Hematite's formation as a Fe_2O_3 crystal was revealed by X-ray diffraction. The use of FTIR revealed different particle functional groups and bands of absorption connected to metal oxygen vibration modes. The Fe_2O_3 nanostructures were prepared at 573K for 4 hours, with an average particle size of about 36.22 nm ^[78].

According to U. Kurtan et al. (2016), nickel ferrite nanoparticles were synthesized using the rapid thermo-decomposition method in the presence of oleylamine in solution, which served as a reducing agent, neutralizer, and stabilizer. X-ray powder diffraction (XRD), Fourier Transform Infrared Spectra (FTIR), and Scanning Electron Microscopy (SEM) were used for structural, morphological, spectroscopic characterization of the product. The XRD analysis revealed the formation of single phase nickel ferrite. Both FT-IR and TGA analyses confirmed the formation of desired nanocomposite. Additionally, FT-IR research revealed the distinctive IR absorption bands of the spinel nickel ferrite phase and oleylamine. SEM research revealed that the product's structural shape is

practically spherical. Finally, the synthetic process can be expanded to synthesize high-quality metal or alloy nanoparticles ^[79].

in 2017, reported the synthesis of stable Ni, Fe, and Co nanoparticle oxides utilizing a chemical method and leaf extraction. The properties such as Structural, biological morphological and magnetic properties were investigated. By using an X-ray pattern, the samples' structure was revealed to be polycrystalline. Diffraction planes of (122), (200) and (200)-oriented crystal structures were revealed by X-ray pattern for Fe₂O₃, NiO and CoO respectively. According to EDS analysis, Ni, Fe, and Co are found in amounts of 71%, 78.8%, and 79%, respectively. SEM is used to identify structures in the Ni, Fe, and Co ^[80].

(T. N. Jebakumar Immanuel Edison, et.al, 2018) work aimed at the synthesis of highly ordered nickel oxide nanoparticles that were electrochemically synthesized on nickel foam (NiOx NPs/Ni foam) by the formation and subsequent heat treatment of nickel hydroxide. FT-IR spectroscopy, X-ray diffraction (XRD) with elemental analysis, and field emission scanning electron microscopy were used to characterize the synthesized NiOx NPs (FE-SEM). The XRD results showed the presence of two different oxide phases with high crystallinity. NiOx NPs were found to be highly organized in the detected FE-SEM pictures. With an average size of 7 nm, the FE-SEM image shows spherical morphology. The results of this study show that electro-synthesized NiOx NPs/Ni foam is a very stable battery-type material that is good binder-free and can be used as a positive electrode for hybrid capacitors ^[81].

(Hassan M. Asoufi, 2018) obtained nanoparticles of iron oxide (Hematite, α -Fe₂O₃) by green route from ferrous chloride tetra hydrate (FeCl₂·4H₂O) and

Ailanthus excelsa leaves extract, which act as reducing and stabilizing agent. Biosynthesized $\text{Fe}_2\text{O}_3\text{NP}$ were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV–vis absorption spectroscopy (UV–vis). $\text{Fe}_2\text{O}_3\text{NPs}$ are spherical in shape, crystalline in nature, with average size 40 nm. This research determined the mortality efficacy of synthesized $\alpha\text{-Fe}_2\text{O}_3\text{NPs}$ onto green peach Aphid ^[82].

(K. Lingaraju , et.al, 2019) discuss the primary physical characteristics of nickel oxide nanoparticles (NiO NPs), which were produced for the first time utilizing an aqueous leaf extract of Euphorbia heterophylla. This leaf extract served as a reducing, capping, and stabilizing agent. The analytical techniques such as XRD, UV-Vis, FT-IR, SEM-EDX and TEM were used to confirm the formation of NiO NPs. Antibacterial, cytotoxic, and blood compatibility assay applications were also tested, and the results show that NPs are made up of nanoholes with different pore sizes ^[83].

(Attiya Rehman, et.al, 2019) reported the comparative study of hematite ($\alpha\text{-Fe}_2\text{O}_3$) and its GO nanocomposites $\alpha\text{-Fe}_2\text{O}_3$ (DTPA) @GO and $\alpha\text{-Fe}_2\text{O}_3$ (EDTA) @ GO using different precursor material EDTA and DTPA for better photocatalytic activity. The composites were fabricated by facile wet chemical route co precipitation method. The XRD analysis explained crystallite size up to 5-10 nm and other lattice parameters confirmed crystal structures. SEM confirmed the composite formation and demonstrated that prepared samples have spherical morphologies. The band gap values were calculated for $\alpha\text{-Fe}_2\text{O}_3$ (DTPA) and $\alpha\text{-Fe}_2\text{O}_3$ (EDTA). MB was used as organic contaminant. The photocatalytic action was observed with hematite/GO nanocomposites. The maximum photocatalytic degradation was 86.06% due to $\alpha\text{-Fe}_2\text{O}_3$ (EDTA) @ GO ^[84].

Using Moringa leaf extract as a reducing agent and capping agent, nickel oxide nanoparticles were synthesized in 2020 using a straightforward, environmentally friendly sonication-assisted method. NiO nanoparticles were examined using a variety of techniques, including X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and a UV-vis spectrometer, to determine their structural, morphological, optical, photocatalytic, and antimicrobial properties. The spherical-shaped nanoparticles with a uniform distribution could be clearly seen in the FESEM. NiO nanoparticles' multifunctional uses in photocatalysis, anticorrosiveness, and antimicrobial activity were also examined. NiO nanoparticles' antibacterial effects on *Escherichia coli* and *Staphylococcus aureus* were investigated [85].

In 2020, studied the preparation of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles via a simple and direct hydrothermal method using three different precursors (iron chloride, iron nitrate and iron sulphate). The FT-IR(Fourier transform infrared spectroscopy), X-ray Diffractometer (XRD), and SEM (Scanning electron microscopy) were used to characterize the rod-shaped hematite nanoparticles produced by chemical synthesis. Iron of oxide nanoparticles were tested for their ability to The catalytic activity on the thermal decomposition of nitrocellulose. Finally, Fe_2O_3 prepared using iron chloride as a precursor may be safely used as an efficient catalyst for nitrocellulose [86].

(Shwetha U R, et.al, 2021) prepared nickel oxide using *Areca catechu* leaf extract via a solution combustion method. The production was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-Visible spectroscopy (UV-Vis). NiO NPs have shown potential antidiabetic and anticancer properties [87].

1.13 Aims of Study

1-Preparation of α -Fe₂O₃ and NiO nanoparticles using green and chemical methods .

2-Preparation of multi α -Fe₂O₃ /NiO nanoparticles with ratio 1:1 using green and chemical methods.

3- Adsorption of sulfur compounds from crude oil by prepared pure and multi metal oxides nanoparticles.

4- Study the kinetic of adsorption process of sulfur components on these adsorbents.

5- Study the thermodynamic functions of adsorption processes of sulfur components on these adsorbents.

6- Determining the best adsorption isotherms for the adsorption of sulfur compounds on prepared adsorbents such as (Langmuir, Temkin, Freundlich, and Redlich-Peterson).