وزارة التعليم العالي والبحث العلمي
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كلية العلوم

تحضير وتشخيص بعض الاكاسيد النانوية واستخدامها لازالة العناصر الثقيلة من مياه المخلفات الصناعية

رسالة مقدمة الى مجلس كلية العلوم- جامعة ديالى وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قبل الطالبة
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1.1: Introduction

Environment means surrounding and everything that affects an organism during its lifetime or it is sum total of water, air and land inter relationships and also their relationship with the human being, other living organisms and property. It involves all the physical and biological surrounding and their interactions [1]. So, pollutants entrance to a natural environment leads to disorder, instability, damage or discomfort of the ecosystem i.e. physical systems or living organisms known as the environmental pollution [2].

There are many types of environmental pollution such as water pollution, light pollution, air pollution, noise pollution, soil pollution, thermal pollution, radiation pollution, and the agents which cause environmental pollution known as pollutants [3]. Three parameters located the pollutant severity including its concentration, its chemical nature, and its persistence [4]. Water pollution, known as the water bodies pollution (for example rivers, lakes, oceans and ground water) is one of the most serious environmental problems. It is caused by a variety of human activities such as industrial, agricultural and domestic takes place when contaminates are sent in direct way or indirectly into water bodies without enough remediation to remove harmful compounds [5].

Wastes of industrial process are different from one industry to other and from certain location to another. Some industries produce wastes containing high level of organic substance, such industries involve food processing plants, dairy and meat-packing houses. The other industries discharge wastes with low level of inorganic substance but which are high in toxic chemicals including: mining facilities, chemical plants, and textile mills [6].

Water industrial contaminants contain many chemicals materials such as aromatic hydrocarbons, organic solvents, pesticides, metals and heavy metals which are one of the pollutants in industrial waste. They are discharged into natural water and tend to be collected in the chain of food. Then they are adsorbed by living organisms because of high solubility in the aquatic environments, so these toxic metals must be removed or are decreased from wastewater before discharging them to environment [7, 8].

Adsorption is a very effective process and economical method for metal ions removal from wastewaters; In order to be a good adsorption process, there must be choice of the type of adsorbent as having many properties such as a good compatibility with adsorbate, high surface area, high adsorption capacity, quick response of adsorption capacity to temperature change, high thermal conductivity, high mass diffusivity and thermal stability [9].

A great change is observed in the adsorbents properties whether chemical, physical, optical and mechanical when the particle size decreases to a nano level. The main change is observed on the surface area of the nanomaterial which increases tremendously and leads to the higher capacity of adsorption for the removal of heavy metals [10].

Metal oxides nanoparticles are classified as the promising adsorbent for removal of heavy metals from aquatic systems due to their large surface areas and high activities , therefore increasing attention has been focused on metal oxide such as iron, aluminum, titanium, manganese, zirconium, and copper oxides [11].

As far as the present study is concerned, iron and copper oxides nanoparticles are prepared and applied to remove heavy metals ions from industrial waste water . Sample analysis is made which contains high concentration of nickel and lead ions and an aqueous solution are prepared of different concentrations of these ions and calculation removal percentage at different contact time. Then determination of the suitable adsorption isotherm model, calculation as well as determination order of the adsorption kinetic are made.

1.2: Heavy Metals

The term ‘heavy metal’ is applied to a group of metals (and metal-like elements) with atomic number above 20 and density greater than 5 g/cm^3 [12]. Twenty metals at least are classified as toxic and fifty percent of these are sent into the environment in magnitude that acts hazard to human health [13]. These elements are naturally found on earth crust and can be introduced into environment as a results of human activities and fast manufacturing [14]. Large amounts of probably toxic heavy metals are introduced into the environment from industrial processes[15]. Many processes such as smelting activities, battery industrial, plating and mining discharge of municipal sewage and industrial wastewater include heavy metals such as chromium, copper, cadmium, lead, nickel, mercury, and zinc [16]. Also heavy metal pollution is present in aqueous effluent of many industries such as refining ores, paint and pigments, chloralkali, sludge disposal, tanneries, radiator manufacturing, and alloy industries [17]. Heavy metals exist in discharged and untreated wastes , pollute water bodies and pose menace to ecosystem [18].

The removal of heavy metals from wastewaters is so important because of their high toxicity and tendency to be collected in living organisms. Moreover, heavy metals cannot be destroyed or degraded [19], and tend to accumulate in living organisms, causing different life threatening disorders [20].

Heavy metal contamination of water and water bodies is a dangerous environmental trouble which affects the quality of water. The consequences are : decrease in water supply and aquatic production, increase in cost of purification and eutrophication of water bodies [21].

The heavy metals include in particular cadmium, lead, copper, zinc and mercury, these elements are highly undegradable, capable to accumulate in various tissues of organisms. Such accumulation in human body may cause damage to kidney structure and function, bones, central nervous system, hematopoietic disorders. It may also influence the course of the fundamental biochemical reactions and have adverse reproductive effects [22].

1.2.1: Nickel element

1.2.1.1: Definition and uses

Nickel, a silver-grayish solid , is found naturally below the crust of earth (volcanic rocks and soils) and has a crystalline structure [23]. It is a one of transition metals. It is ductile and hard [24]. It is highly resistant to attack by air and water [25]. It is 24th most abundant metal the crust of earth and its ores are basically of two types sulphides and oxides [26].

Nickel is one of the five ferromagnetic elements, and it is also a naturally magnetostrictive material, meaning that in the presence of a magnetic field, the material succumb a small change in length, it takes place most commonly in combination with sulphur and iron in pentlandite, with sulphur in millerite, with arsenic in mineral nickeline, and with arsenic and sulphur in nickel glance. Nickel is primarily found combined with oxygen or sulphur as oxides or sulphides found naturally in the earth’s crust. Nickel combined with other elements and is present in all soils, in meteorites, and is emitted from volcanoes [24].

It is found in numerous kind of foods. In spite of nickel content of the soil in which they are grown, widespread items being rich in contents include rye, oats, sunflower seeds, red kidney beans, tea, gelatin, baking powder kippered herrings, soya, strong licorice, peas peanuts, hazelnuts, and whole wheat, cocoa, and dried fruits [27]. Like any other heavy metal, nickel is toxic, non-biodegradable and is usually introduce into environment as a consequence of anthropogenic activities. Other ways of nickel introducing into the environment are through weathering of rocks and soils and leaching of the minerals [23]. Nickel ions and its toxic compounds are water soluble and have a distinctive green color and its compounds have no characteristic of smell or taste [28,29].

Different nickel compounds have been used in many industrial applications which involve stainless steel, aircraft parts, cosmetics, electroplating, automobile, batteries, spark plugs, coins, and production of nickel–cadmium batteries on an industrial scale [23].

Nickel forms many alloys with another metals. Its alloy with iron, nickel steel, is extremely hard and corrosion resistant. For this reason most of the nickel produced world-wide is used for the industry of stainless steel, which is usually used to produce food processing tools and containers. It is also used to fashion jewelry manufacture, machinery parts, coins, finely-divided nickel is used as hydrogenation catalyst [25].

The most widespread metals or alloys are nickel titanium and stainless steel which are used in dentistry for endodontic treatment. However, an essential potential disadvantage of these materials is in corrosion [30].

1.2.1.2: Nickel toxicities and health effect

Nickel, having been classified very toxic represents a dangerous contaminants of environmental trouble. It is the most toxic element, and its elevated concentration lead to symptoms of poisoning like headache, cancer, tightness of the chest, reduction in cell growth, dizziness, nausea, dry cough, chest pain, shortness of breath vomiting, cyanosis, extreme weakness and rapid respiration. In accordance to the World Health

Organization (WHO 2006) the agreeable nickel border is 0.01 and 2.0 mg/L in drinking water and industrial effluent, respectively (WHO 2006) [16]. The toxicity limits for nickel according to WHO are 1.0 mg/m^3 for insoluble nickel compounds, 0.1 mg/m^3 for soluble nickel compounds, 0.05–0.12 mg/m^3 for nickel carbonyl and 1.0 mg/m^3 for nickel sulphide [31].The very common harmful health effect of nickel on people is an allergic reaction. Approximately 10–20% of people is sensitive to nickel. A person can become sensitive to nickel while being in direct contact with jewelry or another substance containing nickel or through lengthy contact with the cuticle. The most common reaction is a skin rash at the site of contact, such as dermatitis, hand eczema; workers who are insecure to nickel by breathing can become sensitized and have asthma attacks. Some sensitized individuals react when they eat nickel in food or water or breathe dust containing nickel. People who are not sensitive to nickel must eat very large amounts of nickel to suffer harmful health effects. Workers who fortuitously drank light-green water including 250 mg/L of nickel from a polluted drinking source are to have stomach aches and suffer from adverse effects such as red blood cells increase and protein increase in the urine in kidneys. This concentration of nickel is more than 100,000 times greater than the amount usually found in drinking water . The most serious harmful health effects resulted from exposure to nickel, such as chronic bronchitis, reduced lung function, lung cancer nasal sinus cancers occurred as a result of being exposed to more than 10 mg $nickel/m^3$ as nickel compounds that are hard to dissolve (such as nickel sub sulfide). Exposure to big concentration of nickel compounds, that soluble easily in water, may also cause cancer. It is due to the existence of nickel compounds or another materials which are cancer producing [28].

Nickel is known to be answerable for ‘Nickel Itch’ a form of skin reactions, conjunctivitis and inflammatory reaction. A concentration of about 30 mg or more of nickel is capable to cause changes in vital organs; such as muscle, brain, lungs, liver and kidney etc. and eventually causes death [31].

1.2.1.3: Properties of nickel element

Some important properties of nickel element are given in **Table (1.1)**.

Table (1.1): Some of important properties of nickel element [32, 33]

Property	
Symbol	Ni
Atomic number	28
Atomic weight	58.6934 g.mol^{-1}
Group, block	group 10, d-block
Period	period 4
Element category	transition metal
Oxidation states	4, 3, 2, 1, 0, −1, −2
Color	silvery-white
Atomic radis	empirical: 124 pm
Electronic configuration	[Ar] 3d^{8} 4s^{2}
Density	8.908 g/cm^{3}
Melting point	1728 K (1455 °C)
Poiling point	3186 K (2913 °C)
Solubility in acids	Dilute HCl & H_2SO_4
Crystal structure	Face-centered cubic
Heat of fusion	17.48 kJ. mol^{-1}
Heat of vaporization	379 k J. mol^{-1}
Electron affinity	112 k J. mol^{-1}
Specific heat capacity	0.44 J.g^{-1} K^{-1}
Molar heat capacity	26.07 J/ (mol·K)
Phase	Solid
Isotopes	Five observationally stable isotopes (^{58}Ni, ^{60}Ni , ^{61}Ni , ^{62}Ni , ^{64}Ni)

1.2.2: Lead element

1.2.2.1: Definition and uses:

Lead is a common heavy metal. It is soft and flexible. Metallic lead has a bluish-white color after cutting it, but when exposed to air its color turns to a dull grayish. It is a bright and silvery metal with a very slight shade of blue in a dry atmosphere. Lead is also the heaviest non-radioactive element. It is harmful and a toxic element that is ubiquitous in environment due to various sources and is found both naturally and anthropogenically. Concentration of lead in the environment increases by pesticide spraying , waste, and cars exhaust [34,35], and many industries generated a big quantities of wastewater including different concentrations of lead such as storage batteries, automotive, aeronautical coating, and steel industries [36], and from lead smelting, tetraethyl lead manufacturing, and the mining, plating, ammunition, ceramic and glass industries [37]. It is also resulted from the industrial wastes of photographic materials, printing, explosive manufacturing, fossil fuels, rubber production, etc.[38] .

Lead is one of the essential contaminated in the wastewater discharged from industries of ore beneficiation, electroplating, tanneries, electrical and electronic, and hydrometallurgical processing [18], and it has been used as raw material in the production of pigments for lead paints [39]. It can be introduced to the food chain and will pose a great threat to human food security. Also it can pollute water, mud and soil because it is released from the breakdown of lead-based paint on buildings: Park tools and soil beside roads may have high lead levels from years of exhaust vapors and pollution from cars that once used leaded gasoline [40]. So all these different sources beside natural ores, deposited lead to the soil, water and air.

1.2.2.2: Lead toxicities and health effect:

Lead has been confirmed to be extremely toxic and its concentration in the environment has to be contained within a specified limit [40]**.** Lead contamination is wide world environmental problem due to its source variety in the environment and its high toxicity which causes a big damage to human beings and ecosystems [41, 42]. Usually lead is listed in the 2nd order between 275 human toxins in the priority list of hazardous substances because of its high toxicity and presence in the environment [43, 44]. Many processes cause lead entrance to human system, such as air breathing in workplace, or places of industries that use lead or eating and drinking water from lead pipes or ingesting polluted dust or air and water near waste places or breathing weed smoke or ingesting polluted food grown on soil containing lead or food covered with lead-containing dust or breathing fumes or eating lead from avocations using lead for example leaded glass and ceramics, etc. [45]. Lead is a extremely dangerous agent among the heavy metals, because of its side effects on the human health even at concentrations as low as 0.01–5 mg/L [19].

Lead does not introduce the metabolism of living organism, so it is considered non-essential and represents a serious cell toxicants even at low concentration percentage[40], 143000 death cases estimated annually along with 600000 new cases of children with intellectual disabilities result from lead exposure according to WHO , and the U.S. Environmental Protection Agency (EPA) has established an action level of 15 μg L^{-1} for lead in public drinking water to protect human health since 1991[46], and it causes plant and animal death and failure to provide adequate protection for food from lead pollution . However, this is causes increase in levels of lead in blood and decreases immunological defenses and impaired psychosocial faculties. Such increase in lead level depletes the body's stores of some major nutrients especially in children, mental deficiency, encephalopathy, brain damage, vomiting, anorexia, anemia, kidney damage, behavioral disturbances, cognitive impairment, and malaise in humans and resultant death [17, 34].

1.2.2.3: Properties of lead element

Some important properties of lead element are given in **Table (1.2).**

Table (1.2): Some of important properties of lead element [32,47]

Property	
Symbol	Pb
Atomic number	82
Atomic weight	207.19
Group, block	group 14 (carbon group) , p-block
Period	period 4
Element category	post-transition metal
Oxidation states	4, 3, 2, 1, 0 ,−1, −2, −4
Color	Bluish-gray
Atomic radis	empirical: 175 pm
Electronic configuration	[Xe] $4f^{14}$ $5d^{10}$ $6s^{2}$ $6p^{2}$
Density	11.34 g/cm^{3}
Melting point	600.4 K (327.4 °C)
Poiling point	2022 K (1740 °C)
Solubility in acid	Nitric acid & Hot conc. sulfuric acid
crystal structure	Face-centered cubic
Heat of fusion	4.77 k $J.mol^{-1}$
Heat of vaporization	179.5 k $J.mol^{-1}$
Electron affinity	35.1 $kJ.mol^{-1}$
Specific heat capacity	0.13 $J.\ g^{-1}\ K^{-1}$
Molar heat capacity	26.650 J/ (mol.K)
Phase	Solid
Isotopes	Four observationally stable isotopes (^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb)

1.3: Heavy Metals Removal from Polluted Aqueous Solution

With heavy metal contamination becoming one of the most serious environmental problems [48], removal of toxic metals such as Cr, Cd, Cu, Pb, Ni, Hg and Zn from waste waters become a necessity due to their toxicity and carcinogenicity [49]. Recently, more and more efforts of researchers all over the world with the best of their abilities have been made on wastewater polluted by toxic metals because it is a public health problem of global concern and severe environmental [16, 50, 51].

In order to tackle the threat caused by heavy metal pollution of water, several options have been adopted. These include oxidation and reduction [57], ion exchange, filtration [19,54,56,57,58,59,60,61], membrane separation, reverse osmosis[16,49,50], solvent extraction [53], electro dialysis[52,54],electrochemical treatments[14,51,52,55],biological methods [18,51], and chemical precipitation[14,16,49,51,52,54,55] is the most commonly used method for heavy metal removal from wastewater streams with high heavy metals concentrations. However, this method is not effective when the heavy metal concentration in the wastewater is lower (less than 100 mg/L) , while adsorption [14,16,49,51,52,54,55,56], gets increasing people’s attention since adsorbents have strong adsorptive ability, high specific surface, , and are appropriate for treating a diversity of heavy metal ions of low concentration of wastewater. So, many studies have been carried out to propose effective and economic metal removal technologies. Some recently techniques tackled increase the interfacial surface area between adsorbent and adsorbate to remove metal ions from dilute solutions [57]. Several researches have been conducted using various materials as adsorbents, some of these adsorbents also contain other toxicants; some are expensive and are characterized with limited surface area for adsorption [52]. Typically, trace quantities of heavy metals in environmental samples are determined using spectrometric techniques such as atomic absorption spectrometry (AAS) or mass spectrometry with inductively coupled plasma (ICP-MS). However, these methods require complex laboratory equipment, expensive chemicals and are hardly available. Instead of the mentioned methods, the electrochemical methods can be used (differential pulse voltammetry and/or cyclic voltammetry). These techniques are one of the best for metal detection because of their low detection limits, metal selectivity, high sensitivity, mobility and low cost [22].

1.4: Adsorption

Untold chemical, biological, and physical, processes occur at the confines between two phases, while others started at that interface. Concentration change of a given materials at the interface as compared with the neighboring phases is an indicating of adsorption [58].

Adsorption is the process whereby molecules from the gas (or liquid) phase are taken up by a solid surface. It is distinguished from absorption which refers to molecules entering into the lattice (bulk) of the solid material. The adsorptive is the material in the gas phase capable of being adsorbed, whereas the adsorbate is the material actually adsorbed by the solid [59].

Adsorption is a phase transport process that is vastly used in practice to eliminate materials from fluid phases (gases or liquids). It can also be observed as natural process in different environmental compartments. The most general definition describes adsorption as an enrichment of chemical species from a fluid phase on the surface of a liquid or a solid. In water remediation , adsorption has been confirmed as an active uptake process for an abundance of solutes [60].

It is one of the very vastly applied methods for environmental treatment. Its kinetics are of great significance to test the rendering of a given adsorbent and gain insight into the underlying mechanisms [61]. The major development of adsorption processes on a large, industrial scale deals mainly with the solid-gas and solid-liquid and interfaces, but in various laboratory separation techniques all types of interfaces are applied [58].

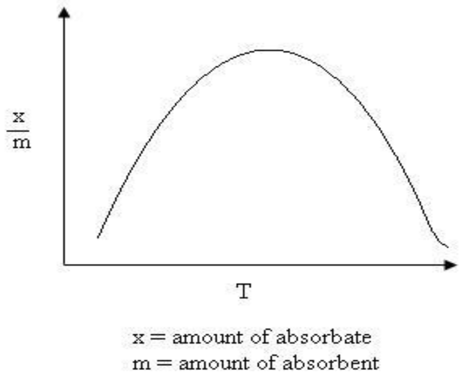
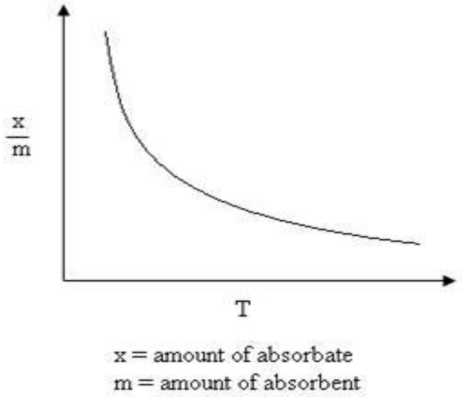
Adsorption is regarded as a practicable separation method for purification or bulk separation in newly developed material production processes, for example, high tech materials and biochemical and biomedical products [62]. The material that adsorbs is the adsorbate and the underlying material that we are concerned within this section is the adsorbent or substrate. The reverse of adsorption is desorption [63]. Purification of gases by adsorption has played a main role in air contamination control, and adsorption of dissolved impurities from solution has been vastly used for water purification. Adsorption is now viewed as a superior method for wastewater remediation and water reclamation. Adsorption applications for chemical processing, air pollution control and water treatment are well known [64].

Adsorption is a spontaneous process because of decreases in free energy of the system i.e. ΔG of the system must have negative value. Also we know, $\Delta G = \Delta H - T\Delta S$ and during this process of adsorption, randomness of the molecule decreases which ΔS is negative, so $\Delta G = \Delta H + T\Delta S$ and this lead ΔH to be negative and $|\Delta H| > |T\Delta S|$ [58].

1.4.1: Types of adsorption

Adsorption may occur in two different ways according to the interactions of the adsorbent and adsorbate. Table (1.3) shows the difference between chemical adsorption and physical adsorption:

Table (1.3): Comparison between chemical adsorption and physical adsorption [59, 63, 65].

Chemical adsorption	Physical adsorption
It arises when adsorbate molecules accumulated on the surface of adsorbent on account of chemical bond (ionic or covalent bond).	It arises when adsorbate molecules accumulated on the surface of adsorbent on account of Van der Waals forces.
The heat of adsorptions is high (40 - 400) K.J.mole^{-1}.	The heat of adsorption is low (20 - 40) K.J.mole^{-1}.
This process occurs at high temperature and increase with the increases in the temperature.	This process is observed under condensation of low temperature and decreased with the increases in the temperature.
It is highly specific.	It is not specific.
This process is irreversible.	This process is reversible, desorption can be occur by increasing temperature or decreasing of pressure.
It is required activation energy.	It does not require activation energy.
Monolayer adsorption, thus adsorbed layer is unimolecular thick.	Multilayer adsorption, thus adsorbed layer is several molecular thick .
It is increasing with the increase of surface area of adsorbent.	It is also increasing with the increase of surface area of adsorbent.
Electron transfer leading to bond formation between sorbent and surface.	No electron transfer although polarization of sorbent may occur.
Surface reactions may take place : Dissociation , reconstruction, catalyst.	No surface reactions.
It is otherwise known chemisorption .	It is otherwise known physisorption
	

1.4.2: Effective factors on the adsorption process

There are many factors which could affect the amount of molecules adsorb on surface:

1.4.2.1: The adsorbent nature and surface area

Adsorption represents surface phenomenon, the extent of adsorption depends upon the specific surface area which is defined as that portion of the total surface area that is exposed for adsorption, so the larger surface area of the adsorbent is simply greater adsorption capacity [66,67,68].

The properties of the adsorbent such as chemical nature, dimension of the pores, and the charge distribution of the adsorbent play an important role in the extent of adsorption. So more finely divided and more porous is solid greater is the amount of adsorption accomplished per unit weight of a solid adsorbent. The essential contribution to surface area is located in the pores of molecular dimension. As the adsorbent porosity increases, the adsorption of small molecules from the solution usually grows. It depended on the surface area and thus the greater the adsorption capacity is the more active sites are available. When the surface area of an adsorbent increases, the adsorption capacity would be the greater [67, 68]. Small particle sizes decrease internal diffusion and mass transfer limitation to the penetration of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly adsorption capability can be attained) [66].

1.4.2.2: The adsorbate nature and concentration .

The physicochemical nature of adsorbate drastically affects both rate and capacity of adsorption, so the amount of material which is adsorbed by the adsorbent at certain temperature increases with the increase in the solute concentration. However, in some cases adsorption may be confined to only one layer of adsorbed solute. Thus increase of concentration of the solute can produce no further adsorption because the surface of the crystal lattice of adsorbent covered [62,63]. Neutral molecules are adsorbed to a large extent than highly ionized molecules [66]. .

The solubility of the solute greatly influences the adsorption equilibrium, material slightly soluble in solvent will be more easily removed from solvent (i.e., adsorbed) than materials with high solubility. Generally, reverse relationship can be predictable between the range of adsorption of solute and its solubility in the solvent where the adsorption occurs [66,67] .When other effects are not present , for a given solvent , the more soluble solute are generally more weakly adsorbed than the less soluble solute [68].The extent of adsorption depends on the adsorbate nature, stereochemistry, size of adsorbed molecule, polarity, and the presence of different substituent groups in the molecule would govern the ability of the molecule to be adsorbed on certain surface [68].

1.4.2.3: Contact time

. The longer contact time is the more complete adsorption will be, therefore, the equipment will be larger [66].

1.4.2.4: The pH effect

The pH of the solution affects the extent of the adsorption because the distribution of the surface charge of the adsorbent can change. Also, the pH of the solution changing has a great effect on the extent of the adsorption through its influence on the adsorbate, the chemical state of the adsorbent, and the solvent. This effect can be observed through the competition on (H^+) and (OH^-) ions and their overlapping with the adsorbent surface or the adsorbate or the solvent. The degree of ionization of a species is affected by pH (e.g., a weak acid or a weak basis). This in turn affects adsorption. As a result of this interaction, the varying extent of adsorption either increases, decreases, or remains unchanged according to the adsorbate functional groups [66,67,68].

1.4.2.5: Temperature

Another important factor is the temperature. Adsorption process is normally exothermic, it is a study of the temperature dependence on adsorption reactions which gives valuable information about the enthalpy and entropy changes during adsorption, thus decrease in temperature result in an increase of adsorption . On the other hand increasing adsorption with a rise in temperature means that process is endothermic. In chemisorption , the quantity adsorbed may increase or decrease with the rising temperature depending on the type of interaction and bonding between the surface and the adsorbed molecule , while in physisorption a decrease in temperature enhances the extent of adsorption [66,67,68].

1.5: Adsorbents

Adsorbents used are of two types either of natural origin or being the result of an industrial production and activation process. Typical natural adsorbents are clay minerals, natural zeolites, oxides, or biopolymers. Engineered adsorbents can be classified into carbonaceous adsorbents, polymeric adsorbents, oxidic adsorbents, and zeolite molecular sieves. Activated carbons produced from carbonaceous material by chemical activation or gas activation are the most widely applied adsorbents in water treatment.

Polymeric adsorbents made by copolymerization of nonpolar or weakly polar monomers show adsorption properties comparable to activated carbons, but high material costs and costly regeneration have prevented a broader application to date.

Oxides and zeolites are adsorbents with strong hydrophilic surface properties. The removal of polar, in particular ionic, compounds is therefore their preferred field of application. In recent decades, an increasing interest in using wastes and by-products as alternative low-cost adsorbents can be observed [60].

In the field of heavy metal removal, adsorption technology is represented as the most promising one among the techniques which are used for this purpose because of its low cost-effective, high efficiency, and being simple to operate for removing trace levels of heavy metal ions. So several types of materials above have been used to adsorb metal ions from aqueous solutions. Although traditional adsorbents could remove heavy metal ions, the low adsorption capacities and efficiencies limit their application deeply. To solve these defects of traditional adsorbents, nanomaterials are used as the novel ones to remove heavy metal ions. With novel size and shape dependent properties, nanomaterials have been extensively investigated over a decade in recent years. The development of nanoscience and nanotechnology has shown remarkable potential for the remediation of environmental problems [69].

1.6: Adsorption Isotherms

Adsorption process is studied through graphs known as adsorption isotherm which show the amount of solute adsorbed on the surface of adsorbent (Q_e) and the equilibrium concentration of the solute in the solution (C_e) at constant temperature [70].

An adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous media or aquatic environments to a solid phase at a constant temperature and pH [71].

Adsorption isotherms can be found in different shapes due to the adsorbent structure complexity and the interaction between each corpuscle as shown in **Figure (1.1)** and the different isotherm classified by Giles et al. (1960) to four types (S, L, H and C types) [70].

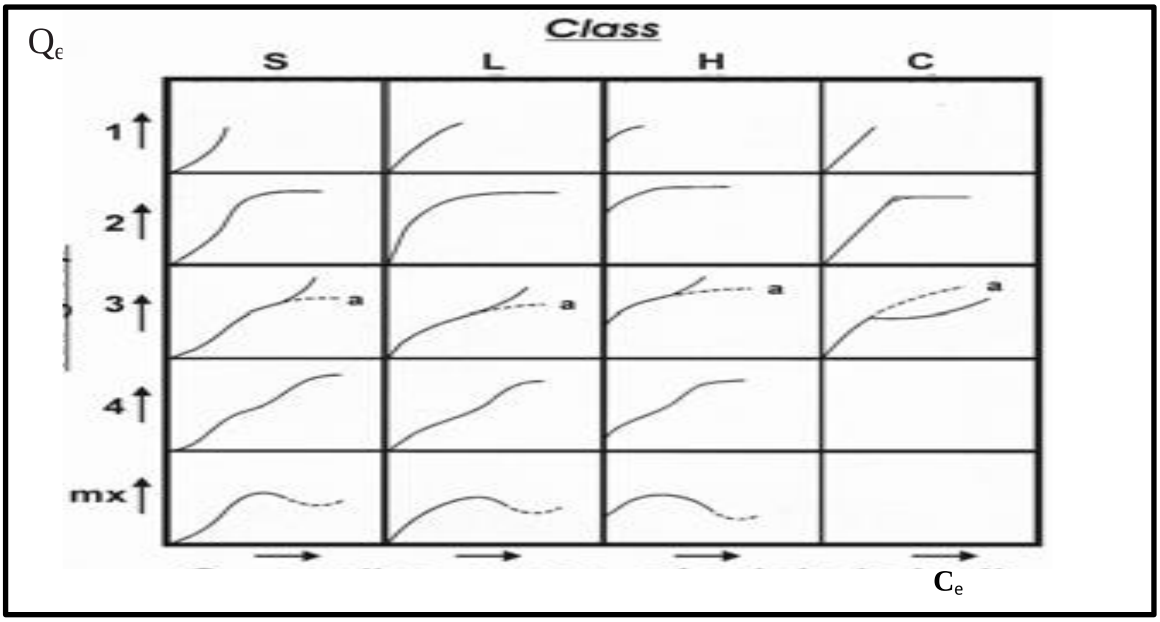


Figure (1.1): Adsorption isotherms as in Giles classification [72].

1. **S-curves :-** The S-curve isotherm is generally characterized by an initially small slope which increases with adsorptive concentration, or if the solvent is strongly absorbed ,there is a strong inter-molecular attraction within adsorbed layer, and the adsorbate which is mono functional
2. **L-curves:-** The L-curve isotherm is generally characterized by an initial slope which does not increase with adsorptive concentration**,** or it may be found when there is no stronger competition from solvent for sites on the surface. Another possibility is that the adsorbate has linear or planar molecules, the major axis is parallel to the surface**,** and it is also called Langmuir type.

3. **H-curves: -** The H-curve isotherm is characterized by a large initial slope suggestion a very high relative affinity of the adsorbent for the adsorbate which is shown even in very dilute solutions.
4. **C-curves: -** The C-curve isotherm is characterized by an initial slope which remain independent on adsorptive concentration until the maximum possible adsorption is achieved, and refers to constant partition linear curves given by substances which penetrate into the adsorbent more readily than the solvent does [72,73,74].

1.7: Type of Adsorption Isotherms

There are several types of adsorption isotherms and the most important one are:

1.7.1: The Langmuir isotherm

The Langmuir equation, which is valid for monolayer adsorption onto a completely homogeneous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules, is represented in the linear form as follows [75,76,77].

$$\frac{Ce}{Qe} = \frac{1}{ab} + \frac{Ce}{a} \qquad (1.1)$$

Where

Q_e: the quantity adsorbed at equilibrium in (mg/g).

C_e : the equilibrium concentration of adsorbate in (mg/L).

a : the Langmuir constant which is a measure of adsorption capacity in (mg/g) .

b : also the Langmuir constant which isa measure of energy of adsorption in (L/mg).

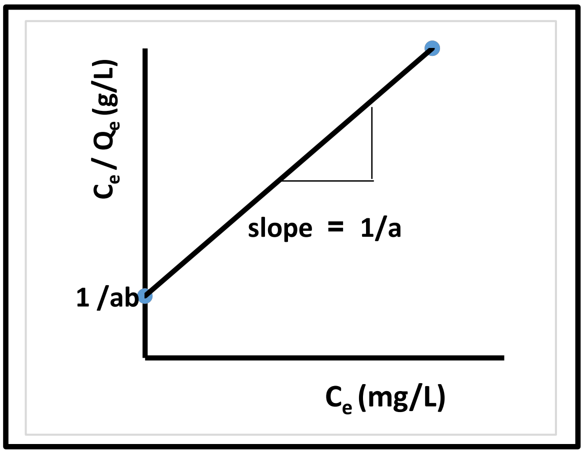


Figure (1.2): The linear form of Langmuir isotherm[77].

This form can be used as a linearization of expermental data by plotting C_e/Q_e against C_e as shown in **Figure (1.2).** The Langmuir constants (a) and (b) can be evaluated from the slope (1/a) and intercept (1/ab) of the linear equation [75].

1.7.2: The Freundlich isotherm

The Freundlich isotherm, assumes a heterogeneous sorption surface and is based on the idea that the adsorption depending on the energy of the adsorption sites. The Freundlich model can be represented as follows [77,78,79]:-

$$Q_e = K_f C_e^{1/n} \quad \ldots\ldots (1.2)$$

Where

Q_e : the quantity adsorbed at equilibrium in (mg/g)

C_e : the equilibrium concentration of the adsorbate in (mg/L).

K_f and **n:** the freundlich constants being indicators of the adsorption capacityand adsorption intensity, respectively.

Take logarithms of equation (1.2) give:

$$\log Q_e = \log K_f + 1/n (\log C_e) \ldots (1.3)$$

If log Q_e is plotted against log C_e a straight line should be obtained as shown in **Figure (1.3).** The slope of the line will give the value of 1/n and the intercept on the Y-axis gives the value of log K_f .

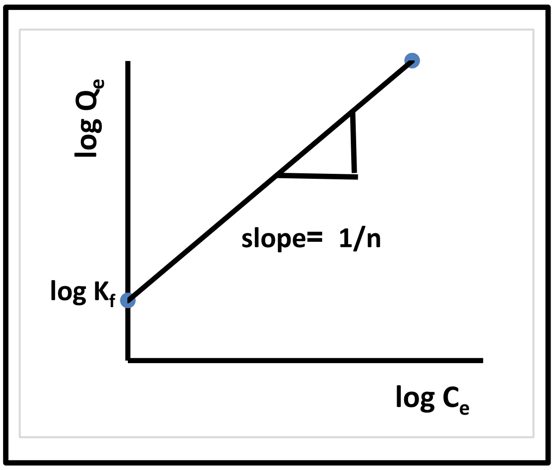


Figure (1.3): The linear relationship Freundlich isotherm[77].

1.8:Nanomaterials

The prefix "nano" has been found in last a century an ever increasing application to different fields of the knowledge. It comes from the ancient

Greek νᾶνος through the Latin nanus meaning literally dwarf and by extension, very small[80]. .

Nano material is defined as a physical substance with one dimension at the lowest between 1-100 nm, (1nm=10^{-9}m) have received considerable interest because of the unique properties different from their bulk counterparts [81, 82]. Nanotechnologies have applications in various disciplines from medicine to many through chemical technology to the construction industry, etc. [22].

Consequently nano metals find applications in diverse fields, such as homogeneous and heterogeneous catalysis, fuel cell catalysis, electronics, optics, magnetism, material sciences and even in medical and biological sciences. Nano-structured materials can be produced by two different approaches, namely, “top down” and “bottom up” approach, as shown in **Figure (1.2)**

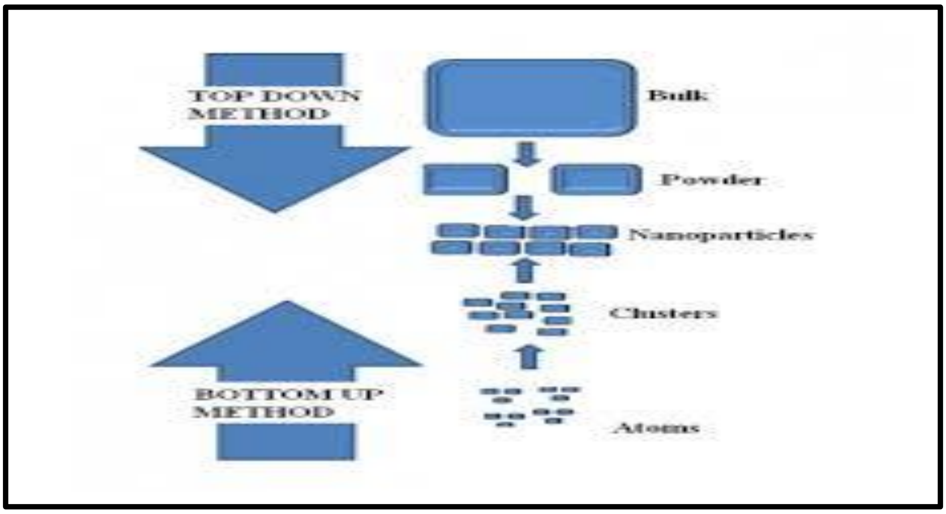


Figure (1.2): Nano materials production

The shape, size and composition of nanoparticles can be tuned depending on reaction conditions, such as pH, temperature, atmosphere, use of surfactants, and ionic strength of the medium or relative ratio of the reagents [83].

With the development of nanoscience and nanotechnology, many of the new nanosorbents are developed for the current water treatment problems and removal of toxic metal very effectively due to large surface to volume ratio and the span life of these nanoparticles are very high. It can enhance huge planar surfaces of nanosorbents which enable and increase interface reactions with pollutants in environment. Various types of nano-sorbents such as metal oxides, clays, carbonaceous nanomaterials, zero-valent metals have been studied for their usefulness in the water treatments [50, 84].

1.9: Metal Oxide Nanoparticles

1.9.1: Iron oxide nanoparticles (Fe_3O_4, Fe_2O_3)

Iron nanomaterials have distinguished themselves by their unique properties, such as larger surface area-volume ratio with another special property of this kind magnetic materials are realized and utilized in the context of environmental remediation [55]. .
Iron oxides nanoparticles take many forms in nature such as magnetite Fe_3O_4, hematite α-Fe_2O_3 and maghemite γ-Fe_2O_3, and also different ferrite compounds are known as materials used in different biological and industrial applications [49,55]. The iron oxide nanoparticles have been utilized in various promising applications, such as catalysis, electronic devices, information storage, sensors, drug-delivery technology, biomedicine, magnetic recording materials, and environmental Remediation, biotechnology, and magnetic separation [56, 84]. It is used in many biological and biomedical applications such as targeted drug delivery, magnetic fluid hyperthermia, magnetic resonance imaging, and tissue engineering. For biological and biomedical applications, magnetic iron oxide nanoparticles are the primary choice because of their biocompatibility and chemical stability [85]. Magnetic nanoparticles are considered potential adsorbents for aqueous heavy metals due to their high

surface area and the unique advantage of easy separation under external magnetic fields [86]. .

Recently, due to the development in nano technology, the exploitation of iron oxide nanomaterials for heavy metal ion removal has attracted much attention because of their demonstrated excellent adsorption capacities and environmentally kindly nature. It has been proposed as inexpensive but efficient adsorbents become a raw material for treating the waste waters and soils, accelerating the coagulation of sewage, removing radionuclides, adsorbing organic dyes and cleaning up the contaminated soils [22,49,50,87].

The synthesis of iron oxide nanoparticles has seen a vast development, and many synthesis methods have been explored such as organic solvent heating method, reverse micelle and micro-emulsion technology, sol-gel synthesis, flow injection, polyol method, electrospray synthesis, the sonochemical method, hydrothermal synthesis or thermal decomposition thermolysis of precursors and co-precipitation method. As such, among the available methods for the synthesis of iron oxide nanoparticles, co-precipitation is the most commonly and the most effective technique which is used for preparing aqueous dispersions of iron oxide nanoparticles because the synthesis is conducted in water due to its simplicity and the possibility of obtaining large quantities of nanoparticles in a single batch . Particles with sizes ranging from 5 to100 nm are obtained [83,85,88]. However, control over particle size, morphology and composition is limited as particle growth is kinetically controlled. Additionally, factors such as the nature of the precursor salts used (chlorides, perchlorates, sulfates, nitrates, etc.), Fe (II) / Fe (III) ratio, pH and ionic strength of the medium are known to affect particle growth [83].

1.9.2: Copper oxide nanoparticles (CuO)

Copper oxide is one of the important metal oxide which has attracted recent research because of its low cost, abundant availably as well as its particular properties [89]. It is one of semiconductors material and gains considerable attentions due to its excellent optical, electrical, physical, and magnetic properties [89, 90]. CuO crystal structures possess a narrowband gap, giving useful photo catalytic and photovoltaic properties [91].

Copper oxide belongs to monoclinic structure system with the brownish-black appearance which finds their significant role in antibacterial agents to fabrics [89]. Copper oxide nanoparticles, have attracted particular attention because it is the simplest member of the family of copper compounds and shows a range of useful physical properties such as high temperature superconductivity, electron correlation effects, and spin dynamics [91].

Copper oxide nanoparticles has a monoclinic structure and semiconductor behavior with an indirect band gap of 1.21 – 1.51 eV. It has the advantage of a lower surface potential barrier than that of metals, which affects electron field emission properties, and is considered as a potential field emitter, an efficient catalytic agent, as well as a good gas sensing material [92]. It is extensively used in the many of fields like catalysis, heat transfer fluids, superconductors, batteries, ceramics as a kind of important inorganic materials etc. [89,90,91].

Copper oxide has gained the most interest because of its wide applications, such as in solar energy conversion, field emission, magnetic storage media, lithium ion batteries, gas sensor, drug delivery, magnetic

resonance imaging, and field emission device. Its treatment is known to induce a disruption of the blood–brain barrier in vivo in mice and rats. Under in vitro conditions, Copper oxide nanoparticles are also found to induce toxic effects in different types of neuronal cells[89]. .
Recently, application of nanoparticles for the removal of pollutants has come up as an interesting area of research. The unique nanosorbents properties provide unprecedented opportunities for the removal of metals in highly efficient and cost-effective approaches, and various nanoparticles and a synthetic polymer with a branching which are for this purpose. Nanoparticles exhibit good adsorption efficiency especially due to higher surface area and greater active sites for interaction with metallic species. Furthermore, adsorbents with specific functional groups have been developed to improve the adsorption capacity [93].

Copper oxide nanoparticles have been prepared with different sizes and shapes via several methods such as sonochemical, alcohothermal synthesis, vapor deposition , electrochemical methods, combustion, colloid thermal synthesis process, and microwave irradiation, thermal oxidation, pulsed wire explosion methods, radiolysis methods, plasma methods, quick precipitation [89,90,94]. There are some methods for the preparation of copper oxide nanoparticles which have been reported recently such as the sol-gel technique, one-step solid state reaction method at room temperature, thermal decomposition of precursors and co-implantation of metal and oxygen ions [95]. Most of these methods are complicated and have drawbacks like use of hazardous organic solvents, expensive reagent, toxic by product, drastic reaction condition, difficult to isolate nanoparticles, longer time etc. [94].

Among these processes, precipitation method is a facile way which attracts considerable interest in industries because of low energy and temperature, inexpensive and cost-effective approach for large scale production and good yield. However, these CuO novel properties can be improved by synthesis in CuO nanostructures which shows excellent performance comparing to bulk counterpart. Different nanostructures of CuO are synthesized in form of nanowire, nanorod, nanoneedle, nano-flower and nanoparticle [90].

1.10: Literature Survey

1.10.1: Literature survey (adsorption and heavy metal ions removal)

(Elshazly and Konsowa , 2003), discussed Ni ions removal from waste water contaminated as $NiCl_2$ using a cation-exchange resin reactor with stirring store. The effect of each temperature, concentration of Ni ion, and stirring degree on the mass transfer coefficient of the diffusion-controlled reaction between Ni ions and the resin. It is example of the factors that was studied. The results showed that using a strong cation-exchange resin for remove of Ni ions is an encouraging technicality for waste water remediation due to get a removing of Ni ion rates up to 88.5% **[96]**.

(Onundi, **et. al 2010),** in their research presented the Cu, Ni and Pb ions adsorption from synthetic semiconductor industrial effluents using palm shell activated carbon . The results indicated that pH of 5 was very appropriate , when the largest adsorbent capacity was at a dosage of 1 g/L, giving an adsorption capacity of 1.337 mg/g for Pb, 1.581 mg/g for Cu and 0.130 mg/g for Ni. Percentage removal of metal was near from equilibrium within 30 min for lead, 75 min for Cu and Ni, with Pb showing 100 %, copper 97 % and nickel 55 % removal, having a trend of $Pb^{2+} > Cu^{2+} > Ni^{2+}$. The correlation coefficient of Langmuir isotherm model had a great value of 0.977, 0.817 and 0.978 for Cu, Ni and Pb respectively **[97]**.

(Jarullah, et. al, 2012), discuss the adsorption of nickel ion by using activated charcoal prepared from dry leaves of bitter orange tree (*Citrus aurantium*).The effects of its concentration, adsorbent dosage, particle size, pH and temperature on uptake of nickel ion have been studied. The adsorption of nickel ion is higher at lower concentration and progression decreases with increasing in the concentration. The pH of 5 was the most suitable. The uptake percentage of nickel ion increases with increase in the adsorbent dosage. The effect of the particle size reveals that the percentage removal of nickel ion decreases with increase in particle size of adsorbent. The effect of temperature shows that as temperature increases, the adsorption rate of nickel ion decreases **[98]**.

(Akkaya and Guzel, 2013), investigated the optimization of Cu and Pb uptake by a novel biosorbent , Cucumber peels biosorption efficiency for Cu and Pb ions were studied in batch mode. The best conditions for adsorption of copper and lead ions were found to be pH of 5, biosorbent dose of 0.1 g, contact time of 60 and 85 minutes, and initial concentration of 100 and 150 mg/L, respectively. The best description of the kinetic data were done by pseudo-second order model. The adsorption process is described by the Langmuir isotherm model. Highest monolayer adsorption capacities were 88.50 and 147.06 mg/g for copper and lead ions, respectively. Thermodynamic factors suggest that the adsorption process is endothermic and spontaneous **[17]**.

(Judith, et.al, 2014), in their research presented the kinetic, equilibrium and mechanistic studies of Ni removal using activated *Pistia stratiotes* leaves, which were prepared by acid remediation was examined for its activity in adsorption of Ni ion. The studied factors of the process involve contact time, temperature, adsorbent dose, initial concentration of Ni ion and pH. Adsorption followed 2nd order. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity obtained from the Langmuir isotherm plot at an initial pH of 6.5 and at 30, 40, 50, and 60℃. The effect of pH on nickel ion removal important and the removal was increased with temperature increasing **[52]**.

(Saravanan, et. al, 2015), studied optimization of process factors for the uptake of Cr (VI) and Ni (II) from aqueous solutions using mixed biosorbents (custard apple seeds and Aspergillus niger) by using response surface methodology . Batch adsorption methods was implemented and it was affected by the different factors such as biomass loading, initial concentration of metal, temperature, and pH, the result showed the best conditions for the adsorption of Cr(VI) to be: pH of 3, Cr(VI) initial concentration was 100 mg/L, biosorbent loading being 10 g/L, and temperature of 36 °C. At these optimized conditions, the highest uptake of Cr (VI) was found to be of 95.7%. The best condition for the uptake of Ni(II) were found to be: pH of 5.6, Ni (II) initial concentration was100 mg/L, adsorbent loading was 10 g/L, and temperature of 30 °C. At these good conditions, the largest uptake of Ni(II) was found to be of 96.41%. Mixed adsorbents reveal best adsorption characteristic towards the removal of Cr (VI) and Ni (II) ions from the aqueous solutions **[29]**.

(Ali, et. al, 2016), studied the Cu (II) uptake from aqueous solutions by the peanut hull as an adsorbent without any physical or chemical remediation . Different factors effect such as particle size, contact time, initial concentration of Cu (II), initial pH, dosage of adsorbent, and temperature were examined for a batch adsorption method. The results indicated that the adsorption process followed the pseudo-second-order and intra-particle diffusion kinetic models, pointing that the adsorption mechanism is chemical and physical adsorption process. Langmuir and Freundlich adsorption isotherms have been tested. The thermodynamic factors were investigated, and it was confirmed that, removal of copper (II) using peanut hulls is nonspontaneous and endothermic. This study convinced that the naturally peanut hulls proved to be an attractive , effective, economic, alternative, and environmentally friendly adsorbent for copper (II) adsorption from aqueous solution **[99]**.

(Al-Homaidan, et. al, **2016)**, investigated the adsorption of lead (II) from aqueous solutions by the nonliving biomass of the microalga (*cyanobacterium*) Spirulina platensis. The biomass was washed, exsiccated and utilized for the investigation. Lead (II) initial concentration of, pH, temperature, adsorbent dose, and effect of contact time on the adsorption of lead by the dry adsorbent were examined. The tests were executed in 250 ml flasks containing 100 ml of solutions using an orbital incubator at 150 rpm. The result showed high rates of lead (II) uptake (more than 91%). The best conditions for a maximum removal by Spirulina platensis were found to be adsorbent dose (2 g), pH of 3, incubation at 26 ˚ C, initial concentration of lead was 100 mg/L, and 60 min contact time. The empirical data fitted well with Freundlich isotherm model with correlation coefficient values greater than 0.97 **[40]**.

(Liu, et. al, 2015), studied the Pb, Cd, Zn and Cu uptake from local solid waste sludge incinerator fly ash by thermal and chlorination remediation. Results showed that without the addendum of chlorinating agents, temperature was a substantial factor and had considerable effect on heavy metal uptake, whilst the residence time had a low effect. Between 900 and 1000 °C for 60 to 300 min, heavy metals reacted with chloride-inherent in the fly ash, and about 80% - 89% of lead, 48% - 56% of cadmium, 27% - 36% of zinc, and 6% - 24% of copper were separated. After adding chlorinating agents, the vaporization percentage of the heavy metals amended dramatically, where the vaporization percentage of copper and zinc were greater than that of lead and cadmium. As the quantity of increment chlorinating agents boosted, the uptake effect of heavy metals increased the effect of the kind of chlorinating agent on the chlorination of heavy metals different frequently, while sodium chloride had the weakest influence on the uptake percentage of copper, cadmium, and zinc. In terms of resource recapture and refinement, magnesium chloride and calcium chloride were the good choices because of their efficient removal of Zn **[100]**.

(Egirani and Wessey, 2015), in their research showed the effect of clay and goethite mineral system on lead removal from aqueous solution, and pH, ionic strength, and particle concentration and residence time related to simulated contaminated waters inclusive effluent discharge. Adsorption isotherms showed that adsorption capacities of the different clay minerals, goethite and their mixtures were dependent on the particle size. Mixed mineral systems of kaolinite / montmorillonite and kaolinite / goethite presented various sorption attitudes from the odd mineral components, constriction lead uptake over the range of pH inspected. Increased ionic strength and solid concentration showed a complex response leading to lower lead sorption. Enhanced lead sorption on some of the mixed mineral systems as ageing increased may be linked to excessed hydroxylation of the mineral surface performing in the fashioning of new reactive sites **[18]**.

1.10.2: Literature survey (nanoparticles)

(Dozier, et. al, 2010), in their research showed the preparation of iron oxide nanoparticles for biomedical and biological applications. It is needed to output nanoparticles that are water soluble and biocompatible. So they report the preparation of iron oxide nanoparticles plated with biological molecules (for example, gluconic acid, lactobionic acid, or polyacrylic acid) by a co-precipitation techniqe. These nanoparticles have small magnitude distribution and are much soluble in water. Due to the biological covering, they will have large potential in abundant biomedical applications such as tissue engineering **[85]**.

(Min, et. al, 2011), investigated the removing of cadmium (II) by composite adsorbent nano iron oxide (Fe_3O_4) / bacterial cellulose, it was prepared through blending method. The process of adsorbing cadmium (II) involves its isotherm and kinetics studies. Results show that the adsorption efficiency is amended because of huge surface area and surface coordination of nano iron oxide (Fe_3O_4) particles. Its adsorption capacity is 27.97 mg/g and the maximum of cadmium (II) uptake is 74%. The adsorption kinetics obeyed pseudo-second equation model and the adsorption equilibrium by Langmuir type. Cd^{2+} can be desorbed effectively by Ethylene diamante tetra acetic acid and hydrochloric acid from the composite adsorbent, which can use it once again **[56]**.

(Cheng, et. al, 2012), studied the enforcement of maghemite (γ-Fe_2O_3) nanoparticles for the eclectic uptake of toxic heavy metals from electroplating influence. The maghemite nanoparticles of 60 nm were prepared by using a co-precipitation technique. Batch tests were implemented for the removal of lead ions from aqueous solutions by maghemite nanoparticles. The effects of contact time, initial concentration of lead ions, pH, and brininess on the amount of lead removed were studied. Result showed a highly dependence on pH and which made the nanoparticles selectively adsorb lead from wastewater. The adsorption of lead ion arrived equilibrium speedily within 15 minutes and the data of adsorption were good agreed with the Langmuir isotherm **[55].**

(Andujar, et. al, 2012), studied illustrating the morphological and structural development of iron oxide nanoparticles created by sodium carbonate in aqueous medium.. They found that by agent for the preparation of uncovered iron oxide nanoparticles, and the reaction yields slowly enough to a detailed research of each of the reaction path and products. Many factors were studied such as temperature and reaction time on particle size, pH, crystalline phase, morphology, and its magnetic properties. The product nanoparticles indicated an increase in average particle size. The optimization of the particle factor leads to super paramagnetic nanoparticles with a high saturation magnetization of 82 A m^2 kg^{-1} at 300 K when prepared at pH of 9 **[83].**

(Predescu and Nicolae, 2012), studied the adsorption of zinc, Copper and cadmium from influence by means of maghmite nanoparticles ,Nano-sized crystals of maghemite iron oxide (γ-Fe_2O_3) were synthesized, with a size of 10 nm. Subsequently, a nano-composite from γ-Fe_2O_3 with cationic exchange resin was prepared. The products have been subjected to characterization with several spectroscopic techniques as well as (TEM) measurements or (XRD) analysis. These investigations emphasize the formation of maghemite nanoparticles on resin surface. The nano-composite indicated remarkable adsorption efficiency in uptake of some toxic metal ions such as zinc, copper, and chromium **[49]**.

(Meng and Shibao, 2012), discussed the uptake of cadmium, lead and copper from water using humic Acid (HA) and thiol functionalized Fe_2O_3 nanoparticles , the humic acid (HA) and 3-mercapto propyl tri ethoxy silane were successfully coated onto Fe_2O_3 (α and γ) nanoparticles surface. Result showed that the sorption of cadmium, lead and copper ions via the nanoparticles can be agreed well by using Langmuir isotherm; and all the adsorbents appeared firmly adsorption ability to cadmium, lead and copper ions in solution. Maximum adsorption and affinity of adsorption on the nanoparticles for lead were usually higher than copper and cadmium, the maximum adsorption for the lead, cadmium and copper followed the order lead > copper > cadmium. Among the nano adsorbents, the Fe_2O_3 (α and γ) nanoparticles covered with HA showed largest adsorption ability to ions of metal than the exposed and thiolated Fe_2O_3 nanoparticles, the adsorption maxima of α-Fe_2O_3 / HA for lead arrived 151.5 mg/g, which was higher than the values of 116.3 and 84.0 mg/g noticed for α-Fe_2O_3 and α-Fe_2O_3/MPTES particles. However, no increasing in the maximum adsorption was noticed for the thiolated Fe_2O_3 nanoparticles (Fe_2O_3/MPTES) for the metal ions compared with the uncovered Fe_2O_3 nanoparticles in this work. The whole capability of Fe_2O_3/HA to adsorb cadmium, lead, copper refers to its potential using another favorable method to treat the metals which polluted the water **[50].**

(Palanisamy, et. al, 2013), discussed the interest of magnetic iron oxide nanoparticles stabilized by carrier oils in uptake of Cu, Ni and Cr, from its aqueous solution by carrier oils intermediate iron oxide nanoparticles filtration , super paramagnetic iron oxide nanoparticles were synthesized by co-precipitation technique by using salts with a various Fe^{3+}/Fe^{2+}. Carrier oils such as olive oil, and flaxseed oil were used as the coating material **[84]**.

(Bhargav and Prabha, 2013), discussed the uptake of heavy metals like As (V) and Cu (II) from the contaminants in wastewater supply by the process of adsorption to make it safer for domestic purpose. For this magnetite (Fe_3O_4) nanoparticles are used for uptake of pollutants in municipal water by applying external magnetic fields. It is synthesized by co-precipitation technique obtained by an aging stoichiometric mixture of ferrous and ferric salts in aqueous medium. Precipitation of Fe_3O_4 is anticipated at a pH between 8 and 14. Magnetite (Fe_3O_4) nanoparticles with size smaller than 30 nm have a great surface area and remain non-magnetized under external magnetic field. The shape and size of the nanoparticles can be controlled by ionic strength, adjusting pH, temperature and the nature of the salts. At optimized pH the obtained Fe_3O_4 nanoparticles are coated with coating agents which develops surface functionalized groups. The sorption of metals like arsenic (V) and copper

(II) take place on these aggregates which are removed with help of external magnetic field leaving the supernatant free from Cu and As **[88]**.

(Phiwdang, K., et. al , 2013), discussed the synthesis of CuO nanoparticles by precipitation technique using various precursors as copper nitrate and copper chloride with post-heating comparing between as prepared and after calcinations. Relevant properties of as prepared nanoparticles were investigated by (XRD), (SEM) and (FTIR) spectroscopy. The results suggest that the formation of CuO nanostructures with various shape, size and morphology can be achieved using different precursors via this process. The improvement in their crystallinity and purification can be further attained by post calcinations process **[90]**.

(Farghali, et. al, 2013), in their research showed the removal of Pb ions from aqueous solutions by using copper oxide nanostructures , Various morphologies of CuO nanostructures (oval, cluster, leaves, small rod, porus nanosheets) have been synthesized by novel simple method using microwave radiation. The produced were characterized by XRD analysis technique, (TEM), surface area analyzer (BET), and energy dispersive spectroscopy (EDS). The ability of CuO nanostructures as adsorbent was leading for adsorptive uptake of lead ions from the aqueous solutions. Different physicochemical factors such as initial concentration of ion, pH, and the equilibrium contact time were investigated. The best pH value for removal of Pb (II) from aqueous solutions was 6.5 and 4 hours was optimum contact time. The adsorption isotherms were obtained using concentrations of the lead ions ranging from 100 to 300 mg/L. It was seen that the process of adsorption was described by pseudo-second-order reaction kinetics, as well as Langmuir and Freundlich adsorption isotherms. The largest capacity of oval, cluster, leaves, small rod and pours nanosheets CuO nanostructures for Pb^2 are 125, 116, 117, 120 and 115 mg/g. Finally it is revealed that CuO nano structures was an active adsorbent for uptake of lead ions from aqueous solutions **[93].**

(Srivastava, et. al, 2013), studied the synthesis and characterization of copper oxide nanoparticles. It was synthesized by the chemical route and calcinations at temperature from 300 ° C to 400 ° C. For the comparison (TEM) and (XRD) measurements, showed a good agreement between data produced by spectroscopy and the microscopic measurements **[92].**

(Predescu, et. al, 2014), investigated the synthesis, characterization and adsorption efficiency of iron oxide nanoparticles covered with cationic resin for wastewater remediation. The magnetic nanoparticles were obtained by co-precipitation method, and then covered with cationic resin. The products were then characterized by (TEM) and (XRD). The removal efficiency was tested on a column with magnetic separation. The results demonstrated the fast adsorption of heavy metal ions on magnetic nanoparticles and the possibility to remove with high efficiency the toxic materials from wastewaters **[51].**

(Nithya, et. al, 2014), studied the preparation and characterization of copper oxide nanoparticles by modified sol-gel method using sodium dodecyl sulphate as a surfactant. Calcination temperature effect on particle size, band-gap, crystallinity and morphology of the nanoparticles were studied with the help of particle size analysis, UV-Spectroscopy, (XRD) and (SEM) studies. Also the prepared nanoparticles were tested for their activity towards gas sensing **[89].**

(Ahamed, et. al, 2014), studied the structural and antimicrobial properties of CuO nanoparticles synthesized by a simple precipitation method. Copper (II) acetate was used as a precursor and sodium hydroxide as a reducing agent. X-ray diffraction pattern showed the crystalline nature of copper oxide nanoparticles. Field emission scanning electron microscope (FESEM) and field emission transmission electron microscope (FETEM) demonstrated the morphology of CuO nanoparticles. The average diameter of CuO nanoparticles calculated by TEM and XRD was around 23 nm. Energy dispersive X-ray spectroscopy (EDS) spectrum and XRD pattern suggested that prepared CuO nanoparticles were highly pure. CuO nanoparticles showed excellent antimicrobial activity against various bacterial strains. Moreover, *E. coli* and *E. faecalis* exhibited the highest sensitivity to CuO nanoparticles while *K. pneumonia* was the least one **[91]**.

(Devi and Singh, 2014), discussed the preparation of copper oxide nanoparticles by using *Centella asiatica* (L.) leaves extracts at room temperature. This method is completely a green method, free from toxic and harmful solvent. Copper oxide particles such prepared are in nano scale and there morphology and size are characterized using SEM, UV–Visible spectroscopy, IR spectroscopy and EDX. Copper oxide nanoparticles synthesized by this method can be used for the photo catalytic degradation of methyl orange. These nanoparticles can reduce methyl orange in aqueous medium in the absent of reducing agents. It is more economic as compared to other methods. This catalytic effect of copper oxide nanoparticles can be contributed to its small size **[94]**.

1.11: The Aims of The Study

1- Preparation of (${Fe}_3O_4$) nanoparticles, (${Fe}_2O_3$) nanoparticles , and (CuO) nanoparticles by a simple precipitation method, and Characterization them by using X-ray diffraction (XRD) , scanning electron microscopic (SEM), and atomic force (AFM).

2- Measuring the efficiency of these oxides to remove nickel and lead ions from industrial wastewater after analyzing by using aqueous solutions containing these ions.

3- Determining the best adsorption of nickel and lead ions by using the three oxide nanoparticles (adsorbent) with a batch method at different contact time and initial concentration of aqueous solutions (adsorbate) with other constant condition such as pH value ,adsorbent dosage ,and temperature being the same .

4- Determining a suitable adsorption isotherm for each oxide to fit the adsorption and calculating the orders of the adsorption kinetics.