SYNTHESIS OF MAGNESIUM HYDROXIDE AND ITS APPLICATION IN HEAVY METAL REMOVAL

A thesis submitted in partial fulfilment of the requirements for the degree of

Master of Technology in Nanoscience and Technology

by

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Certificate

This is to certify that the entitled “**SYNTHESIS OF MAGNESIUM HYDROXIDE AND ITS APPLICITION IN HEAVY METAL REMOVAL”** has been carried out by Mr **Utpal Sarkar (**Registration No 141058 of 2017-2018**)** under my guidance and supervision and accepted in partial fulfilment for the degree of Master of Technology in Nano science and Technology, Jadavpur University. To the Best of our knowledge the contents of this thesis or any part thereof have not been previously submitted for the award of any degree or diploma.

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This foregoing thesis is hereby approved as a credible study of an engineering subject carried out and presented in a manner satisfactorily to warranty its acceptance as a prerequisite to the degree for which it has been submitted. It is understood that by this approval the undersigned do not endorse or approve any statement made or opinion expressed or conclusion drawn therein but approve the thesis only for purpose for which it has been submitted.

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I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of his **“SYNTHESIS OF MAGNESIUM HYDROXIDE AND ITS APPLICATION IN HEAVY METAL REMOVAL”** studies.

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Abstract

Magnesium hydroxide is synthesized using magnesium salt & ammonium hydroxide in presence of a non-ionic compounds respectively the group of poly ethyl glycols as surface modifier. Obtain magnesium hydroxide samples are characterize by XRD, FESEM & HRTEM. FESEM images reveal flower like structure morphology.

Presence of heavy metal like cadmium ions in water is very harmful for human health & permissible limit set by world health organisation (WHO) in drinking water 0.003 mg/l. The magnesium hydroxide nanostructure surface pores are able to adsorb the cadmium ions from 10 mg/l concentration to 0.201 mg/l concentration for a given amount magnesium hydroxide. The adsorption of cadmium ions will be more with the increased magnesium hydroxide amount & time of adsorption. So magnesium hydroxide may be an important material for water purification systems.

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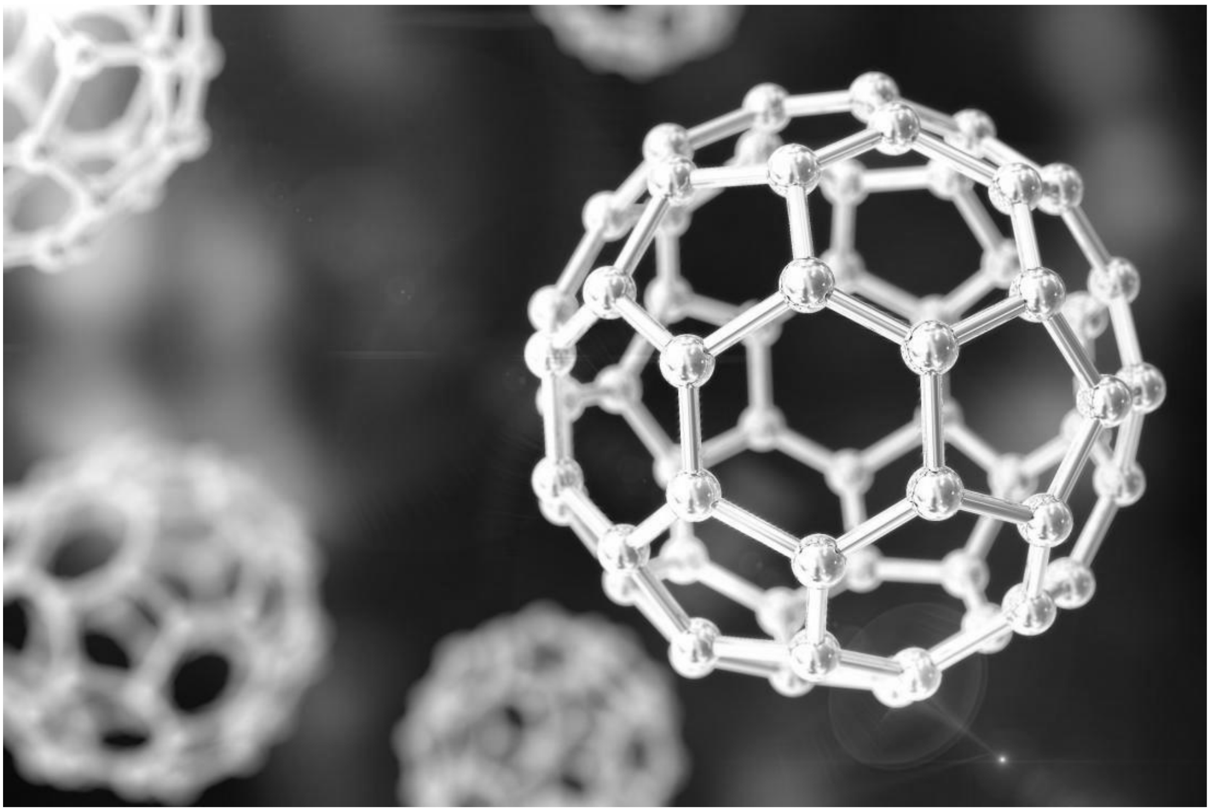

Chapter 1

Introduction to nanotechnology

1. Introduction

1.1 Introduction to Nanoscience & Nanotechnology :

Nanotechnology is science, engineering, and technology conducted at the nanoscale, which is about 1 to 100 nanometers. One nanometer is a billionth of a meter, or 10^{-9} of a meter. Nanotechnology is manipulation of matter on an atomic, molecular, and supramolecular scale. Nanotechnology as defined by size is naturally very broad, including fields of science as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, energy storage, microfabrication, molecular engineering, etc. The associated research and applications are equally diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to direct control of matter on the atomic scale.

1.1.1 What is nanotechnology?

Most definitions revolve around the study and control of phenomena and materials at length scales below 100 nm and quite often they make a comparison with a human hair, which is about 80,000 nm wide.

It seems that a size limitation to the 1-100 nm range, the area where size-dependant quantum effects come to bear, would exclude numerous materials and devices, especially in the pharmaceutical area, and some experts caution against a rigid definition based on a sub-100 nm size. This definition reflects the fact that quantum mechanical effects are important at this quantum-realm, and so the definition shifted from a particular technological goal to a research category inclusive of all types of research and technologies that deal with the special properties of matter which occur below the given size threshold. It is therefore common to see the plural form "nanotechnologies" as well as "nanoscale technologies" to refer to the broad range of research and applications whose common trait is size.

Another important criteria for the definition is the requirement that the nano-structure is man-made, i.e. a synthetically produced nanoparticle or nanomaterial. Otherwise we would have to include every naturally formed biomolecule and material particle, in effect redefining much of chemistry and molecular biology as 'nanotechnology‘.

1.1.2 How it started?

The ideas and concepts behind nanoscience and nanotechnology started with a talk entitled ―There‘s Plenty of Room at the Bottom‖ by physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology on December 29, 1959; long before the term nanotechnology was used. In his talk, Feynman described a process in which scientists would be able to manipulate and control individual atoms and molecules. Thus, physicist Richard Feynman is called the father of nanotechnology.

1.1.3 Who coined the term Nanotechnology?

The term was coined in 1974 by Norio Taniguchi of Tokyo Science University to describe semiconductor processes such as thin-film deposition that deal with control on the order of nanometers. It wasn't until 1981, with the development of the scanning tunneling microscope that could "see" individual atoms, with which modern nanotechnology began.

Inspired by Feynman's concepts, K. Eric Drexler used the term "nanotechnology" in his 1986 book Engines of Creation: The Coming Era of Nanotechnology, which proposed the idea of a nanoscale "assembler" which would be able to build a copy of itself and of other items of arbitrary complexity with atomic control [2,3].

Today, scientists and engineers are finding a wide variety of ways to deliberately make materials at the nanoscale to take advantage of their enhanced properties such as higher strength, lighter weight, increased control of light spectrum, and greater chemical reactivity than their larger-scale or bulk counterparts.

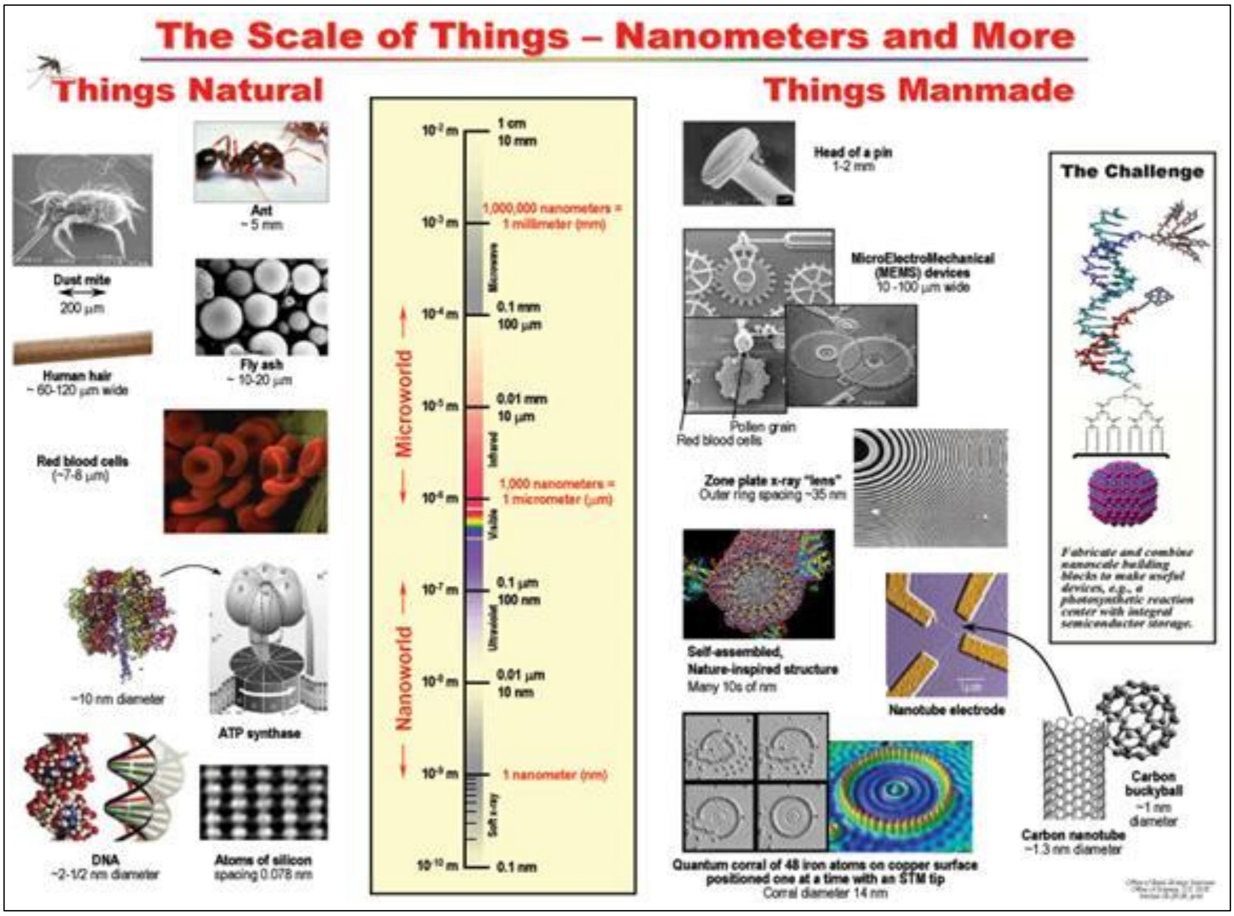

Figure 1: Schematic diagram of nanotechnology and its size comparison

1.1.4 A brief history of nanotechnology:

- **2000 years ago**: Sulphide Nano crystals used by Greeks and Romans to dye hair.
- **1000 years ago (middle ages):** Gold nanoparticles of different sizes used to produce different colours in stained glass windows.

- **1959:** Physicist Richard Feynman gave a radical lecture at an American Physical Society meeting at Caltech titled ―There is plenty of room at the bottom‖.

- **1974:** 'Nanotechnology'- Professor Norio Taniguchi for the first time uses the term nanotechnology [4].

- IBM develops Scanning Tunnelling Microscope [5].
- **1985:** 'Buckyball'- Scientists at Rice University and University of Sussex discover Fullerene (C60) [6].

- **1986:** 'Engines of Creation'- First book on nanotechnology by K. Eric Drexler [7]. Atomic Force Microscope invented by Binnig, Quate, and Gerbe.

- IBM logo made with individual atoms.
- **1991:** Carbon Nanotubes discovered by S. Ijima.
- **1999:** "Nano medicine"- First Nano medicine book by R. Freitas.
- **2000:** 'National Nanotechnology Initiative' was launched.

1.1.5 What distinguishes nanomaterial from bulk?

While most micro structured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometre dimensions are significantly different from those of atoms and bulk materials. Among the characteristics of nanomaterial that distinguish them from bulk materials, it is important to note the following:

- Large fraction of surface atoms;
- High surface energy;
- Spatial confinement
- Reduced numbers of imperfections that do not exist in the corresponding bulk materials [1].

1.1.6 Classification of Nanomaterials

This classification is based on the number of dimensions of a material, which are outside the nanoscale (<100 nm) range.[1]

Accordingly,

- In zero-dimensional (0D) nanomaterials all the dimensions are measured within the nanoscale (no dimensions are larger than 100 nm). Most commonly, 0D nanomaterials are nanoparticles.
- In one-dimensional nanomaterials (1D), one dimension is outside the nanoscale. This class includes nanotubes, nanorods, and nanowires.
- In two-dimensional nanomaterials (2D), two dimensions are outside the nanoscale. This class exhibits plate-like shapes and includes graphene, nanofilms, nanolayers, and nanocoatings.
- Three-dimensional nanomaterials (3D) are materials that are not confined to the nanoscale in any dimension. This class can contain bulk powders, dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multi-nanolayers.

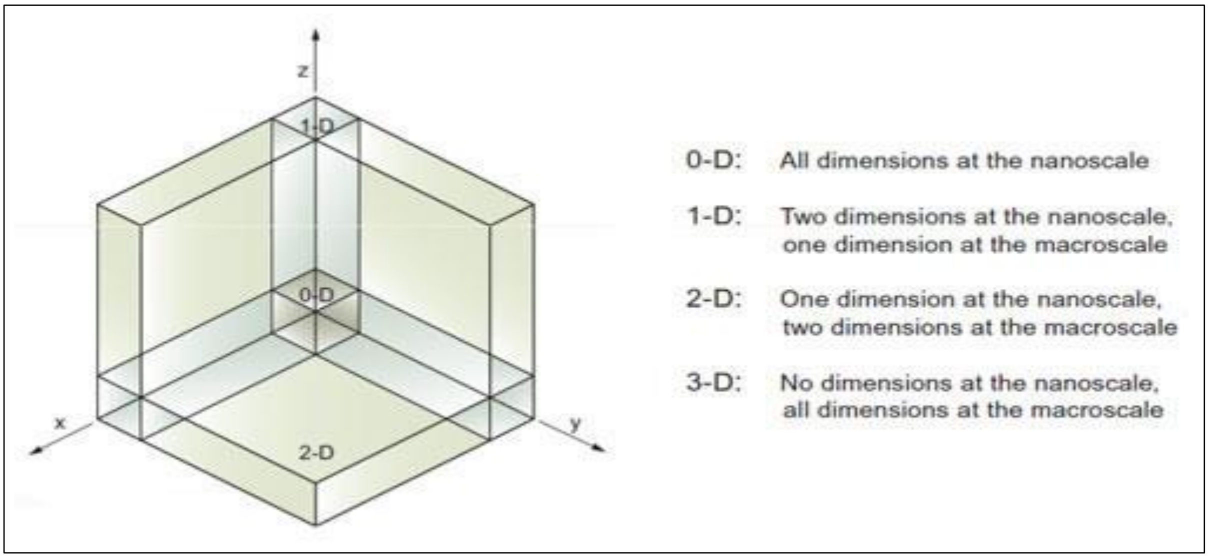

Figure2: Classification of nanoscale dimensions. (Source: Tallinn University of Technology)

1.1.7 Synthesis of Nanomaterials

In order to explore the unique physical properties & phenomena and also to realize the useful applications of nanostructures and nanomaterial, the ability to fabricate and process nanomaterial and nanostructures is the first hurdle in nanotechnology. The following schematic diagram in Fig3 shows the two significant approaches in the synthesis of nanomaterial.

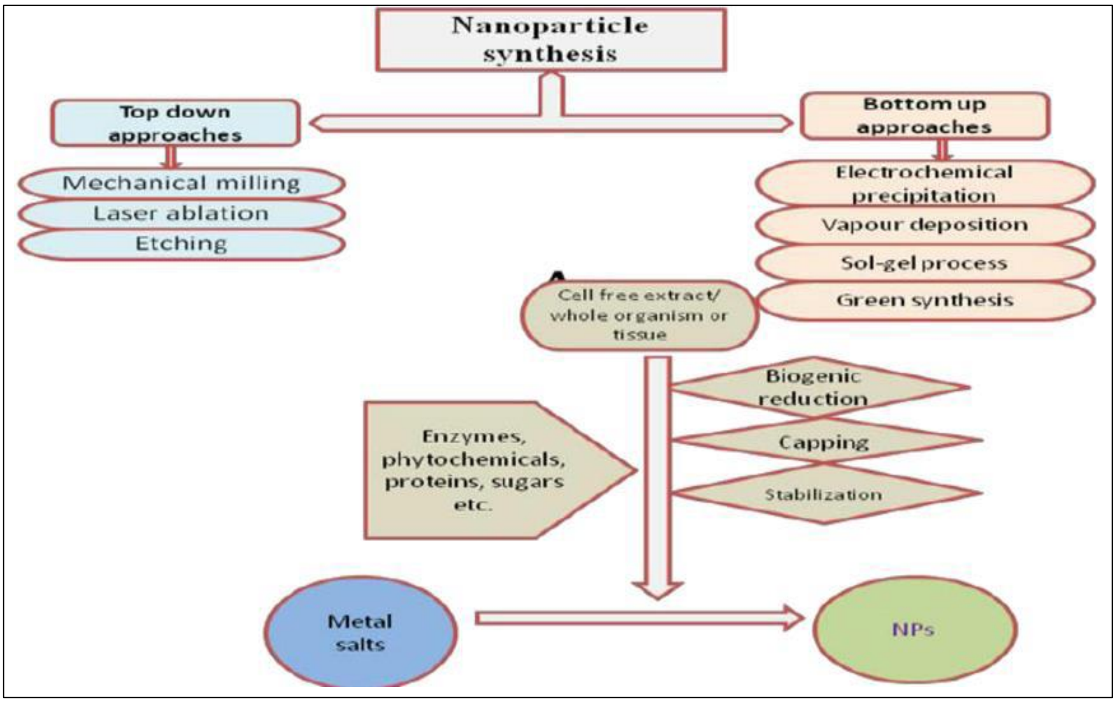

Figure3: Schematic diagram of different synthesis approaches of nanomaterials

For the fabrication and processing of nanomaterial and nanostructures, the following challenges must be taken care of [1]:

- Overcome the huge surface energy, a result of enormous surface area or large surface-to- volume ratio.
- Ensure all nanomaterial with desired size, uniform size distribution, morphology, crystallinity, chemical composition, and microstructure which result in desired physical properties.

- Prevent nanomaterial and nanostructures from coarsening through either Ostwald ripening or agglomeration.

Many technologies have been explored to fabricate nanostructures and nanomaterial. These technical approaches can be grouped in several ways like growth media or the form of products.

Top Down' and 'Bottom Up Approach':

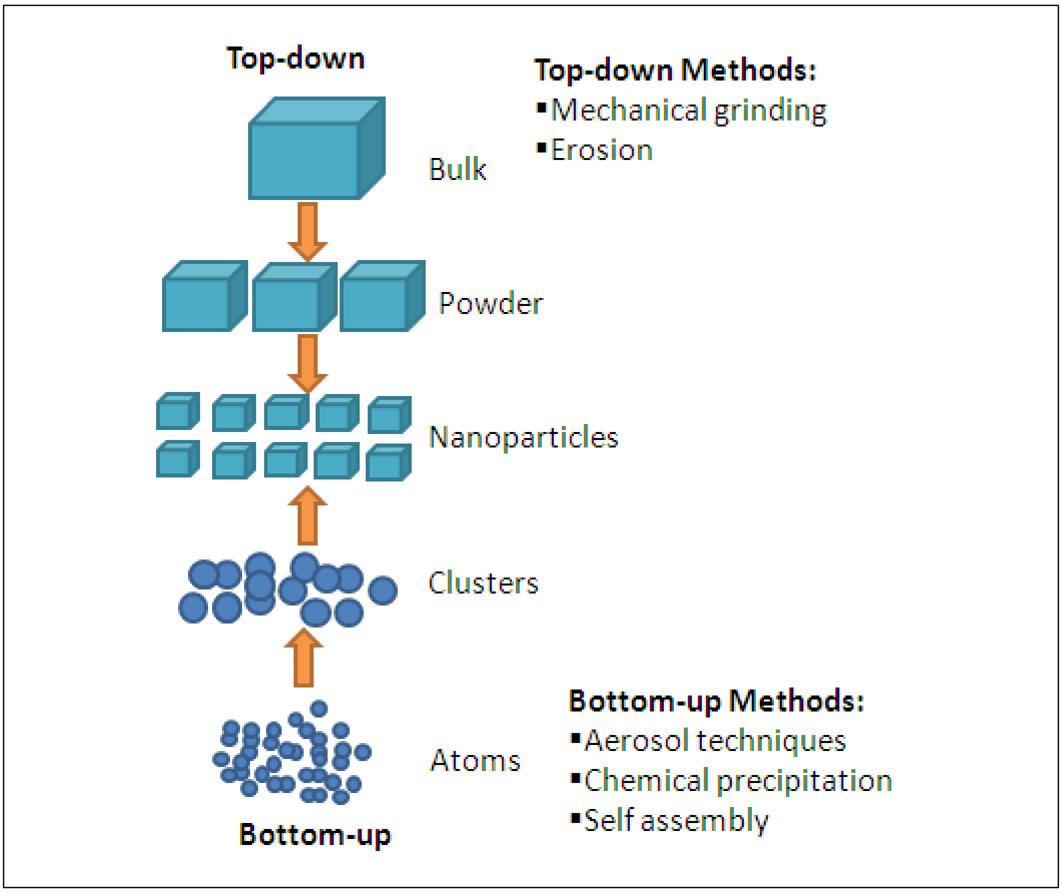

Fig4: Schematic diagram of Top Down and Bottom Up Approach [7]

The top down approach uses traditional methods to guide the synthesis of Nano scale materials [1, 8]. The paradigm proper of its definition generally dictates that in the top down approach it all begins from a bulk piece of material, which is then gradually or step by step removed to form objects in the nanometre-size regime. Well known techniques such as photo lithography and electron beam lithography, anodization, ion and plasma etching all belong to this type of approach. The bottom up approach is exactly the opposite of top down approach. In this case instead of starting with large materials and chipping it away to reveal small bits of it, it all begins from atoms and molecules that get rearranged and assembled to large nanostructures. It is the new paradigm for synthesis in the nanotechnology world as the bottom up approach allows a creation of diverse types of nanomaterial, and it is likely to revolutionize the way of material fabrication. Schematic representation of Bottom up and Top down approach is shown in Fig4.

1.2 Applications of Nanotechnology

1.2.1 Nanotechnological processes for wastewater treatment

1.2.1.1 Nanomaterials for adsorption of pollutants

Nanoparticles possess two important characteristics that make them very good adsorbents. These are the large specific surface of nanomaterials and surface multifunctionality or the ability to easily chemically react and bind to different adjacent atoms and molecules (Figure 9). These characteristics make nanoparticles not only effective adsorbents for various contaminants in wastewater but also allow for long-term stability, as this also results in adsorbent degradation (with the addition of catalytic properties of nanoparticles) and improves the adsorption efficiency.

In addition, nanomaterials possess unique mechanical, electrical, chemical, optical and many other characteristics that allow them to have much better adsorption properties for some contaminants (heavy metals and organic pollutants). This is why they are called the "material of the 21st century"[9,10]

1.2.1.2 Nanomaterials for water disinfection

In addition to having excellent adsorption and catalytic properties, some nanomaterials have proven to have great antimicrobial activity as well. Such materials include chitosan, silver nanoparticles, titanium dioxide, fullerene nanoparticles, carbon nanotubes, etc. All these nanomaterials are mild oxidants and are relatively inert in water, and are therefore note expected to create harmful by-products. There are several ways of applying the nanomaterials in water disinfection processes:[11]

1.2.1.3 Nanofiltration

Membrane filtration plays an important role in removing various types of contamination and enables high level of water purification. Until recently, its biggest problem was a substantial investment cost (about 70 % of the total investment cost refers to membranes). As the price is lowering, the membrane wastewater treatment process becomes more and more popular in the market, mainly due to its high efficiency in the removal of solid waste materials, monovalent and divalent ions, various pathogens, etc. Nanofiltration (with reverse osmosis, RO) is a high-pressure membrane treatment process. But unlike the RO, it requires a much lower drive pressure (7 to 14 bar), and so allows lower energy consumption. Centrifugal pumps are most often used for the pressure and circulation of wastewater within the nanomembrane.[12]

1.2.2 Nanotechnology in Energy and Environment:

Energy crisis and environmental pollution in present days have severe negative impact in human life. To provide sufficient energy to the developing world, nanotechnology is the key factor because less expensive improved energy can be produced through suitable nanomaterial.

- Fuel cell (e.g. CNT) for hydrogen storage and related automobile applications.
- Cheap, light weight and more efficient metal oxide nanomaterial photovoltaic application for the purpose of water splitting and efficient dye sensitized solar cell.
- Nanotechnology can be used to the further reduction of combustion engine pollutants by nanoporous filters; this can clean the exhaust mechanically.
- Solid state lightening is a powerful tool to reduce total electricity consumption by 10% and cut carbon emission by the equivalent of 28 million tons/year.

1.2.3 Nanotechnology in Health and Medicine:

Nanotechnology has a high impact on the research and applications related to biology and medicine. Nano-drug delivery is the safest procedure for medication because small quantity of nanomaterial can help to recover with reducing side effects. Nano medicine has also the potential to enable early detection and prevention, and to essentially improve diagnosis, treatment and follow-up of diseases with the help of bio-sensors.

- Carbon nanotubes have promising application for the development of advanced biosensors with novel features.
- Nano devices can make gene sequencing more efficient.
- Tissue engineering makes use of artificially stimulated cell which can help in transplantation of organs or artificial implants.
- The technology is also being used to develop sensors for cancer diagnostics.

1.2.4 Nanotechnology in Transportation:

Nanomaterial is used as faster and cost effective new fuel source. The main advantage of using nanomaterial is light weight so that easy to carry in fuel chamber of cars and aeroplanes.

- Suitable Nanomaterials can effectively reduce the emission of pollutants in the process of incomplete combustion in engine. Nano Twin Technologies has recently released an air filter to remove hazardous chemicals from the air in car cabins.
- Nanoparticles of inorganic clays and polymers are an effective alternative for carbon black tires results in environmental friendly, wear resistant tires. Frictional resistant tires are also made possible through Nano science.

- Nano coating of metallic surfaces such as steel to achieve super-hardening, low friction, and enhanced corrosion protection.

1.2.5 Nanotechnology in Defence and Security:

Nanotechnology will lead to higher protection, more lethality, longer endurance and better self-supporting capacities of future combat soldiers. Substantial advantages are expected to be gained which include threat detection, novel electronic display and interface systems, as well as a pivotal role for the development of miniaturised unmanned combat vehicles and robotics. Nanotechnology will also enable small portable sensor systems capable of identifying chemical, biological and nuclear, radiation, or explosive threats.

1.2.6 Nanotechnology in Information & Communication:

Electronic memory designs in the past have largely relied on the formation of transistors. The miniaturization of electronic industry has been the driving force behind the rapid research and development of Nano science and technology. Continuing to shrink silicon chips is getting expensive and difficult. Chips built using the molecular transistors are the industry's best hope for building faster, cheaper computers well into this century. "With the electronics we're talking about, we're going to make a computer that doesn't just fit in your wristwatch, not just in a button on your shirt, but in one of the fibres of your shirt," says Philip Kuekes, a computer architect at Hewlett-Packard Laboratories. According to the manufacturers, NRAM (Nanotube-based/Non-volatile random access memory) is a universal memory chip suitable for countless existing and new applications in the field of electronics. In the modern communication technology traditional analog electrical devices are increasingly replaced by optical or optoelectronic devices due to their enormous bandwidth and capacity. Two promising examples are photonic crystals and quantum dots. Quantum dots are nanoscale objects, which can be used for the construction of lasers.

1.3 Introduction to Heavy Metal Removal

The environmental issues due to globalization and rapid industrialization are becoming more and more nuisance for human being. Therefore efficient and effective methods are needed especially for chemical industries. Heavy metals present in wastewater and industrial effluent is major concern of environmental pollution. Heavy metals are generally considered those whose density exceeds 5 g per cubic centimeter. Most of the elements falls into this category are highly water soluble, well-known toxics and carcinogenic agents. Heavy metals are considered to be the following elements: Copper, Silver, Zinc, Cadmium, Gold, Mercury, Lead, Chromium, Iron, Nickel, Tin, Arsenic, Selenium, Molybdenum, Cobalt, Manganese, and Aluminum. They represent serious threats to the human population and the fauna and flora of the receiving water bodies [13]. They can be absorbed and accumulated in human body and caused serious health effects like cancer, organ damage, nervous system damage, and in extreme cases, death. Heavy metals such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium are generated in electroplating, electrolysis depositions, conversion-coating, and anodizing-cleaning, milling, and etching industries.

As the low amounts of these metals are highly toxic, removal of heavy metals from wastewater has recently become the subject of considerable interest owing to strict legislations.Wastewater regulations were established to minimize human and environmental exposure to hazardous chemicals[14]. These include limits on the types and concentration of heavy metals that may be present in the discharged wastewater. The Maximum Contaminated Level (MCL) standards, for those heavy metals, established by USEPA [15].

1.4 Introduction for Magnesium hydroxide Synthesis

Magnesium hydroxide and magnesium oxide have been extensively studies. Magnesium and its alloys posses unique properties such as low weight and non toxicity [16]. These properties are advantageous for various device in the field of electronics, aerospace, automobile applications and biomedicine.it has also been used as acidic waste neutralizer in environmental protection, in paper manufacturing, as a fertilizer additive [17,18] and most important waste water treatment. The synthesis of magnesium hydroxide using different magnesium salt and ammonium hydroxide is possess. The reaction was perfoed in the presence of non inonic compounds representing the group of poly as modifiers. Dispersive properties of the product were characterised by polydispersity indes, particle size, as well as FESEM and HRTEM and the crystallinity of the product can be measured by XRD techniques.

Different synthesis process of magnesium hydroxide

1.4.1 Synthesis of Magnesium Hydroxide Using a Spinning Disk Reactor

Magnesium hydroxide, so-called brucite, is usually used in flame retardant composite formulations because of its ability to undergo endothermic dehydration in fire conditions.[19] Many methods for synthesizing magnesium hydroxide nanoparticles, including the precipitation method,[20] hydrothermal method,[21,22] and sol-gel method,[23,24] have been developed, but most of them are in laboratory scale. Furthermore, these methods are time-consuming or expensive and difficult to scale up. , it is usually used in fire-resisting bricks orcrucibles. It is also an exceptionally important material for use in catalysis and toxic waste remediation, or as an additive in paint and superconductor products[22]. Higee equipment has

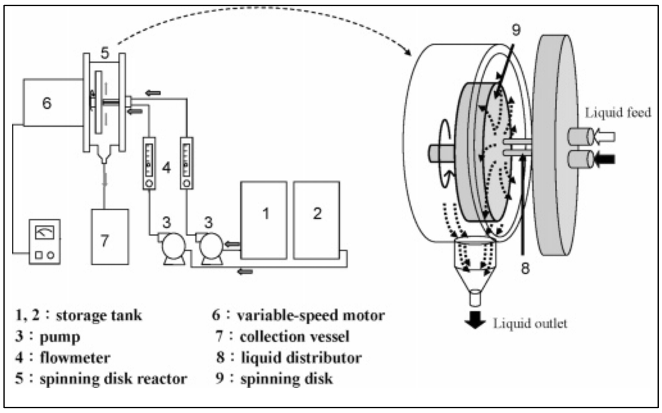

Figure 5: A schematic diagram of the Higee

been developing for many years[25]. There are two types of devices, i.e., the high-gravity rotating packedbed reactor (RPBR) and the spinning disk reactor (SDR). Compared with an RPBR, an SDR is a simpler type of equipment, in which the liquid spreads over a disk to form a thin film due to the high centrifugal force caused by spinning.

The chemical reactions involved in the formation of magnesium hydroxide and oxide are as follows:

$$\mathbf{MgCl_2(aq) + 2NaOH(aq) \text{ --}\!\rightarrow Mg(OH)_2(s) + 2NaCl(aq)}$$

1.4.2 Synthesis of Magnesium Hydroxide via cathodic Electrodeposition

Metal hydroxide was synthesized by cathodic reduction of its nitrate solution potentiostatically at appropriate negative voltage using indium tin oxide (ITO)-coated conductive glass slides (≈200 Ω/□) as a working electrode. A platinum wire was used as the counter electrode; the working electrode potential during electrolysis was measured with respect to a saturated calomel electrode (SCE). Electrolysis of magnesium salt solutions was performed in a single conventional compartment cell. Prior to electrodeposition, the glass substrate was cleaned in a standard procedure. In a typical run, 5.12 g of $Mg(NO_3)_2{\cdot}6H_2O$ and 4.04 g of KNO_3 were dissolved in 200 Ml of deionized water to make a stock solution, all experiments were carried out on potentiostatic electrolysis (CHI660B potentiostat/galvanostat) at ambient temperature duration time of 1.5 h and the product formed on glass substrate. The deposited films were rinsed thoroughly with deionized water to remove the residual and dried to a constant weigh at 50 °C for further physical characterization[26].

1.4.3 Synthesis of Magnesium Hydroxide nanorods by liquid–solid arc discharge technique:

The 0.5 mol NaCl was used as electrolyte during liquid–solid arc discharge. Two strips of metal magnesium performed as two electrodes. The distance between them was about 3 cm. The end of one electrode was held tight into the cell while another one was put in and off solvent periodically. The interval is about 5 s. This process was keeping for 5 min. The changeable pulse voltage could be adjusted in the range of 50–200 V. To preserve the reaction at a constantly low temperature, the electrolytic cell was put in an bigger circulating water flume. After being centrifuged, the white participate was washed by distilled water and absolute alcohol several times to remove the residue of NaCl, then dried in vacuum at 80 C.

During the process of liquid–solid arc discharge, high heat was emitted from instantaneous circulation between two electrodes, making the metal Mg electrode melted. The metal colloid has high concentration near the electrode [27]. Their activity could let them reacted with the OH to form $Mg(OH)_2$ in the natural or basic electrolyte. The mechanism of the formation of the $Mg(OH)_2$ nanorods is supposed as follow:

$$\mathbf{Mg\ (metal)\ \text{-----}\!\rightarrow Mg\ (colloid)\ \text{------}\!\rightarrow Mg^{2+}}$$

$$\mathbf{\text{-----}\!\rightarrow Mg(OH)_2\ (metal)}$$

1.4.4 Synthesis of Magnesium Hydroxide using nanosecond pulsed laser ablation in liquids:

Pulsed laser ablation in liquid media (PLAL) is a promising technique for the controlled fabrication of nanomaterials via rapid reactive quenching of ablated species at the interface between the plasma and liquid. PLAL is a versatile technique for preparing various kinds of nanoparticles (NPs) such as noble metals, alloys, oxides and semiconductors.[28] The features of PLAL are as follows. Well crystallized NPs can easily be obtained in one-step procedures without subsequent heat-treatments [29,30] because of the high energetic state of ablated species. Certain pure NP colloidal solutions can be formed without the formation of by-products. In addition, chemicals such as surfactants can be added to liquids in order to control the size and the aggregation state of NPs by changing the surface charge of the nuclei. The entire product can be completely collected in solutions, and the obtained colloid solution is very easy to handle. The production system does not require costly vacuum chambers.

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Chapter2. Literature Survey

2.1. Heavy Metal Toxicity

Heavy metals are elements having atomic weights between *63.5* and 200.6, and aspecific gravity greater than *5.0*.Most of the heavy metals are dangerous to health or to the environment. Heavy metals in industrial wastewater include cadmium, lead, chromium, mercury, uranium, selenium, zinc, arsenic, silver, gold, and nickel.The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO. Heavy metals are major pollutants in marine, ground, industrial and even treated wastewater. Most of the point sources of heavy metal pollutants are industrial wastewater from mining, metal processing, tanneries, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, lumber and wood products. Heavy metal exposure has been implicated in several diseases and may increase the risk of cancers.

2.2. Source of Heavy Metal

Heavy metal	Source	Effect
Cadmium	Usage of phosphate fertilizer, NiCd batteries, colour pigment and plastic industries, metal painting	Kidney damage, renal disorder, human carcinogen, disestive system, respiratory system
Arsenic	Pharmaceutical and glass industries, incineration of preserved wood products such as play structure, boardwalks	

Copper	Water pipes; Copper water heaters, Alcoholic beverages, Pesticides, Insecticides, fungicides, Copper Jewelry, Copper cooking pots	Mental disorders, Anaemia; Arthritis, Hypertension, vomiting, Autism, Postpartum Inflammation and enlargement of liver, heart problem.
Chromium	Steel and textile industry	Skin rashes, respiratory problems, acute renal failure, weakened immune systems, kidney and liver damage, lung cancer,
Nickel	Effluents of silver refineries, electroplating, zinc base casting and storage battery industries.	Dermatitis, Encephalopathy, cancer of lungs, nose and bone, headache, dizziness, nausea and vomiting, chest pain, rapid respiration.
Lead	Industries such as mining, steel, automobile, batteries and paints, Pollutants arising from increasing industrialization	Headache and vomiting, Learning difficulties, Mental retardation, Vertigo, kidney damage, Birth defects, Muscle weakness, Thyroid dysfunction, Insomnia, Fatigue.
Mercury	Industries like chloro-alkali, paints, pulp and paper, oil refining, rubber processing and fertilizer,	Tremors, Birth defects, Kidney damage, Tooth loss

Table 1: Sources and toxicological effects of some heavy metals: [1].

Heavy metal	Cadmium	Arsenic	Copper	Chromium	Nickel	Lead	Mercury
MCL(mg/l)	0.01	0.05	0.25	0.05	0.20	0.006	0.00003

TABLE 2. The MCL standards for the most hazardous heavy metals [2]

2.3. Importance of Heavy metal Removal.

Heavy metal pollution has become one of the most serious environmental problems today. The treatment of heavy metals is of special concern due to their recalcitrance and persistence in the environment. The environmental issues due to globalization and rapid industrialization are becoming more and more nuisance for human being. (Gunatilake S.K.Department of Natural Resources Sabaragamuwa University of Sri Lanka Belihuloya, Sri Lanka). Most of the elements falls into this category are highly water soluble, well-known toxics and carcinogenic agents. Heavy metals are considered to be the following elements: Copper, Silver, Zinc, Cadmium, Gold, Mercury, Lead, Chromium, Iron, Nickel, Tin, Arsenic, Selenium, Molybdenum, Cobalt, Manganese, and Aluminum. They represent serious threats to the human population and the fauna and flora of the receiving water bodies [3]. They can be absorbed and accumulated in human body and caused serious health effects like cancer, organ damage, nervous system damage, and in extreme cases, death. Wood processing industries where a chromated copper-arsenate wood treatment produces arsenic containing wastes; inorganic pigment manufacturing producing pigments contain chromium compounds and cadmium sulfide; petroleum refining generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and ferrocyanide. All of these generators produce a large quantity of wastewaters, residues, and sludge that can be categorized as hazardous wastes requiring extensive waste treatment [4].

2.4. Various Conventional Methods of Heavy Metal Removal

Non-biodegradable contaminants pose a serious health and environmental hazard and removal of these wastes cannot be achieved using secondary methods. Hence, tertiary/advanced wastewater treatment methods such as ion exchange, precipitation, membrane separation, electrolysis and adsorption_ can be used to remove these recalcitrant wastes. So far, a number of efficient methods have been developed for heavy metal removal.[5] reviewed various methods for the removal of heavy metals such as chemical precipitation, adsorption, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, nanofiltration, coagulation, flocculation, floatation, etc. Generally, these processes are efficient in removing the bulk of metals from solution at high or moderate concentrations. Instead of using commercial activated to remove heavy metal researchers have worked on inexpensive materials, such as magnesium hydroxide[6], chitosan, zeolites, and other adsorbents. This process brief introduction given below

2.4.1 Chemical Precipitation:

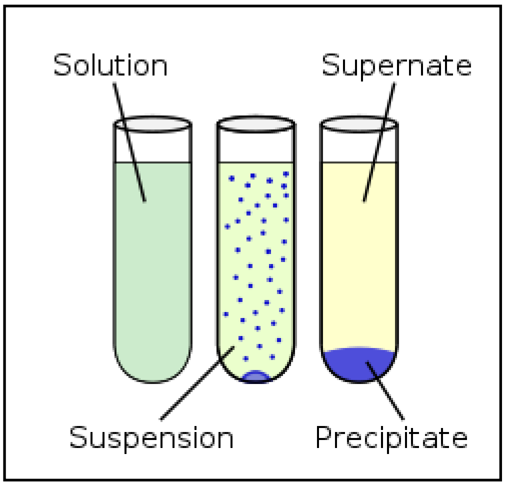
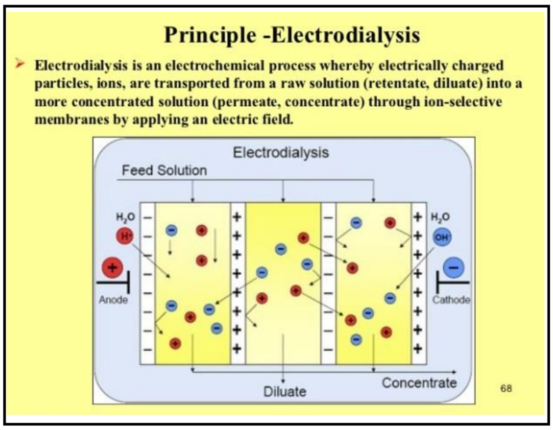


Figure1: Chemical precipitation

Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The large amount of sludge containing toxic compounds produced during the process is the main disadvantage.

2.4.2 Electrodialysis



Principle -Electrodialysis

- **Electrodialysis is an electrochemical process whereby electrically charged particles, ions, are transported from a raw solution (retentate, diluate) into a more concentrated solution (permeate, concentrate) through ion-selective membranes by applying an electric field.**

Figure 2: Principle of Electrodialysis

In this process, the ionic components (heavy metals) are separated through the use of semi-permeable ionselective membranes. Application of an electrical potential between the two electrodes causes a migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes, cells of concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides, which clog the membrane.

2.4.3 Adsorption

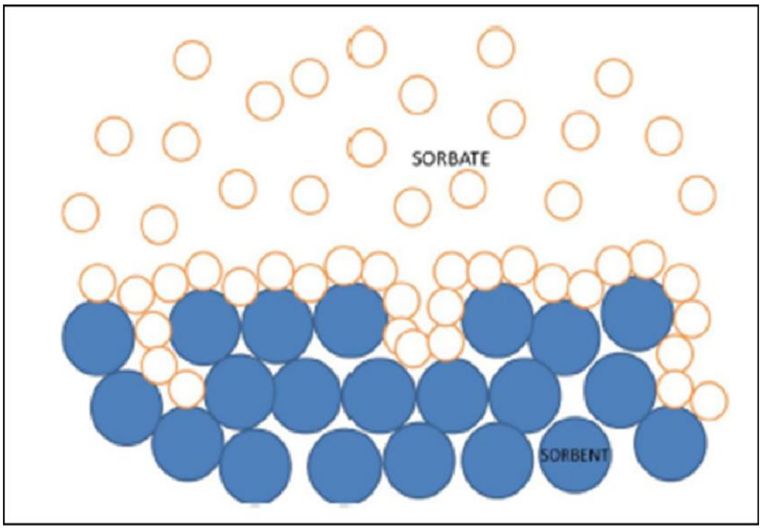


Figure3: Adsorption principle

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Among these methods, adsorption is currently considered to be very suitable for wastewater treatment because of its simplicity and cost effectiveness . Adsorption is commonly used technique for the removal of metal ions from various industrial effluents [7].

Magnesium Hydroxide is most widely use adsorbent. It is highly porous material and synthesis process is cost effective. Figure3: adsorption principle

2.4.4 Coagulation/ flocculation

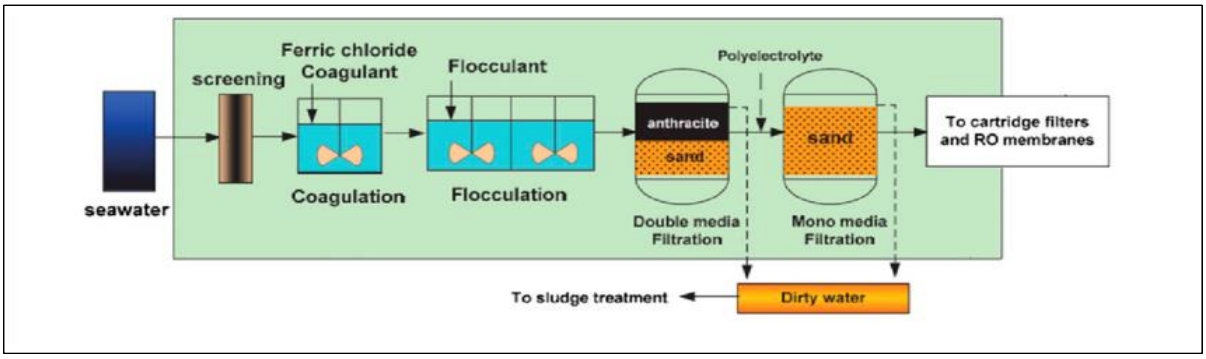


Figure4: principle of Coagulation

Coagulation and flocculation are an essential part of drinking water treatment as well as wastewater treatment. Coagulation is the chemical reaction which occurs when achemical or coagulant is added to the water. The coagulant encourages the colloidalmaterial in the water to join together into small aggregates called “flocs”. Suspendedmatter is then attracted to these flocs. Flocculation is a slow gentle mixing of the waterto encourage the flocs to form and grow to a size which will easily settle out. The basic mechanisms involved in the removal of organic contaminants by coagulation. Kuo et al. studied the effects of initial pH and turbidity, alum and pre ozonation doses, and flocculation time on the removal of dis solved organic matter during alum coagulation.[8]

2.4.5 Ultrafiltration

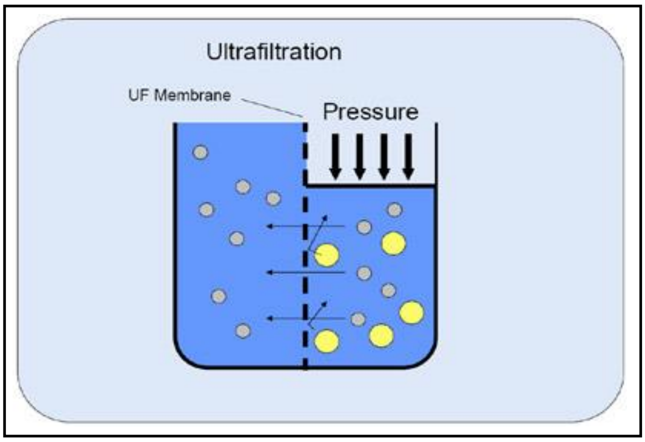


Figure5: Principle of Ultrafiltration

Ultrafiltration is a separation process using membranes with pore sizes in the range of 0.1 to 0.001 micron. Typically, ultrafiltration will remove high molecular-weight substances, colloidal materials, and organic and inorganic polymeric molecules. It is a pressure-driven purification process in which water and low molecular weight substances permeate a membrane while particles, colloids, and macromolecules are retained. The primary removal mechanism is size exclusion, although the electrical charge and surface chemistry of the particles or membrane may affect the purification efficiency.

2.4.6 Reverse osmosis

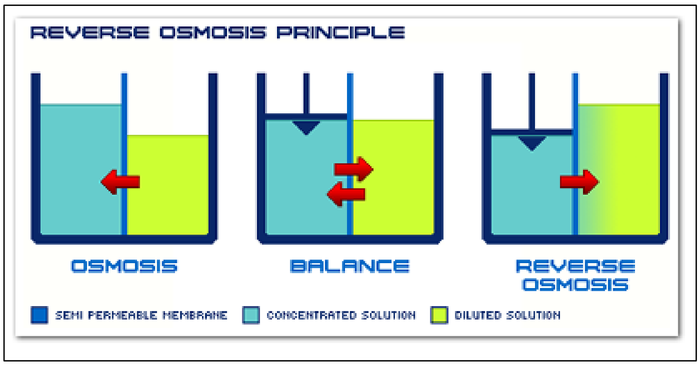


Figure6: Principle of Osmosis

In this RO process when a pressure is applied to the concentrated side of the membrane forcing purified water into the dilute side, the rejected impurities from the concentrated side being washed away in the reject water. Applications that have been reported for RO processes include the treatment of organic containing wastewater, wastewater from electroplating and metal finishing, pulp and paper, mining and petrochemical, textile, and food processing industries, radioactive wastewater, municipal wastewater, and contaminated groundwater [9].

2.4.7 Ion Exchange

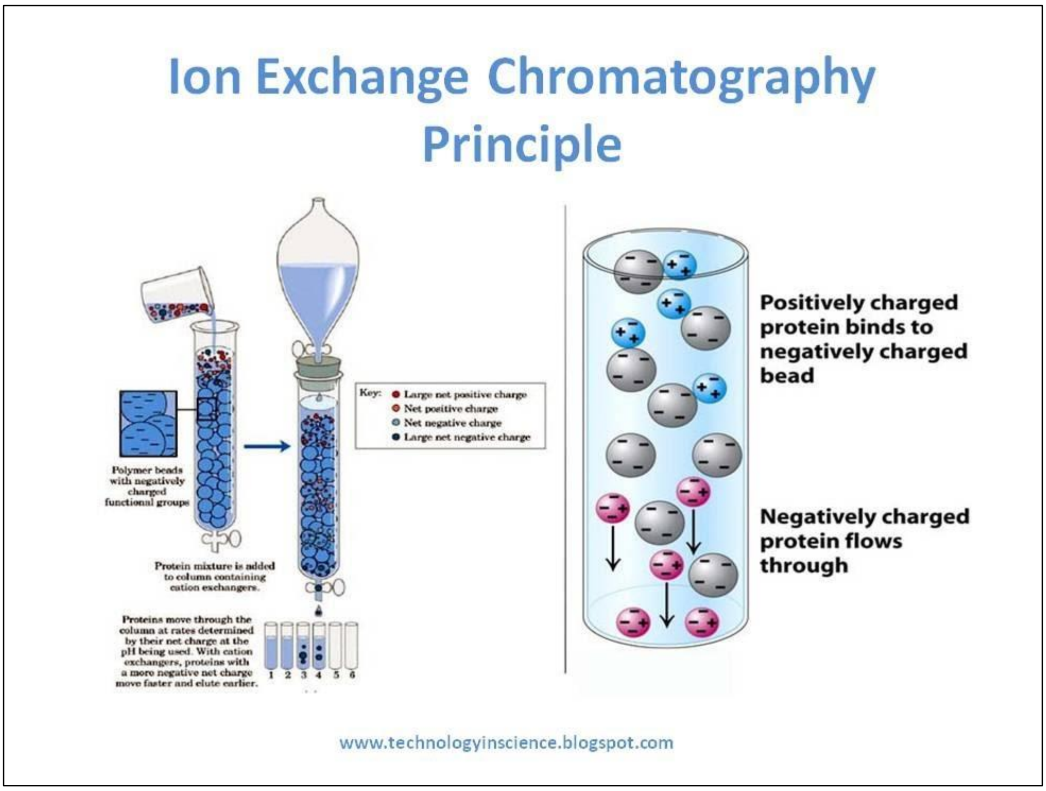


Figure7: Principle of Ion Exchange

Ion exchange can attract soluble ions from the liquid phase to the solid phase, which is the most widely used method in water treatment industry. As a cost-effective method, ion exchange process normally involves low-cost materials and convenient operations, and it has been proved to be very effective for removing heavy metals from aqueous solutions, particular for treating water with low concentration of heavy metals [10, 11]. In this process cations or anions containing special ion exchanger is used to remove metal ions in the solution.

2.5. Adsorption

i) Adsorption is the adhesion of atoms, ions or molecule from a gas, liquid or dissolved solid to a surface.

ii) This process creates a film of the adsorbate on the surface of the adsorbent.

This process differs from absorption in which a solute is dissolved by a liquid or solid.

iii) Adsorption is a surface based process while adsorption involves the whole volume of the material.

iv) Adsorption is present in many natural, physical, biological and chemical system and is widely used in industrial application such as activated charcoal computing and using waste heat to provide cold water for air conditioner, waste water purification.

2.6. Different adsorbent materials

The most important property that a good adsorbent [12,13] should possess is a porous structure resulting in high surface area. In addition, the time taken for adsorption equilibrium to be established should be as small as possible so that it can be used to remove contaminants in lesser time. Thus, for removal of pollutants, one looks to adsorbents with high surface area and porosity and showing fast adsorption kinetics. Some of the important adsorbents which are generally used in industry and for pollution control are discussed now.

2.6.1 Clay

There are three main groups of clays: kaolinite, montmorillonite-smectite, and mica. The montmorillonite has the highest cation exchange capacity and its recent market price is found to be 20 times cheaper as compared to activated carbon. Their heavy metals removal capacity is less as compared to zeolites but their easy availability and economical properties give back their less efficiency. Efficiency for heavy metal removal by clay could be improved by modifying them to clay-polymer composites [14,15].

2.6.2 Bauxite and Alumina

Bauxite is a naturally occurring porous crystalline alumina contaminated with kaolinite and iron oxides in varying proportions, depending on the place of origin. It is widely used in place of alumina, and it has been experimentally demonstrated that it removes most aerobic andanaerobic bacteria. Its surface area[16] ranges from 25 to 250 m^2g^{-1}. Alumina is a synthetic porous crystalline gel, which is available in the form of granules of different sizes. It is found to have a surface area[17] ranging from 200–300 m^2g^{-1} and is used in industries requiring the removal of water from gas streams, decolorization, and refining of petroleum oils and waxes.

2.6.3 Silica Gel

It is prepared by the coagulation of colloidal silicic acid, which results in the formation of porous and noncrystalline granules of different sizes. It shows a higher surface area as compared to alumina, which ranges from 250 to 900 m^2g^{-1}. The gel is considered a good adsorbent and is used in many industries for drying of gases and liquids, purifying of hydrocarbons, etc.[18,19]

2.6.4 Peat moss

Abundant in nature and has a very high organic content. Its large surface area ($\geq$ 200 m^2/g) and high porosity makes it an effective agent for heavy metal removal from wastewater. It was observed that peat moss plays an important role in treatment of metal-bearing industrial effluents such as Cu^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} [20]. The adsorption capacity of sphagnum peat moss was found to be 132 mg of Cr^{6+}/g at a pH range of 1.5-3.0. The most striking benefit of this adsorbent in treatment is the easiness of the system, low cost, and the capability to acknowledge a wide variation of effluent composition [21].

2.6.5 Zeolites and Ion Exchange Resin

Zeolites are important microporous adsorbents that occur naturally and are also prepared synthetically. They are also considered to be selective adsorbents and show ion exchange property [22,23] as well as molecular adsorption,[24,25] Zeolites are crystalline tectosilicates capable of undergoing reversible base-exchange reactions. Earlier zeolites were formed by fusing weighed amounts of feldspar, clay, and soda ash. Later on, synthetic zeolites obtained from mixtures of caustic soda, sodium silicate, and bauxite were also developed. Natural zeolites generally show low surface area; however, the apparent surface area[26]of some synthetic zeolites can be as high as 700 m^2g^{-1}.

2.6.6 Activated Carbon

Activated carbon [16] is the oldest adsorbent known and is usually prepared from source material, such as coal, coconut shells, lignite, and wood, using one of two basic activation methods:

2.6.6.1 Physical activation- This is a process in which the precursor is developed into activated carbons [27−30] using gases. The precursor is usually subjected to carbonization followed by activation or using either. Carbonization is the first stage where the precursor is pyrolyzed in the temperature range 600–900◦C,

2.6.6.2 Chemical activation- This is the other method used for the preparation of activated carbons[27,28,30,31] and involves impregnation with chemicals such as H_3PO_4, KOH, or NaOH, followed by heating under a gas (usually nitrogen) flow in the temperature range 450 to 900◦C.

2.7. Magnesium hydroxide

Magnesium hydroxide is the inorganic compound with the chemical formula $Mg(OH)_2$. It occurs in nature as the mineral brucite. It is a white solid with low solubility in water($K_{sp} = 5.61\times10^{-12}$). Magnesium hydroxide is a common component of antacids, such as milk of magnesia, as well as laxatives. Magnesium atomic number 12 so its electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2$, valence number 2 and oxygen atomic number 8 so its electronic configuration is $1s^2\ 2s^2\ 2p^4$ so valence number 2 and last hydrogen valence number 1 so it forms magnesium hydroxide. Magnesium hydroxide is a very porous structure material and it has large specific surface area.

Mganesium hydroxide is very attative compound of a wide range of its important application. Besides, $Mg(OH)_2$ is one of the most important precursor of magnesium hydroxide. It is used as a nutraliser of acidic pollutants of water and grases, filter in paper industry, antibacterial agent, and fertiliser additive [31].its non toxic character and high thermal stability make it an attractive additive to polymers used to restrict polymers flammability. The appearance of many papers on polymers used to restrict polymer flammability. One of its interesting properties is the diversity of its microstructure. It crystallise as needls , plate ,road, tubves and flowers. The presences of many papers on $Mg(OH)_2$ indicate increasing interest in this inorganic fillers. According to the recent literature reports, the properties of the final product, in particular its morphology, are closed related to type of precursor and the precipitating agents.

Precipitation process and Condition			Dispersive properties		Adsorptive propertices		
Sample no	Type of salt	Mean molecular weight	Particle diameter nano ZS(nm)	pdI	BET surface area (m^2/g)	Total volume of pore (cm^3/g)	Mean size of pore(nm)
S_unmod	Magnesium sulfate	-	21-106	0.225	21	0.01	2.7
1s_mod		200	59-220	0.668	28	0.01	2.6
2s_mod		400	59-142	0.346	42	0.22	28.2
3s_mod		8000	68-459	0.435	30	0.01	2.6
4s_mod		20000	79-255	0.387	32	0.01	2.7
Cl_unmod	Magnesium chloride	-	220-396	0.196	3.3	0.02	2.8
1CL_mod		200	51-459	0.287	10	0.01	3.5
2CL_mod		400	122-459	0.312	8	0.01	3.5
3CL_mod		8000	68-2670	0.571	12	0.02	3.6
4CL_mod		20000	59-342	0.496	6	0.01	3.1
N_unmod	Magnesium nitrate	-	106-255; 110-1990	0.365	3	0.01	1.5
1N_mod		200	33-396	0.380	4	0.01	2.2
2N_mod		400	51-825	0.428	4.5	0.01	2.6
3N_mod		8000	79-3090	0.520	7	0.01	2.5
4N_mod		20000	68-190	0.321	6	0.01	2.1

Table3 table 1 Physicochemical properties of magnesium hydroxide precipitated with the use of 5% solution of a magnesium salts, ammonium hydroxide in stoichiometric amount and a 2% solution of one of the following non-ionic compounds PEG 200, 400, 8000, 20000[32]

So functionalization of magnesium hydroxide (precipitated with the use of a magnesium salt and ammonium hydroxide) with non-ionic compounds from the group of poly(ethylene glycols) has not brought favourable changes in the dispersive properties of the products. The size of particles in the modified samples was greater or comparable to that in the unmodified magnesium hydroxide. The modification with PEG has resulted in increased specific surface areas BET of all samples. Relatively large specific surface area was obtained for the samples synthesized with the use of magnesium sulfate. The best dispersive properties (particle size range from 59 to 142 nm) and adsorptive properties (surface area BET of 42 m^2/g) were found for sample 2S_mod., modified with PEG 400.

2.8. Different synthesis process $Mg(OH)_2$

A variety of methods for yielding nanostructured $Mg(OH)_2$ have been reported. These include hydrothermal/solvothermal techniques, precipitation routes and microwave-assisted methods. Further, the use of surfactants and templating agents has been explored as a means to obtain $Mg(OH)_2$ nanocrystals with different morphologies, from hexagonal nanoplates through nanotubes, nanorods and nanosheets to mixture of nanosheets and nanoparticles.

Different synthesis routes are,

2.8.1 Conventional hydrothermal/solvothermal synthesis

Hydrothermal and solvothermal methods have been widely employed to produce nanostructured $Mg(OH)_2$. These methods often involve the use of surfactants such as Poly(ethylene glycol) (PEG) or ethylendiamine (en), which are considered to play an important role in the mechanism of the nanostructure formation, acting either as templates or growth inhibitors. One of the major drawbacks of these synthetic procedures however is the relatively long reaction time, which is typically of 6 to 24 h or more. The synthesis of $Mg(OH)_2$, nanorods by solvothermal treatment was first reported in 2000 by Li et al[33].

$$\mathbf{Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2}$$

The key influence in the crystal growth mechanism is believed to be the presence of the en molecules, which are likely to act as bidentate ligands to form a complex with Mg^{2+} cations, thereafter controlling the nucleation and growth of the nanorods.

2.8.2 Synthesis via microwave-assisted methods

The use of microwaves as an alternative to conventional heating for material synthesis in the solid state as well as in solution has attracted considerable attention.[34,35] In fact, using microwave (MW) heating can enable reaction times to be dramatically decreased from days to even a matter of minutes when compared to conventional heating approaches. Great progress has been made over the past decade in terms of the MW preparation of nanostructured $Mg(OH)_2$ (Table 2).

Mg source	Solvent/additives	Power/W	Time/h	Morphology	Dimensions
$Mg(NO_3)_2$	Water/NaOH	20	120	Fibrous	Dia:20–40nm length:100-150 nm.
$MgCl_2$, $6H_2O$	Water/NaOH/urea	1000	0.5	Spherical/lamellar	Sphere dia 30 µm; thickness plate: 95 nm.
$Mg(SO)_4$	Water/NaOH	206	0.25	Lamellar	Thickness 5nm
Mg (rod)	Water	160	1	Lamellar	Dia: 25-125nm
Mg (powder)	Water	180	0.13	Lamellar	Dia:100-1000 Nm thickness: 36-45 nm

Table 4 Effect of selected experimental parameters on MH products in microwave-assisted synthesesa [36,37]

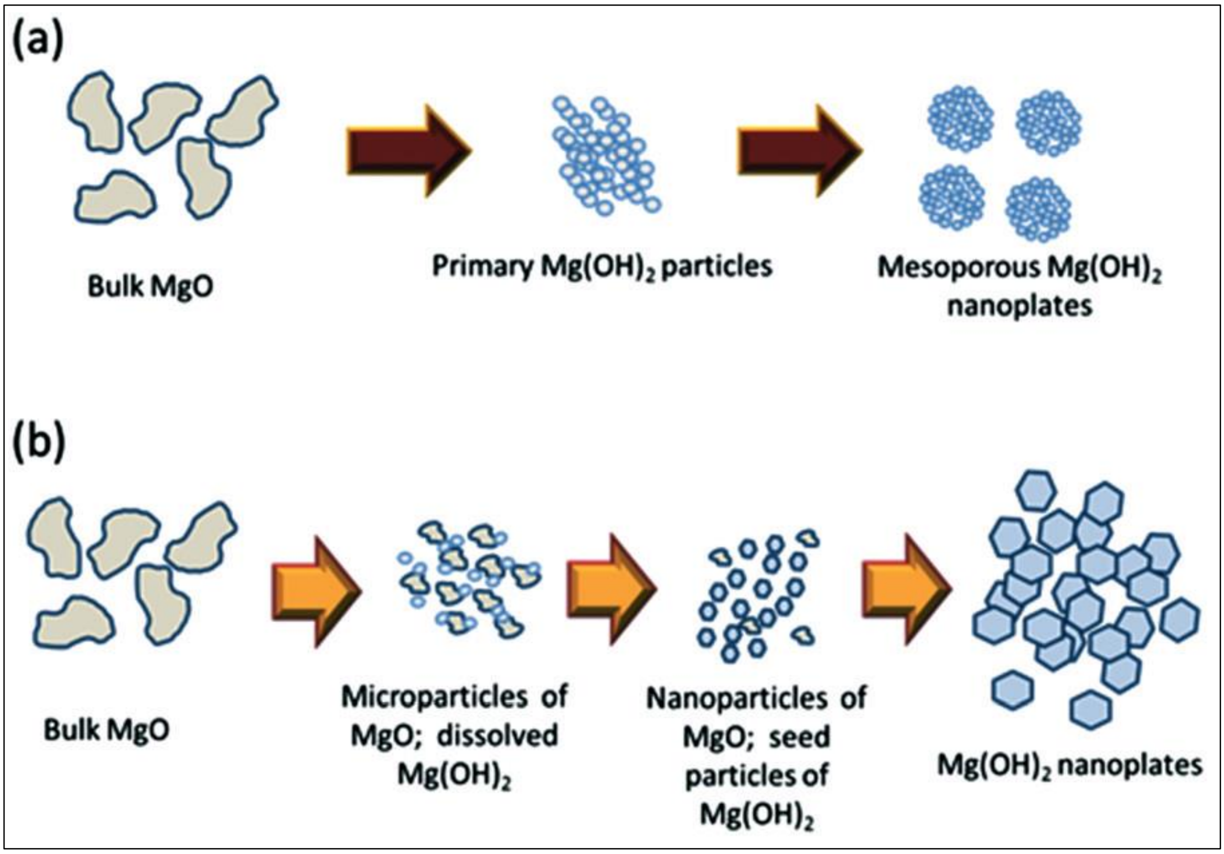


Fig. 8 Proposed growth processes for (a) conventional hydrothermal synthesis proposed by Yu et al.[38] and (b) MW-hydrothermal synthesis proposed by Hanlon et al. reproduced from ref.[39] with permission from the Royal Society of Chemistry.

2.8.3 Precipitation methods

Solution based precipitation and co-precipitation methods are attractive ways to prepare MH under relatively mild conditions. Routes with and without the use of surfactants and surface modifiers have been explored as means to obtain nanostructures with controlled size and morphology. Magnesium hydroxide nanoparticles with three structural morphologies, needle-, lamellar- and rod-like, were synthesized individually through solution precipitation in the presence of complex dispersants [40]. MH nanocrystals synthesized by the wet precipitationprocedure were distinctly characterized according to their sizes and morphologies, which are strongly affected by water-soluble polymers,

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CHAPTER3.1 INSTRUMENTS AND APPARATUS

3.1.1 MAGNETIC STIRRER

A magnetic stirrer or magnetic mixer is a laboratory device that employs a rotating Magnetic field to cause a stir bar immersed in a liquid to spin very quickly and thus stirring the liquid. The rotating field created by a rotating magnet placed beneath the vessel with the liquid.

Purpose of magnetic stirrer:

- The main purpose of magnetic stirrer is to mix several substance, either solids or liquids which result into a homogeneous liquid mixture
- Some of the practical uses include bacteria growth and also buffer solution.
- The magnetic stirrer work in a unique method using an external magnetic field. This external magnetic field rotates the small magnetic bar that need to be placed the mixture.
- One the main advantages of using a magnetic stirrer is that there is almost no risk contamination occurring.

Figure1: Magnetic Stirrer

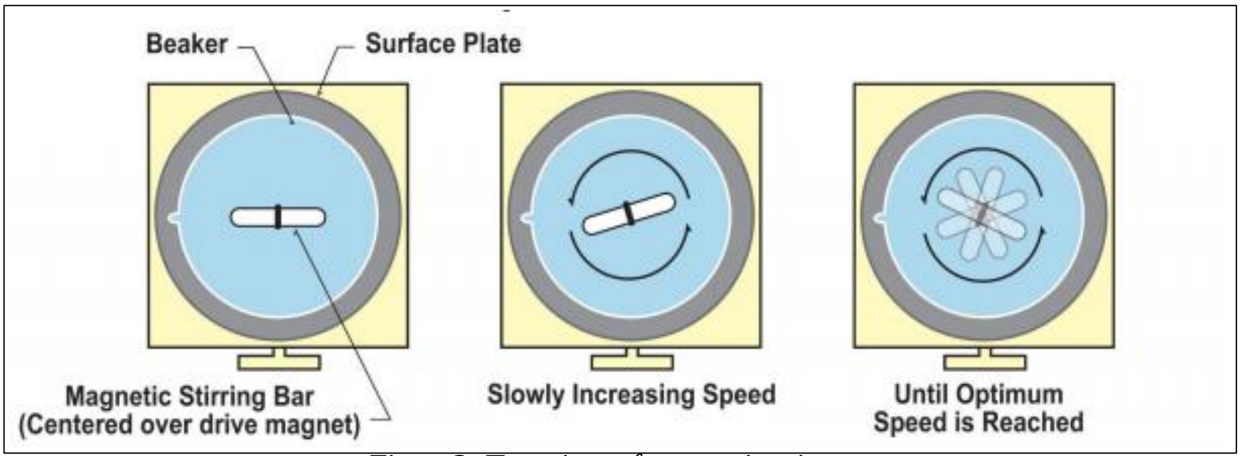

Figure2: Top view of magnetic stirrer

3.1.2 ATOMIC ADSORPTION SPECTROSCOPY

Atomic adsorption spectroscopy is based on the same principle as the flame test used in qualitative analysis. In the flame test, when a small amount of a solution of a metal ion is placed in the flame of a Bunsen burner, the flame turns a colour that is the characteristic of the metal ion. A sodium solution gives a yellow colour, a potassium solution result in violet colour, a copper solution gives a green colour, etc. when more than one metal ion is present, viewing the flame a coloured glass filter can help mask any interference. The phenomenon just describe is an “atomic emission “phenomenon.

The reason for calling it atomic emission lies in the process occurring in the flame. One of the steps of the process is an **atomization step**. That is the **flame converts the metal ion into atoms.** When a solution of sodium chloride is placed in the flame, for example the solvent evaporates leaving behind solid crystalline sodium chloride. This evaporation is then followed by the dissociation of the sodium chloride crystals into individual ground state atoms- a process that is termed atomization. Thus, sodium atoms are actually present in the flame at this point rather than sodium ions, and the process of light emission actually involves these atoms rather than the ions.

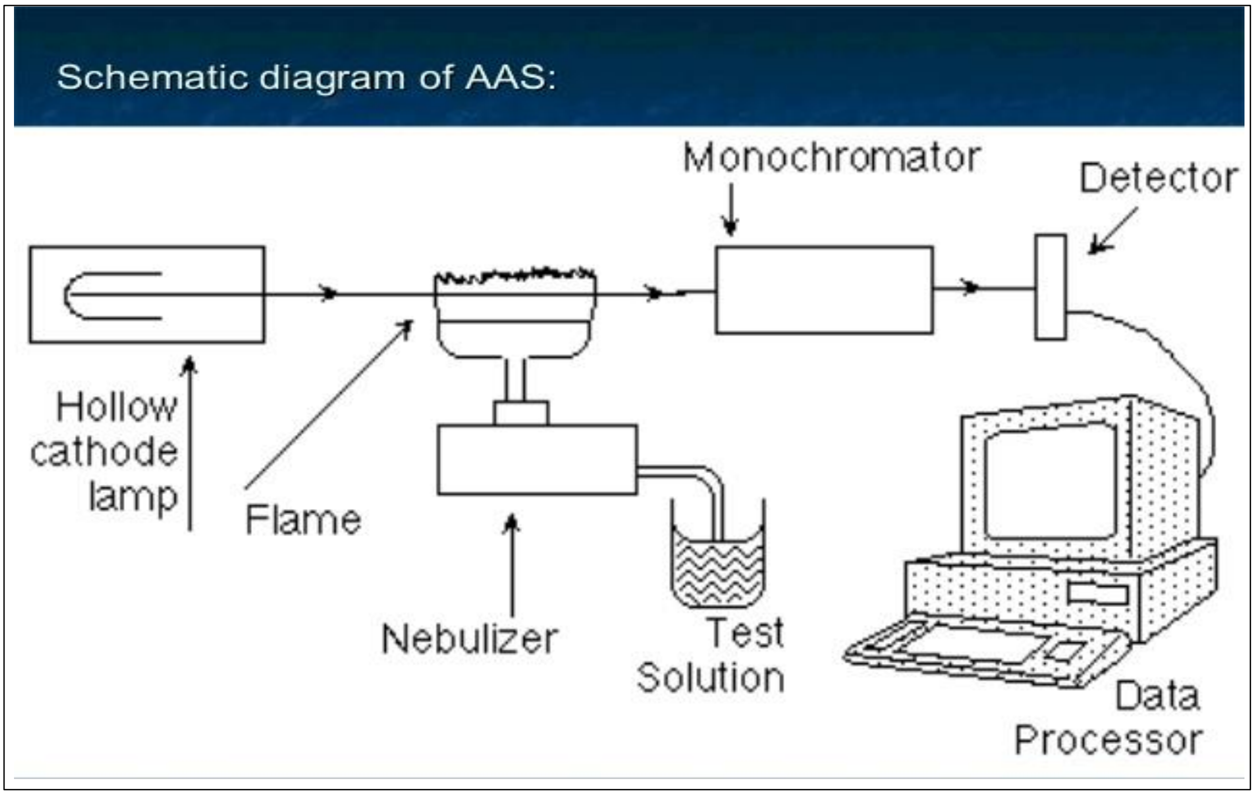

Figure3: Schematic diagram of AAS

Following atomization, a small percentage of the atoms absorb sufficient energy from the flame so as to be promoted to an excited state. These atoms quickly return to a lower state, and light corresponding to the energy that is lost in the process. It is this light that our eye perceives.In the instrumental technique, a monochromator replaces the coloured glass filter, and a photocell detector/readout replace our eye. Also the burner design is more sophisticated in that the sample is continually fed into the flame by aspiration.

Atomic adsorption spectroscopy is an analytical technique that measures the concentration of the sample. Atomic adsorption is so sensitive that it can measure down to parts per million (ug/ml or mg/l) in a sample. Only a very small number of the atoms in the flame are actually present in an excited state at any given instant. Thus, there is a large percentage of atoms that are in the ground state and available to be excited by some other means, Such as a beam of light from a light source. Atomic adsorption (AA) takes advantage of this fact and uses a light beam to excite these ground state atoms in the flame. Thus, in AA light adsorption (by these ground state atoms) is measured and related to concentration.

The light source called a hollow cathode tube (HCL lamp), is a lamp that emits exactly the wavelength required for the analysis (without the use of a monochromator0. The light is directed at the flame containing the sample, which is aspirated from the sample container. The flame is typically wide(4-6 inches), giving a reasonably long path length for detection small concentration of atoms in the flame. The light beam then enters the monochromator, which is tuned to a wavelength that is adsorbed by the sample. The detector measures the light intensity.

The concentration of an adsorbing species in a sample is determined by applying **lambert-beer's law.** Linear relationship between absorbance and concentration of an absorbing species, now

$$\text{Absorbance, } A = €.c.d$$

Where, € = wavelength- dependent molar absorptivity coefficient

C = concentration of the sample

D = path length

Absorbance is determined using following equation:

$$\text{Absorbance} = -\log (I_t/I_0)$$

I_t = transmitted radiation

I_0 = incident radiation

Hollow cathode tube emits exactly the wavelength required for the analysis because of the metal to be tested are present within the lamp, and when the lamp is on, these atoms are supplied with energy, which causes them to elevate to the excited states. Upon returning to the ground state, exactly the same wavelengths that are useful in the analysis are emitted, since it is the analysed metal with exactly the same energy levels that undergoes excitation.

Mechanism of the lamp: this lamp contains a tungsten anode and cylindrical hollow cathode made of the element to be determined. The lamp itself is a sealed glass envelope filled with argon or neon gas. When the lamp is on, argon atoms are ionized with the electrons drawn to the anode (+ charge electrode)., while the argon ions, Ar^+ , "bombard" the surface of the cathode (- charge electrode).The metal atoms in the cathode are elevated to the excited state and are ejected from the surface as a result of this bombardment. When the atoms return to the surface as a result of this characteristic line spectrum of that atom is emitted.

Nebulizer:

- Sucks up the liquid sample
- Creates a fine aerosol (fine spray) for introduction into the flame
- Mixes aerosol, fuel and oxidant thoroughly, creates a heterogeneous mixture

The larger drops fall out and drain off while smaller vaporise in the flame. Only approx. 1 % of the solution nebulized.

Gas use in flame: The fuel is acetylene and the oxidant can be compressed air or nitrous oxide. The combination will be "acetylene + air or acetylene + nitrous oxide". To ignite the flame.

Gas required	Acetylene	(Oxidant) compress air	(Oxidant) nitrous oxide
purity	99.9%	O_2 21% N_2 78%	99.5%
Minimum pressure	55KPa(8psi	330KPa(47psi)	330KPa(47psi)
Maximum pressure	96KPa (14 psi)	370KPa(53psi)	370KPa(53psi)
Minimum Flow rate	12l/min	24l/min	24l/min

Calibration: A calibration curve is used to determine the unknown concentration of an element, eg cadmium in the solution. The instrument is calibration curve is produce which is continually rescaled as more concentrated solutions are used the more concentrated solution absorb more radiation upto a certain absorbance. The calibration curve shows the concentration against the amount of radiation absorbed.

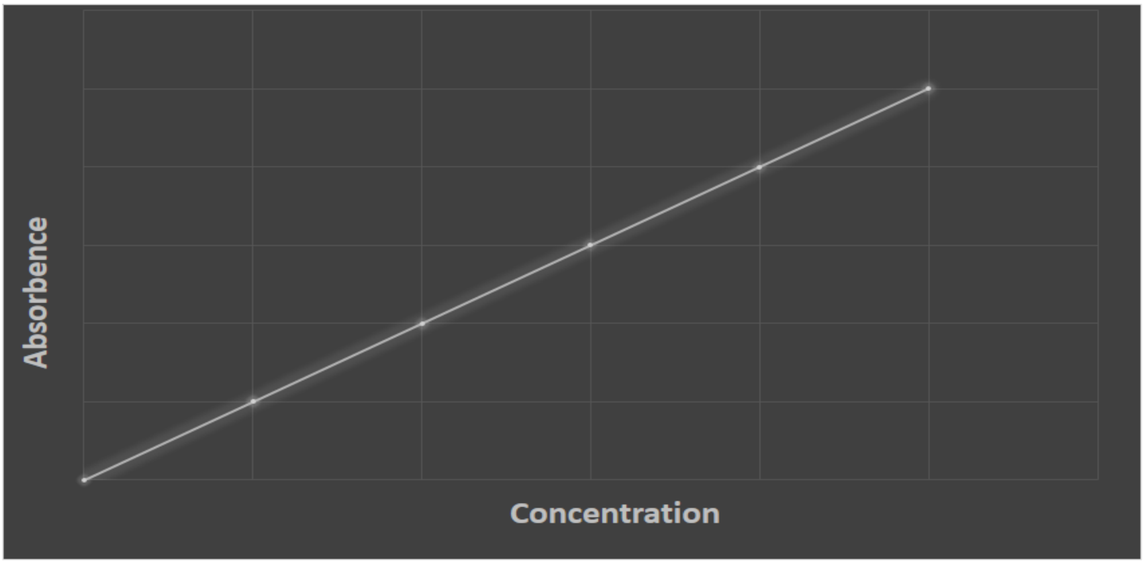

Figure4: Calibration curve for standard solution of AAS

The sample solution is fed into the instrument and the unknown concentration of the element, eg cadmium is then displayed on the calibration curve.

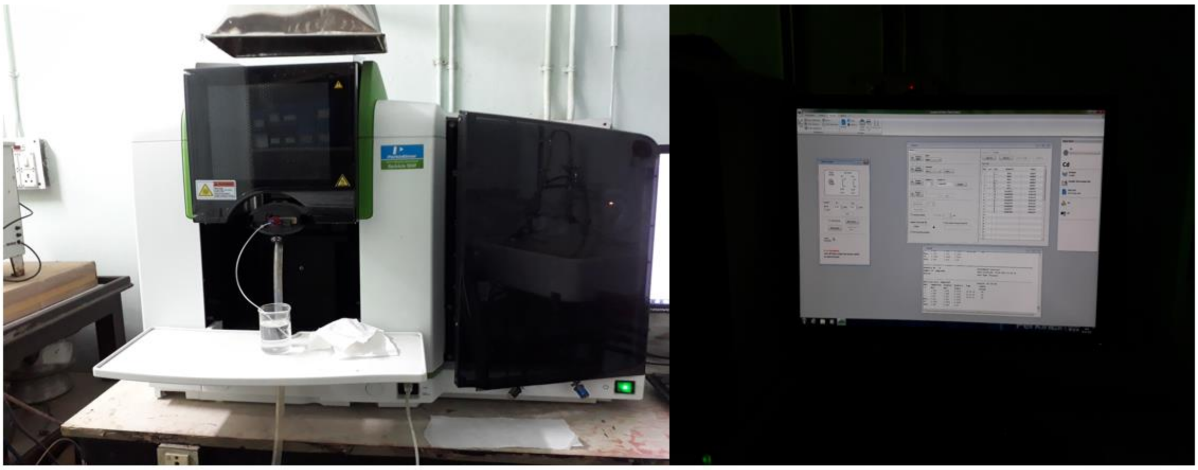

Figure5: Image of Atomic Adsorption Spectroscopy

3.1.3 FUME HOOD

Working principle: The most common fume hoods are bypass hoods. These are designed to operate at a constant volume of air. There are numerous kinds of bypass fume hoods including auxiliary air, high performance, and reduced air volume hoods. The fume hoods have an efficient air exhaust system that allows expulsion of toxic gases.

Some fume hoods are specially made to handle specific corrosive substances such as hyperchloric acid. Others have specifications that enable handling of radioactive materials and are fitted with filters to prevent the release of these elements to the environment.

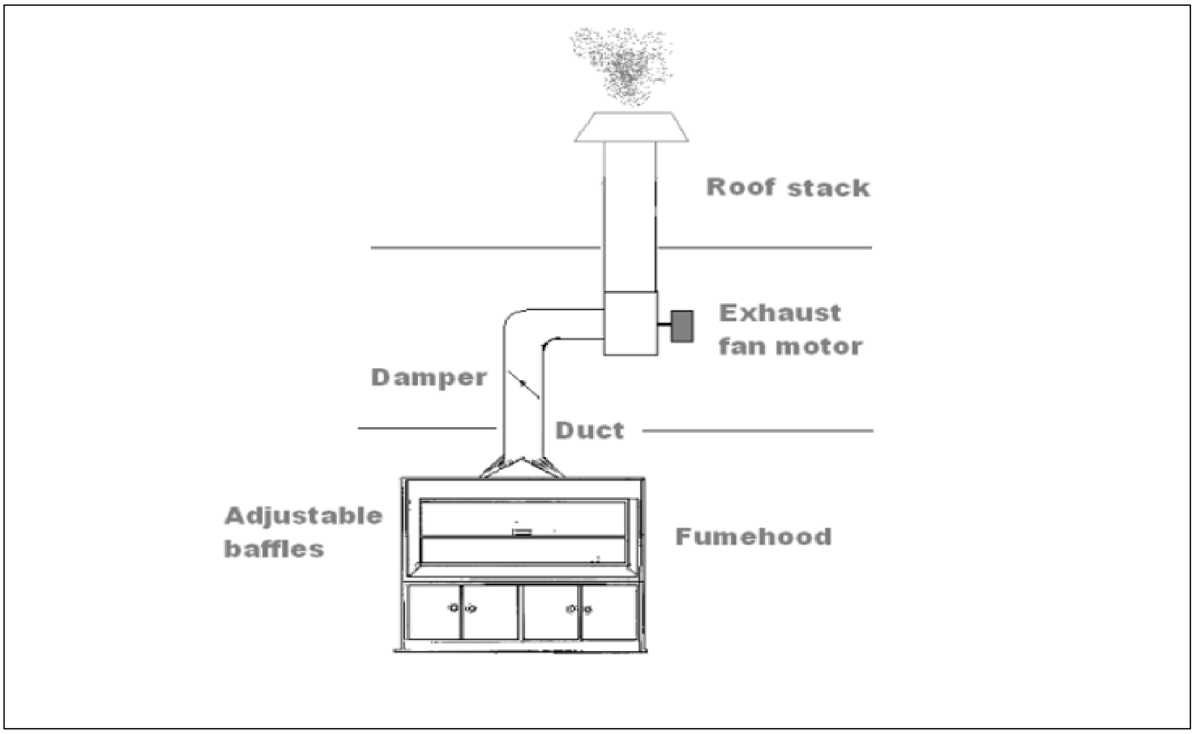

Figure6: A schematic diagram of fume hood

Uses

A laboratory fume hood is widely found in many analytical chemistry labs where experiments that release toxic gases such as sulfur dioxide gas are released. It is also ideal for performing experiments that involve chemicals that easily sputter out during heating. Such compounds can easily burn the lab technician and other lab occupants when conducted in the open space.

3.2 CHARACTERIZATION INSTRUMENTS

3.2.1 X-Ray Diffraction

Introduction

Max von Laue and Co., in 1912, discovered that crystalline substances act as three dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice.

X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample

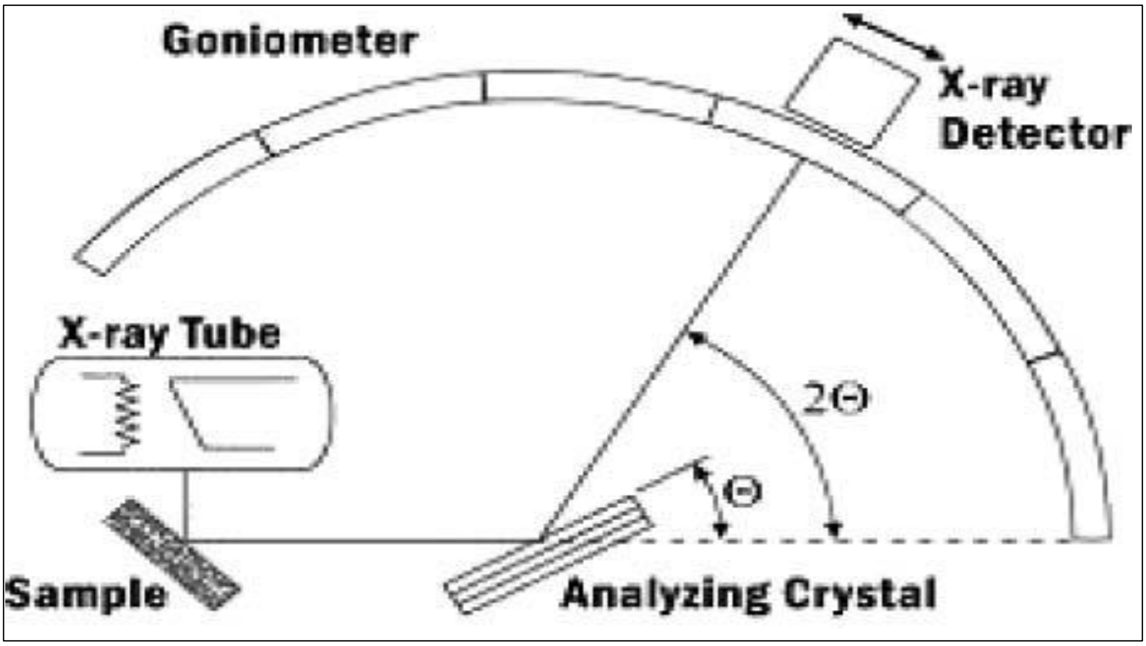

Figure7: Schematic diagram of a diffractometer system.

The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's law:

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

where n is an integer, λ is the wavelength of the X-rays, d is the interplanar spacing generating the diffraction, and θ is the diffraction angle. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed, and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the compound because each compound has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns. The crystallite size, D can be calculated from the Scherrer's formula $D=(k\lambda/\beta\cos\theta)$ where β is full width of height maximum(FWHm) of a diffraction peak, k is the Scherrer constant and θ is the diffraction angle [1–3]. X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K_α and K_β. K_α consists, in part, of $K_{\alpha1}$ and $K_{\beta2}$. $K_{\alpha1}$ has a slightly shorter wavelength and twice the intensity of $K_{\alpha2}$. The specific wavelengths are characteristic of the target material (Cu,Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha1}$ and $K_{\alpha2}$ are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuK_α radiation = 1.5418 Å.

These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies Bragg’s law, constructive interference occurs and a peak in intensity appears. A detector records and processes this X-ray signal and converts the signal to a count rate, which is then output to a device such as a printer or computer monitor. The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ. The instrument used to maintain the angle and rotate the sample is termed a goniometer. For typical powder patterns, data are collected at 2θ from 5 to 90, angles that are preset in the X-ray scan. X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g., minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering, and biology. Other applications include characterization of crystalline materials, identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically, determination of unit cell dimensions, and measurement of sample purity.

With specialized techniques, X-ray diffraction (XRD) can be used to determine crystal structures by using Rietveld refinement, determine modal amounts of minerals (quantitative analysis), characterize thin film samples, and make textural measurements, such as the orientation of grains, in a polycrystalline sample (Brindley and Brown, 1980).

There are some strengths and some limitations of X-ray powder diffraction (XRD):

Strengths:

- Powerful and rapid (<20 min) for identification of an unknown material
- Provides unambiguous mineral determination in most cases
- Requires minimal sample preparation
- Wide availability of XRD units
- Non-destructive, fast, and easy sample preparation
- High accuracy for d-spacing calculations
- Can be done in situ

XRD Theoretical Aspects

Instrumentation: The instrumentation that is used for powder diffraction measurements has not changed much from that developed in the late 1940s. The major difference found in modern instrumentation is the use of the minicomputer for control, data acquisition, and data processing. Figure 2 illustrates the geometry of the system, showing the layout of a typical diffractometer with system source F, Soller slits P and RP, sample S, divergence slit D, and receiving slit R. The axis of the goniometer is at A.

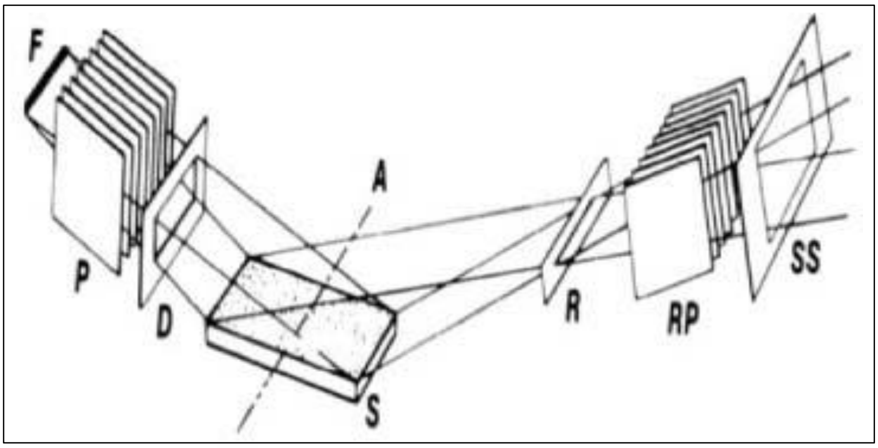

Figure8: Geometry of the Bragg-Brentano diffractometer.

Figure9: Image of XRD machine Rigaku Ultima III.

Sample Preparation

Proper sample preparation is one of the most important requirements in the analysis of powder samples by X-ray diffraction. This statement is especially true for soils and clays that contain finely divided colloids, which are poor reflectors of X-rays, as well as other types of materials such as iron oxide coatings and organic materials that make characterization by XRD more difficult.

Applications

Pharmaceutical Industry, Forensic Science, Geological Applications, Microelectronics, Industry Glass Industry

3.2.2 Field emission scanning electron microscope (FESEM):

Overview of the FESEM system

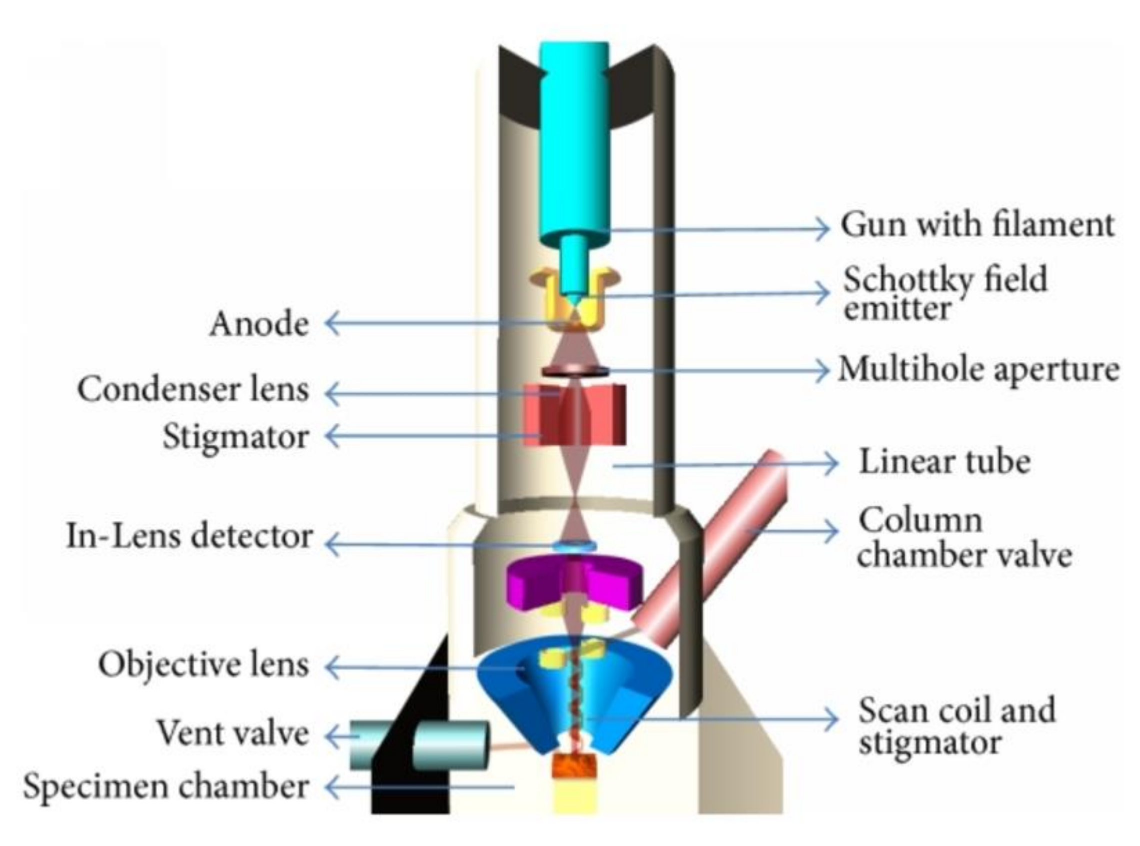

Figure10: Diagram of FESEM System

- FESEM uses a focused beam of electron to generate an image or to analyse the specimen
- For operation, the gun head, the column and specimen chamber have to evacuated
- The pre- vacuum and turbo pump evacuated the chamber. Vacuum in the specimen chamber is measured by penning gauge.
- Column chamber valve remain closed until the detector pressure are ready for operation. After vent command, column chamber valve closes and N_2 gas flow into the chamber through vent valve.

Principle of the operation

In standard electron microscopes, electrons are mostly generated by heating a tungsten filament (electron gun). They are also produced from a crystal of LaB_6. The use of LaB_6 results in a higher electron density in the beam and a better resolution than that with the conventional used device. In a field emission (FE) electron microscope, no heating but a so–called "cold" source is used. Field emission microscope is a type of electron microscope that is usually employed to investigate the surface of a sample by scanning it with a high energy beam of electrons. Here, the wave properties of electrons ($\lambda = h/p$, λ associated with a beam of electrons of momentum p) are used to obtain resolution.[4-5]

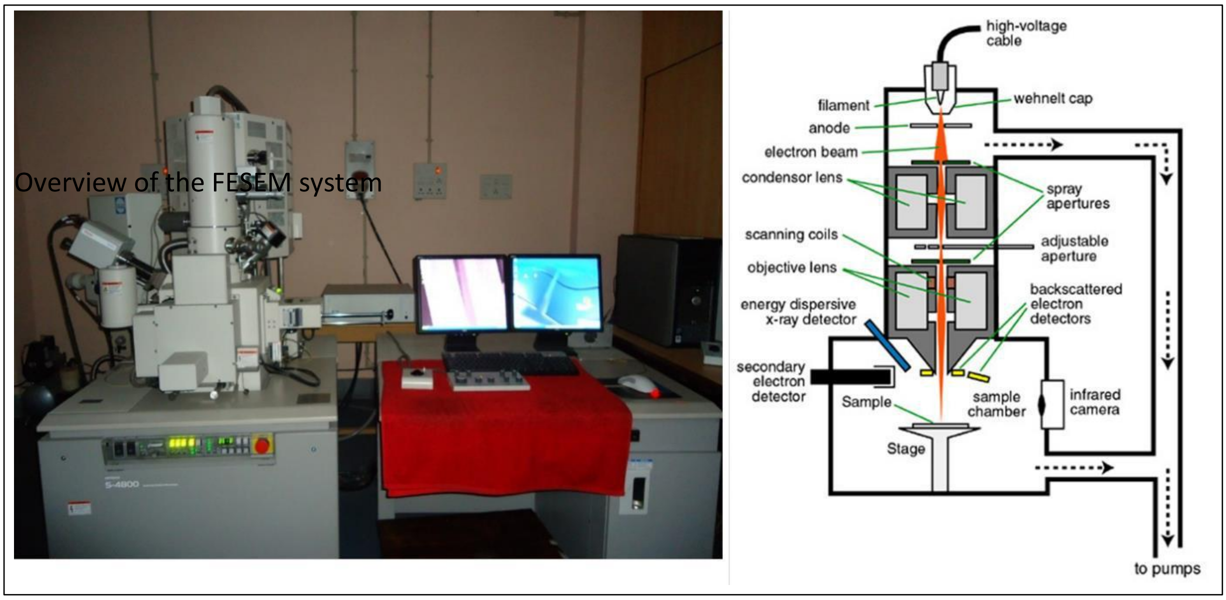

Figure 11: Left: Hitachi S4800 FESEM with EDX attachment, Simple schematic of FESEM

In FESEM, the electron beam passes through objective lens deflect horizontally and vertically so that the beam scans the surface of the sample [Figure 11 (right)]. As the electrons penetrate the surface of the sample, a number of interactions occur that can result in the emission of electrons or photons from or through the surface. The generated secondary electrons are collected by the detector and converted into voltage. The amplified voltage is applied to the grid of the CRT which changes the intensity of the spot light. In this way an image is produced on the CRT; every point that the beam strikes on the sample is mapped directly onto a corresponding point on the screen. The schematic diagram of FESEM is presented in figure 11 (right). When an electron beam interacts with the atoms of a nano structures sample, each incident electron undergoes two types of scattering elastic and inelastic. In elastic scattering, only the trajectory changes and the kinetic energy and velocity remain constant. In the case of inelastic scattering, the incident electrons displace electrons from the sample orbits around nuclei of atoms. The electron interacts with the sample produces signal about the sample’s morphology, composition and other properties. The morphologies of the synthesized nanomaterials are characterized with the help of field emission scanning electron microscopy (FESEM, S–4800). The photograph of the instrument is shown in figure 11 (left). Energy Dispersive X–Ray (EDX) is one of the most versatile tools for analyzing the compositions of the synthesized samples. It is sometimes referred to also EDS or EDAX analysis. EDX is the integrated feature of both SEM and TEM. During EDX analysis, the specimen is bombarded with an electron beam inside electron microscope. The bombarding electrons collide with the specimen atom and knock some of them off in the process. The electrons vacated from the inner shell are eventually filled with the higher energy outer shell electrons and emit X–ray in this method. In this run, X–rays emitted from atoms represent the characteristics of the elements, and their intensity distribution represents the thickness– projected atom densities in the specimen. EDAX is a very important tool for identifying the chemical composition of a specimen.

3.2.3 Introduction to Transmission Electron Microscopy (TEM)

Transmission electron microscopy is used to reveal sub-micrometre, internal fine structure in solids. Materials scientists tend to call this microstructure while bioscientists usually prefer the term ultrastructure. The amount and scale of the information which can be extracted by TEM depends critically on four parameters. The first and second of these depend largely on the depth of your pocket – the more you spend, the better the microscope parameters. The third is usually determined by your experimental skill while the last depends on luck or your choice of experimental system.

The parameters are as follows:

- The resolving power of the microscope (usually smaller then 0.3 nm)
- The energy spread of the electron beam (offers several eV)
- Thickness of the specimen (almost always significantly less then 1μm)
- The composition and stability of the specimen

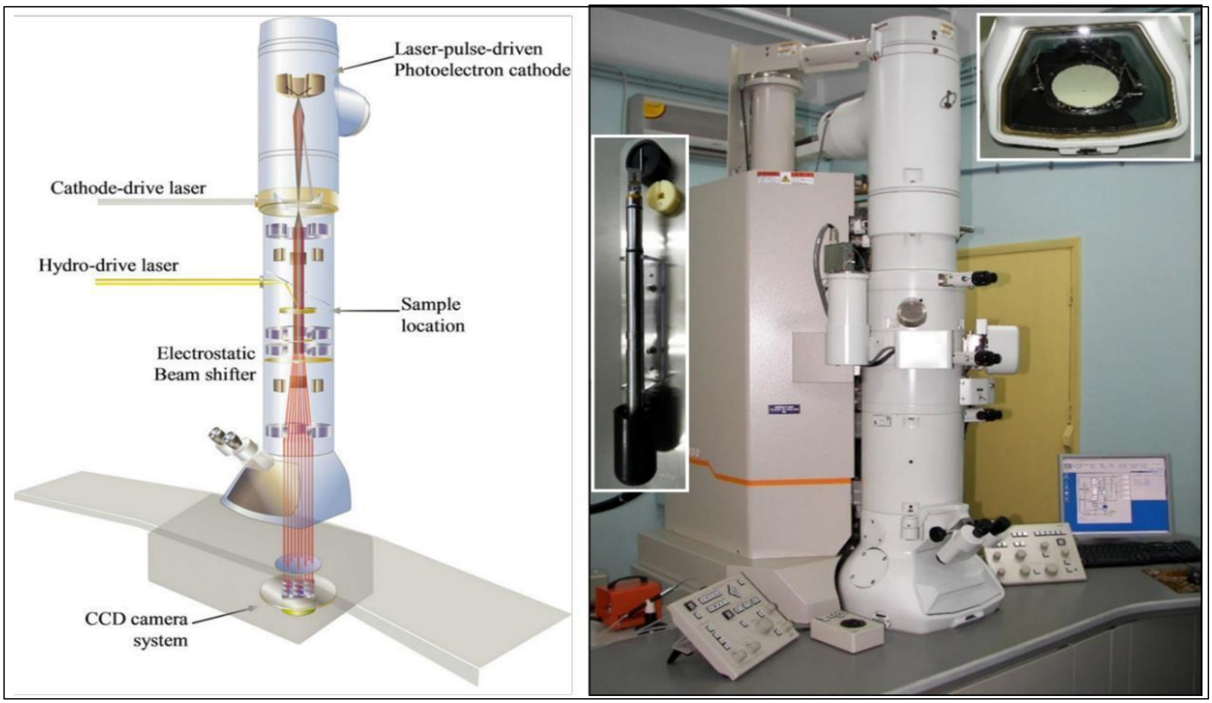

Figure12: layout of optical components of basic TEM instrument, JEOL JEM 2100 HRTEM

The two available types of TEM – CTEM and STEM – differ principally in the way they address the specimen. The conventional TEM (CTEM) is a wide-beam technique, in which a close-to-parallel electron beam floods the whole area of interest and the image, formed by an imaging (objective) lens after the thin specimen from perhaps 106 pixels, is collected in monitor device .

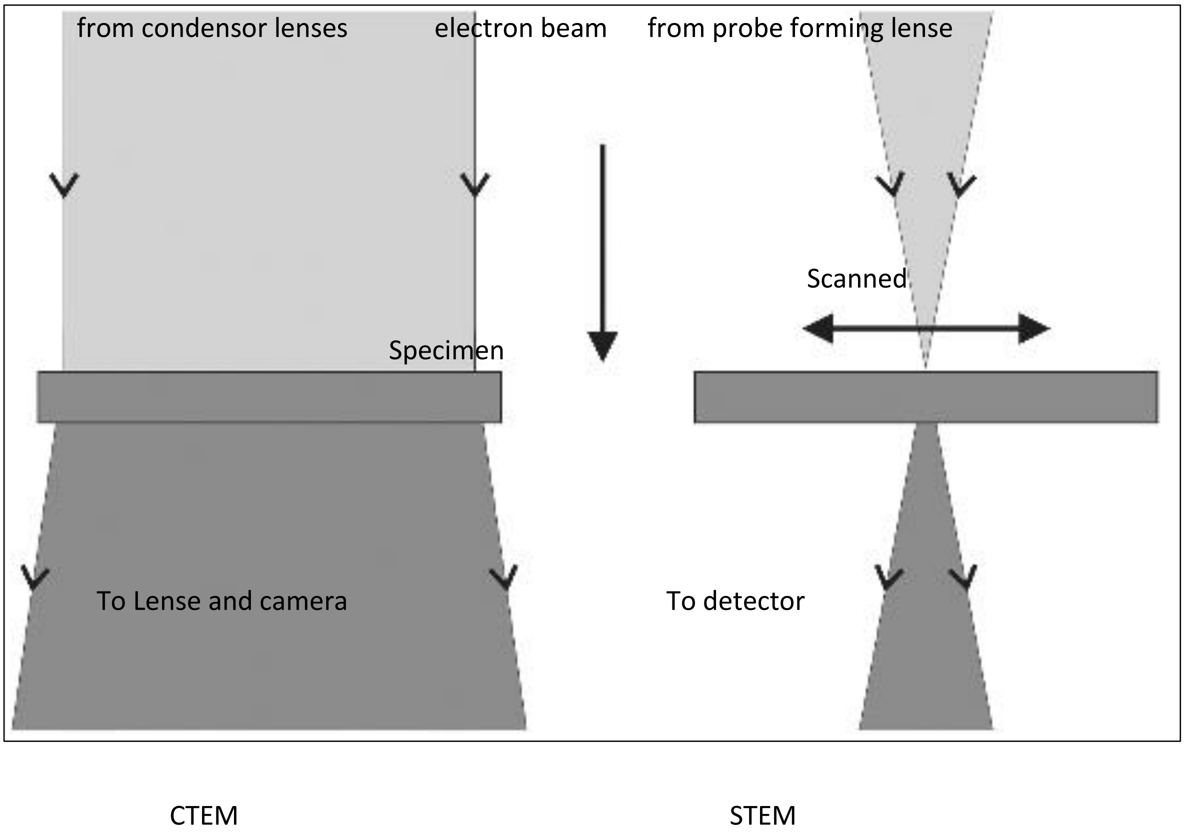

Figure13: The electron beam in CTEM and STEM instruments. Note that in many STEM instruments the beam actually travels upwards rather than down as shown here.

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CHAPTER4. Experiments, Results and discussion

4.1 Experiment procedure:

Magnesium hydroxide synthesized in two different methods. In the first process hydrated magnesium chloride ($MgCl_2$, $6H_2O$) and ammonium hydroxide NH_4OH are used as the precursor and PEG 200 is used as a modifier. In the second process hydrated magnesium sulfate ($MgSO_2$, $7H_2O$ and ammonium hydroxide NH_4OH are used as the precursor and PEG 400 is used as modifier. Magnesium hydroxide is obtained from the reaction of 5 % solution of magnesium salt with a solution of ammonium hydroxide taken in the stoichiometric ratio.

4.1.1 Preparation of $Mg(OH)_2$ from $MgCl_2$, $6H_2O$ [sample 1]

10 mg magnesium chloride and 200ml double distilled water are mixed in a beaker and 6.68 ml of 25% of ammonium hydroxide solution is mixed with another 200ml double distilled water. 1ml PEG200 and 49 ml double distilled water are mixed in a 500ml capacity beaker and this beaker is placed on a high speed magnetic stirrer (Remi 2MLH). Magnesium salt solution and ammonium hydroxide solution both are simultaneously dosed into the PEG solution at a rate of 2ml/min with the help of micropipette. This reaction is carried out at constant temperature 80^0C and at 1800rpm. The precipitate is washed out and filtered (whatman41 filter paper). The residue is collected in a petri dish and oven dried at 105^0C for about 8 hours.

$$\mathbf{MgCl_2 + 2\,NH_4OH \text{----------}\rightarrow Mg(OH)_2 + (NH_4)Cl_2}$$

Stoichiometric calculation for NH_4OH:

Molar weight of MgCl2 , 6H2O = 203.3 gm/mol

Mole of $MgCl_2$ = 5/203.3 [5 gm for 5% magnesium salt]

= 0.02459 mole

Mole ammonium hydroxide = (2* 0.02459) = 0.04918 mole

Weight of ammonium hydroxide = 0.04918 * 17 = 0.83606 gm

We have 25% ammonium hydroxide solution

So $V_2 = (S_1 * V_1)/ S_2$ = (0.83606 * 100)/25 = 3.344 ml (for per 100ml)

4.1.2 Preparation of $Mg(OH)_2$ from $MgSO_4 ,7H_2O$ [sample 2]

10 mg magnesium sulfate and 200 double distilled water are mixed in a beaker and 5.52 ml of 25% of ammonium hydroxide solution is mixed with 200ml double distilled water. 1ml PEG400 and 49 ml double distilled water are mixed in 500ml capacity beaker and this beaker is placed on high speed magnetic stirrer(Remi 2 MLH). Now magnesium salt solution and ammonium hydroxide solution both are simultaneously does into the PEG solution at a rate of 2ml/min respectively with the help of micropipette. This reaction is carried out at constant temperature 80^0C and constant 1800 rpm. The precipitate is washed out and filtered (whatman41 filter paper). The residue is collected in petri dish for oven dried at 105^0C about 8 hours.

$$\mathbf{MgSO_4 + 2\,NH_4OH \text{ ----------}\rightarrow Mg(OH)_2 + (NH_4)_2SO_4}$$

Stoichiometric calculation for NH_4OH:

Molar weight of $MgSO_4$, $7H_2O$ = 246.47 gm/mol

Mole of $MgSO_4$ = 5/246.47 = 0.0203 mole [5 gm for 5% magnesium salt]

Mole ammonium hydroxide = (2* 0.0203) = 0.04057 mole

Weight of ammonium hydroxide = 0.04057 * 17 = 0.6897 gm

We have 25% ammonium hydroxide solution

So $V_2 = (S_1 * V_1)/ S_2$ =(0.6869 * 100)/25 = 2.7589 ml (for per 100ml)

4.2 Preparation of cadmium stock solution

1000 ml of cadmium nitrate solution is made with concentration 10 mg/l.

For 0.01gm cadmium we have to take = (311.5858*0.01)/112.411

= 0.0277 gm cadmium nitrate [$Cd(NO_3)_2$, $4H_2O$]

So 0.0277 gm cadmium nitrate mixed with 1000 ml double distilled water.

4.3 Preparation of the Standard cadmium Solutions for AAS

Three standard cadmium solutions are prepared in the range of 0.5-10 mg/l in 100 ml volumetric flasks. One of the solutions should have concentration 5.0 mg/l of cadmium, this solution is used to check the performance of the instrument.

4.4 Experiments on Heavy metal (cadmium) removal by $Mg(OH)_2$

Amount of Mg(OH)2 , time of adsorption and different volume of cadmium stock solutions are used three different parameter in the removal of cadmium by $Mg(OH)_2$

4.4.1 Variables 1: Amount magnesium hydroxide [$Mg(OH)_2$]

To see the effect of the amount of $Mg(OH)_2$ on the adsorption of cadmium , 30ml of cadmium stock solution with cadmium concentration 10mg/l is treated with 5mg, 10mg, 20mg.30mg,40mg and 50mg of $Mg(OH)_2$ and stirred with magnetic stirrer at 400rpm for 4 hours. After that cadmium concentration of 6 different solution are measured using AAS

4.4.2 Variables 2: Time of adsorption & different volume of Cd stock solution

100ml stock solution of cadmium of 10 mg/l concentration is treated with 50mg of $Mg(OH)_2$ and stirrer with magnetic stirred at 400rpm for 3hours. To see the effect of adsorption, 10ml of solution is taken out after 30 minute interval and the concentration of cadmium measured in AAS. The same process is repeated for 200ml & 300ml of cadmium stock solution to the effect of adsorption $Mg(OH)_2$.

4.5 Characterization of the Material

The dried samples are collected, crushed and ground to fine powders and a particle characterized using X-ray powder diffraction (XRD), FESEM and HRTEM. XRD is carried out in RIGAKU ULTIMA (III) XRD machine with a scan speed 5^0 / min from 20^0- 80^0 using CuKα radiation (λ= 1.5418 Å), and the operational voltage and current maintained at 40KV and 40 mA respectively. Field Emission Scanning Electron Microscopic (FESEM) is used to observed the details of surface morphology by using Hitachi S4800 FESEM operated at a beam energy of 20.0 KV. High resolution transmission electron microscopic (HRTEM) images are obtained by JEOL JEM 2100 microscopic machine with an electron voltages of 200KV.

4.5.1 XRD ANALYSIS:

Sample1:

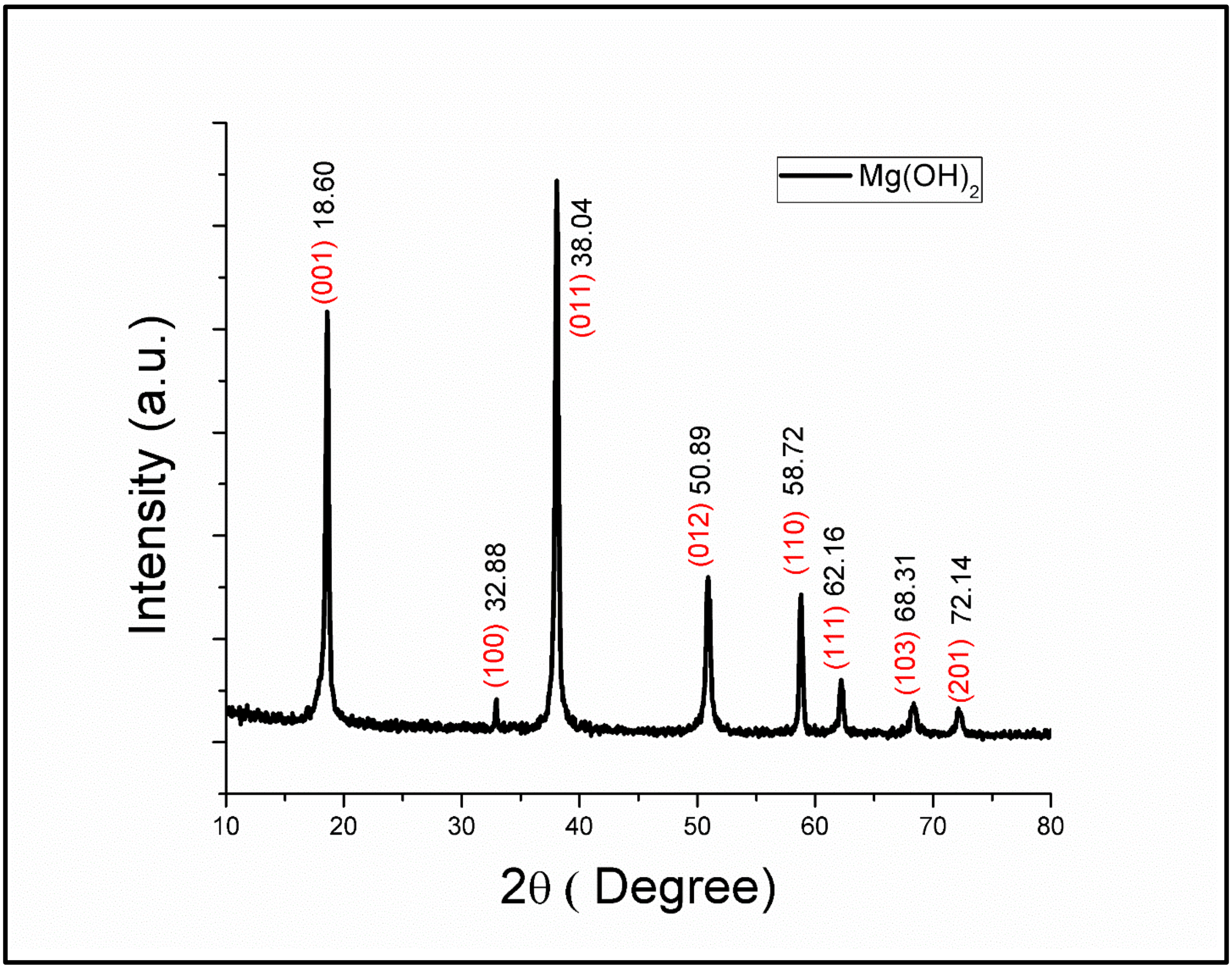

Figure 1(a): XRD pattern of the sample 1

Fig 1(a) represents the XRD pattern of sample 1. The 2θ values and d value of the peaks in the XRD pattern agree with JCPDS data of $Mg(OH)_2$. The XRD patterns in the fig 1(a) confirming the formation of Magnesium Hydroxide to a pure hexagonal phase [space group 76-0667] with calculated lattice constants a = 3.142 Å and c = 4.766 Å, mineral name brucite in agreement with the reported data (JCPDS 7-239).

Sample 2:

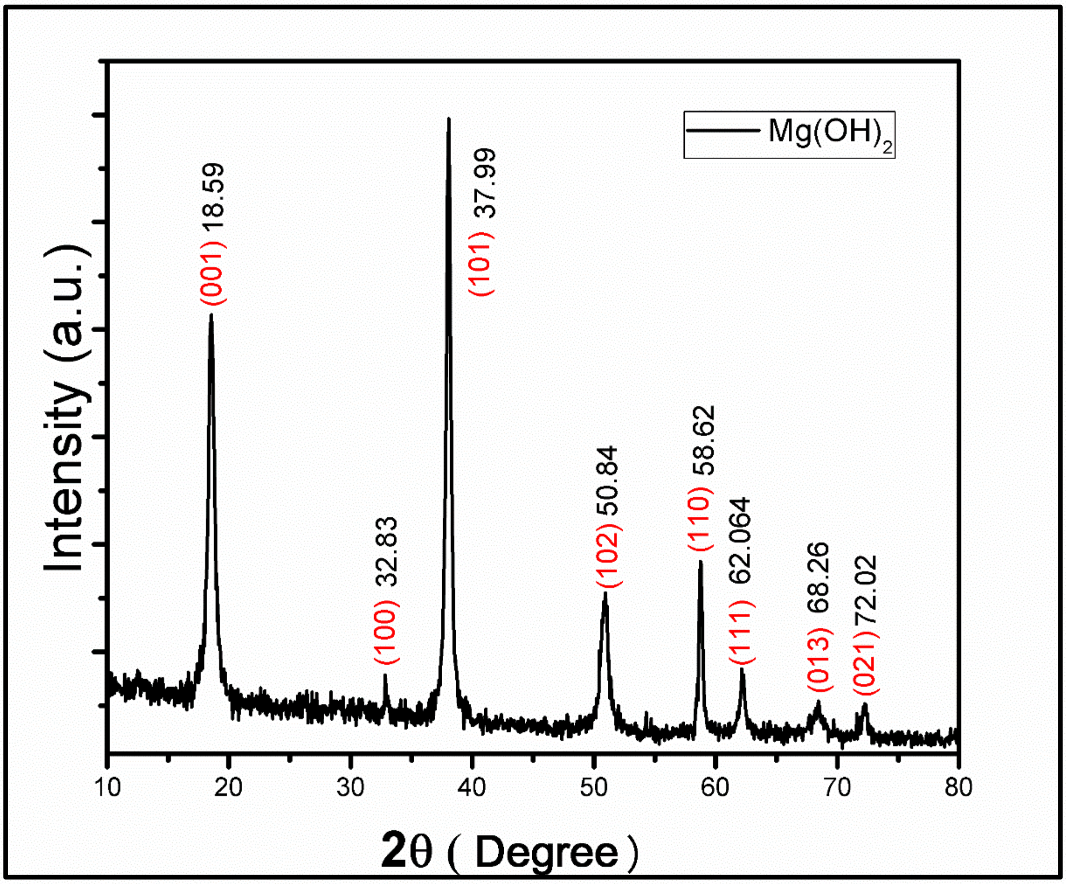

Figure 1(b): XRD pattern of the sample 2

Fig1(b) represents the XRD pattern of sample 2. The 2θ values and d value of peaks in the XRD pattern agree with JCPDS data of $Mg(OH)_2$. The XRD patterns in the fig 1(b) conforming the formation of Magnesium Hydroxide to a pure hexagonal phase [space group 74-2220] with calculated lattice constants a = 3.147 Å and c = 4.768 Å, mineral name brucite in agreement with the reported data (JCPDS 7-239).

4.5.2 FESEM Analysis

Sample 1:

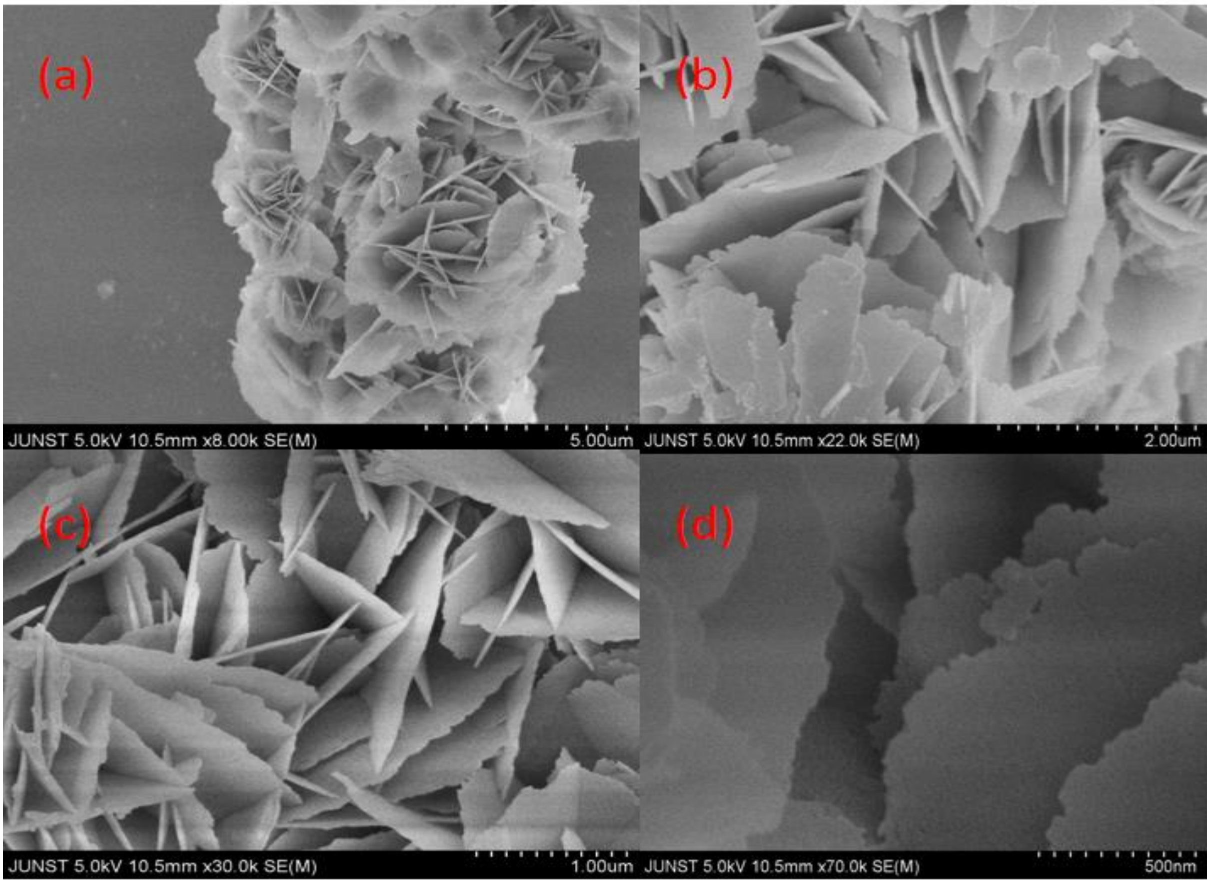

Figure 2: FESEM image of $Mg(OH)_2$ (sample 1) at magnification (a) 5 µm, (b) 2 µm, (c) 1 µm and (d) 500 nm

Fig 2 shows the FESEM image of $Mg(OH)_2$ prepared using MgCl2, 6H2O as the precursor. The image confirms flower like structure. The average diameter is 1.782 µm and thickness 34 nano meter (imageJ softwear).

Sample 2:

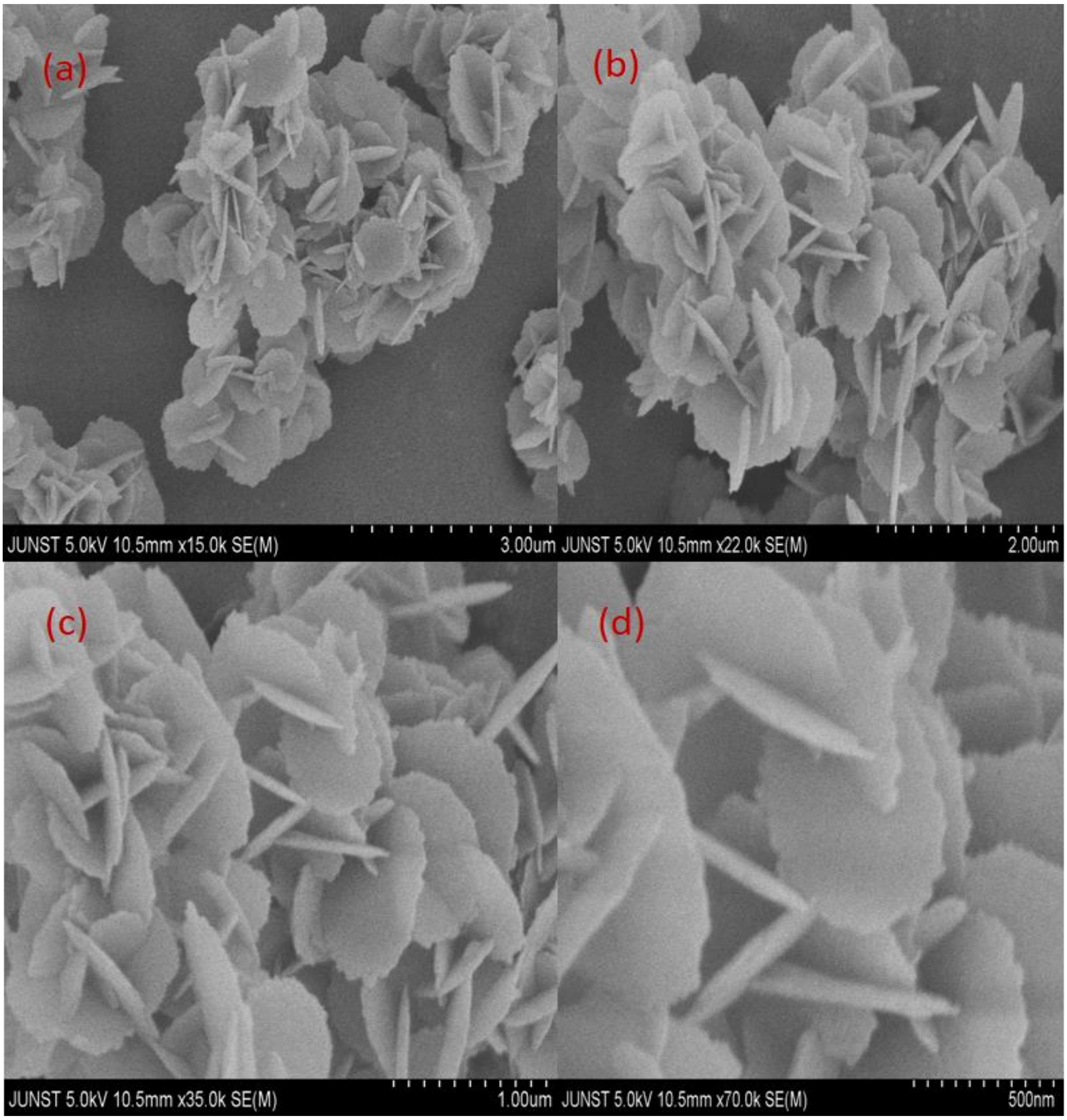

Figure 3: FESEM image of $Mg(OH)_2$ (sample 2) at magnification (a) 3 µm, (b) 2 µm, (c) 1 µm and (d) 500 nm

Fig 3 shows the FESEM image of $Mg(OH)_2$ prepared using MgSO4 ,7H2O as the precursor. The image confirms the flower like structure. The average diameter is 0.742 µm and (imageJ softwear) and thickness 22 nano meter. So we have seen that synthesized particle of $Mg(OH)_2$ more small as compare to sample1 where we used $MgSO_4$ as precursor.

4.5.3 HRTEM Analysis

Sample 1:

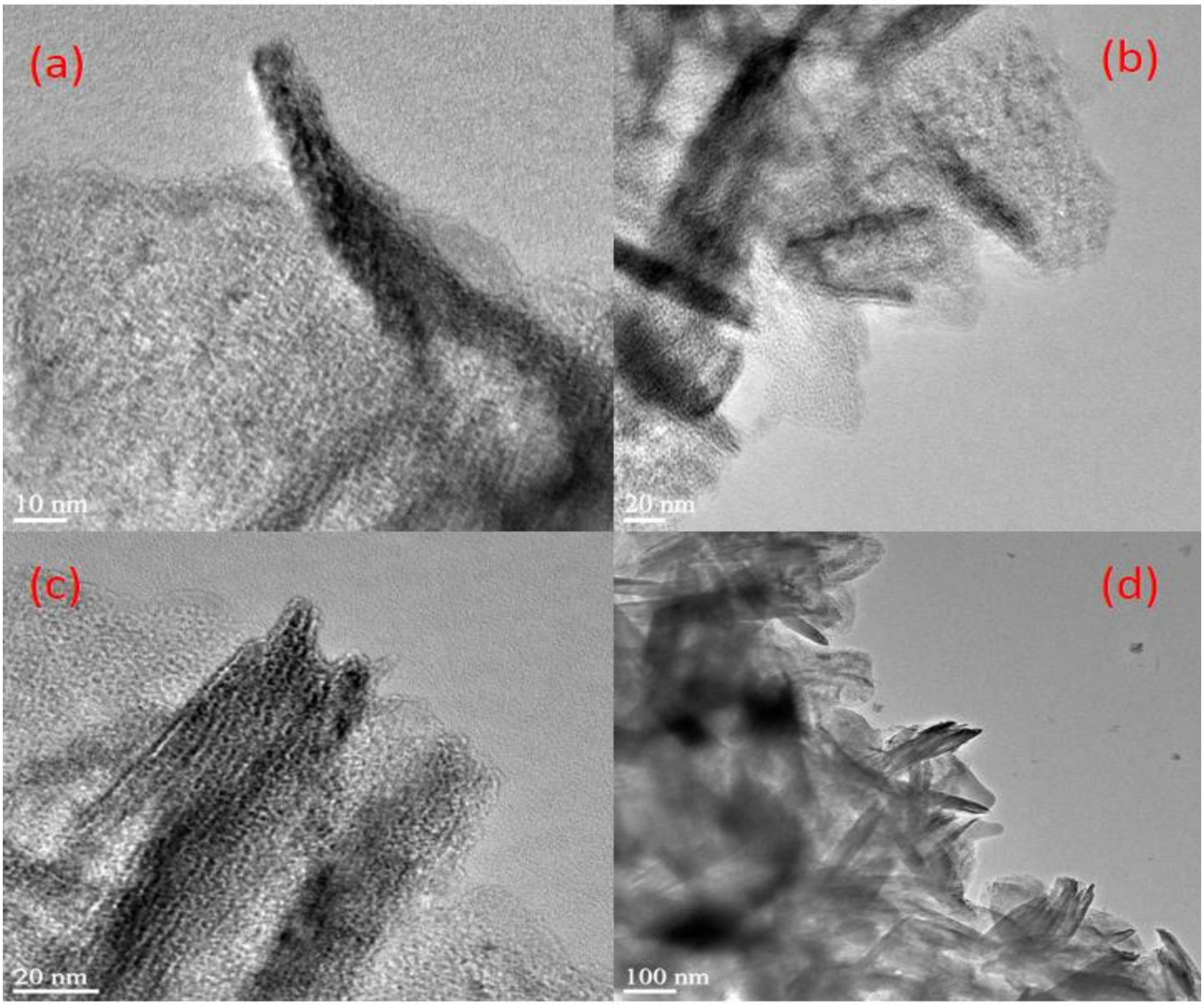

Figure 4: HRTEM image of magnesium hydroxide (sample 1) at magnifications (a) 10nm, (b) 20nm, (c) 20nm, (d) 100nm

The morphology and structure of the $Mg(OH)_2$ is further examined with high resolution transmission electron microscopy (HRTEM). TEM image of the Mg(OH)2 at different magnification shows the presence of fine size pores on the surface.

Sample 2:

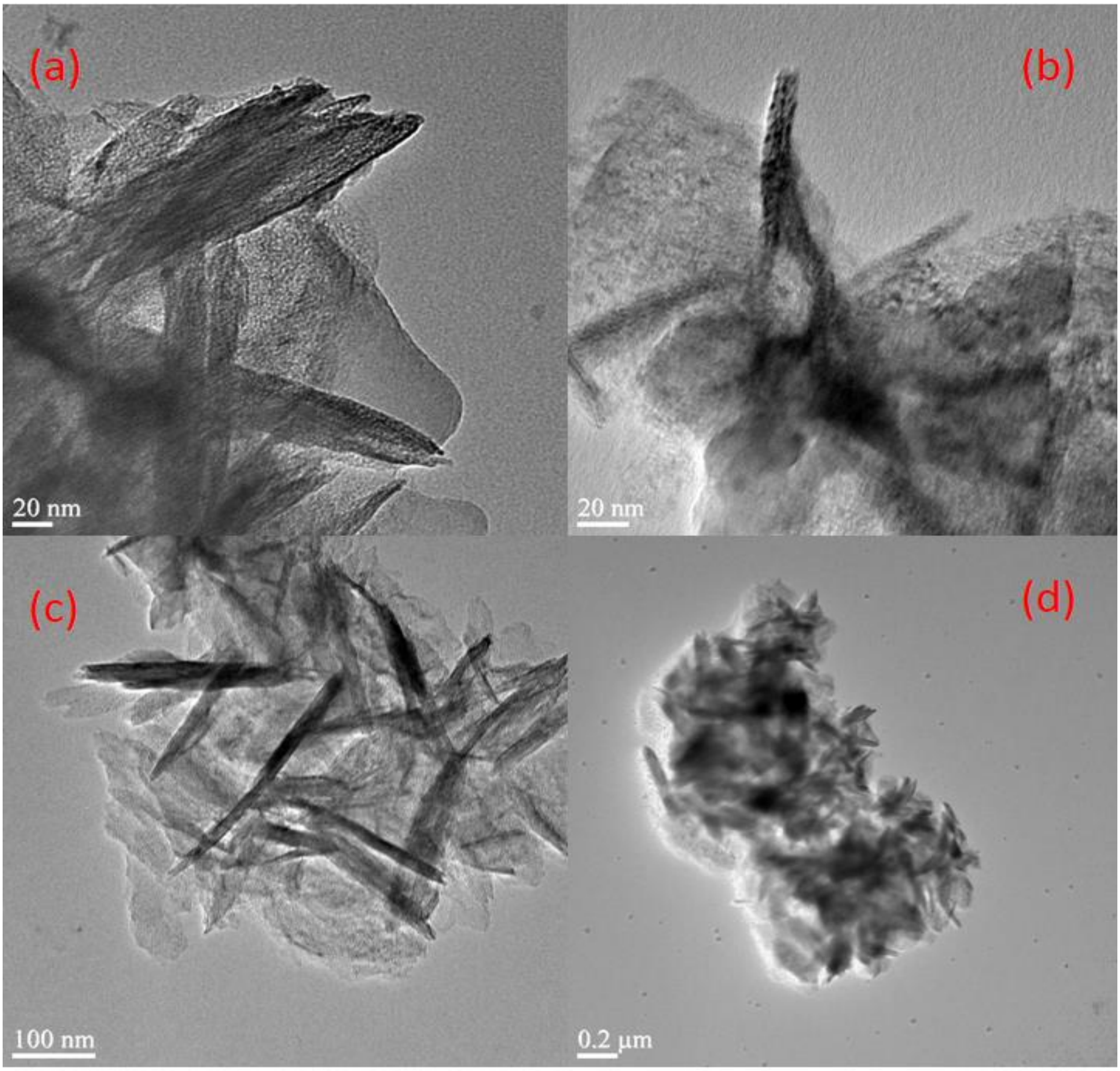

Figure 5: HRTEM image of magnesium hydroxide (sample 2) at magnifications (a) 20nm, (b) 20nm, (c) 100nm, (d) 0.2µm

The morphology and structure of the $Mg(OH)_2$ is further examined with high resolution transmission electron microscopy (HRTEM). TEM image of the Mg(OH)2 at different magnification shows the fine size pores on the surface.

To see the effect of amount of magnesium hydroxide on the adsorption of the cadmium from the solution, 30ml of cadmium stock solution with 10 mg/l concentration of cadmium is treated with different amount of magnesium hydroxide and concentration of the solution is measured in each case after 4 hours. The initial and final concentration of the cadmium in the solution is given in table 1

SL NO	Amount of $Mg(OH)_2$	Amount of Cd stock solution	Initial; concentration (mg/l)	Final concentration (mg/l)	Average concentration (mg/l)
1	5mg	30ml	10	0.866	0.916
				0.966	
2	10mg	30ml	10	0.740	0.7705
				0.801	
3	20mg	30ml	10	0.572	0.592
				0.612	
4	30mg	30ml	10	0.363	0.378
				0.393	
5	40mg	30ml	10	0.270	0.280
				0.290	
6	50mg	30ml	10	0.207	0.212
				0.217	

Table1: Effect of variation of amount Mg(OH)2 on the adsorption of cadmium

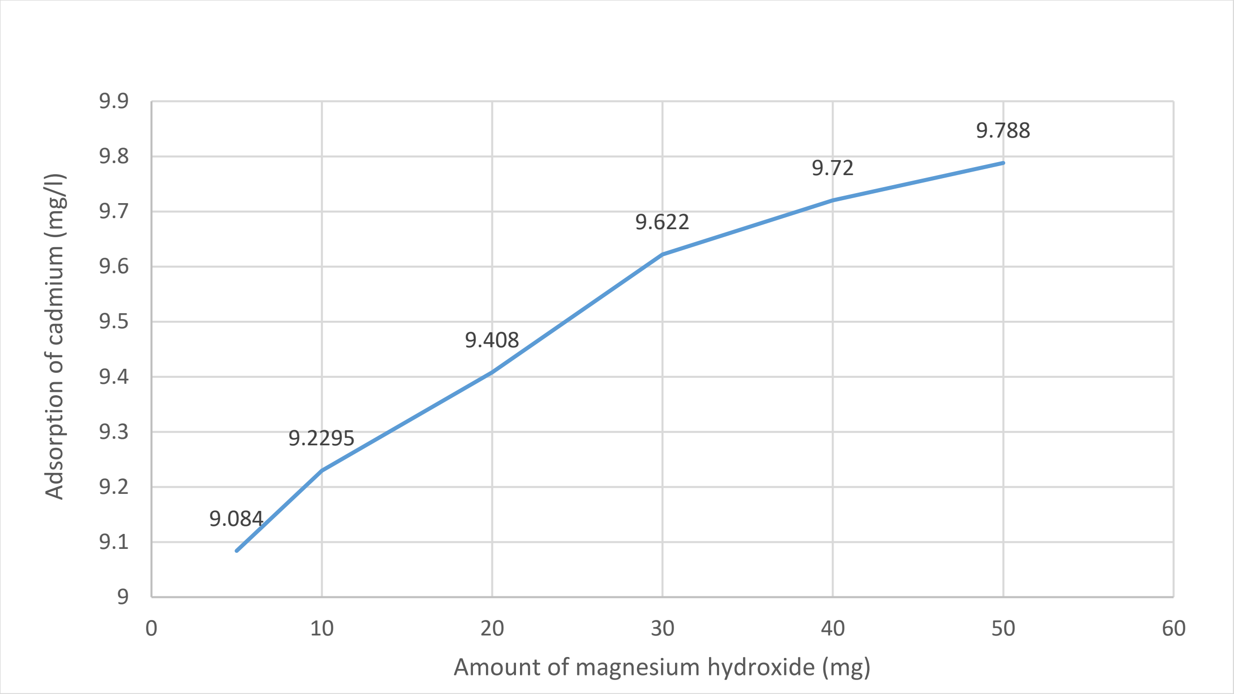

Figure 6: Adsorption of cadmium at different amount of magnesium

Analysing the data it is observed that with increasing the $Mg(OH)_2$ mount from 5mg to 50mg the concentration of cadmium in the solution is reduce from 0.916 mg/l to 0.212 mg/l in case of 5mg $Mg(OH)_2$ adsorption of cadmium ions 9.084 mg/l and for 50mg $Mg(OH)_2$ adsorption of cadmium ions 9.788 mg/l.

To see the effect of time on the adsorption of cadmium from the cd stock solution, 100ml of cadmium stock solution with 10mg/l concentration of cadmium is treated with 50mg of Mg(OH)2 . The concentration of cadmium in the solution is measured by taking 10ml of solution after 30 minutes interval by AAS. The initial and final concentration is given in the table 2.

The same process is repeated for 200ml and 300ml cadmium stock solution, initial and final concentration of cadmium in the solution is given in the table 3 and table4 respectively.

SL No	Time interval (min)	Cd stock solution (ml)	Amount of $Mg(OH)_2$ (mg)	Initial concentration (mg/l)	Final concentration (mg/l)	Adsorption of Cadmium (mg/l)
1	0	100	50	10	10	0
2	30	100	50	10	0.772	9.228
3	60	100	50	10	0.478	9.522
4	90	100	50	10	0.311	9.689
5	120	100	50	10	0.294	9.706
6	150	100	50	10	0.245	9.755
7	180	100	50	10	0.232	9.768

Table 2 : Effect of time on the adsorption of cadmium ions for 100ml cadmium stock solution

SL No	Time interval (min)	Cd stock solution (ml)	Amount of $Mg(OH)_2$ (mg)	Initial concentration (mg/l)	Final concentration (mg/l)	Adsorption of Cadmium (mg/l)
1	0	200	50	10	10	0
2	30	200	50	10	1.526	8.474
3	60	200	50	10	1.356	8.644
4	90	200	50	10	1.191	8.809
5	120	200	50	10	1.076	8.924
6	150	200	50	10	1.055	8.945
7	180	200	50	10	0.976	9.024

Table 3 : Effect of time on the adsorption of cadmium ions for 200ml cadmium stock solution

SL No	Time interval (min)	Cd stock solution (ml)	Amount of $Mg(OH)_2$ (mg)	Initial concentration (mg/l)	Final concentration (mg/l)	Adsorption of Cadmium (mg/l)
1	0	300	50	10	10	0
2	30	300	50	10	1.988	8.012
3	60	300	50	10	1.830	8.17
4	90	300	50	10	1.718	8.282
5	120	300	50	10	1.624	8.376
6	150	300	50	10	1.546	8.454
7	180	300	50	10	1.483	8.517

Table 4: Effect of time on the adsorption of cadmium ions for 300ml cadmium stock solution

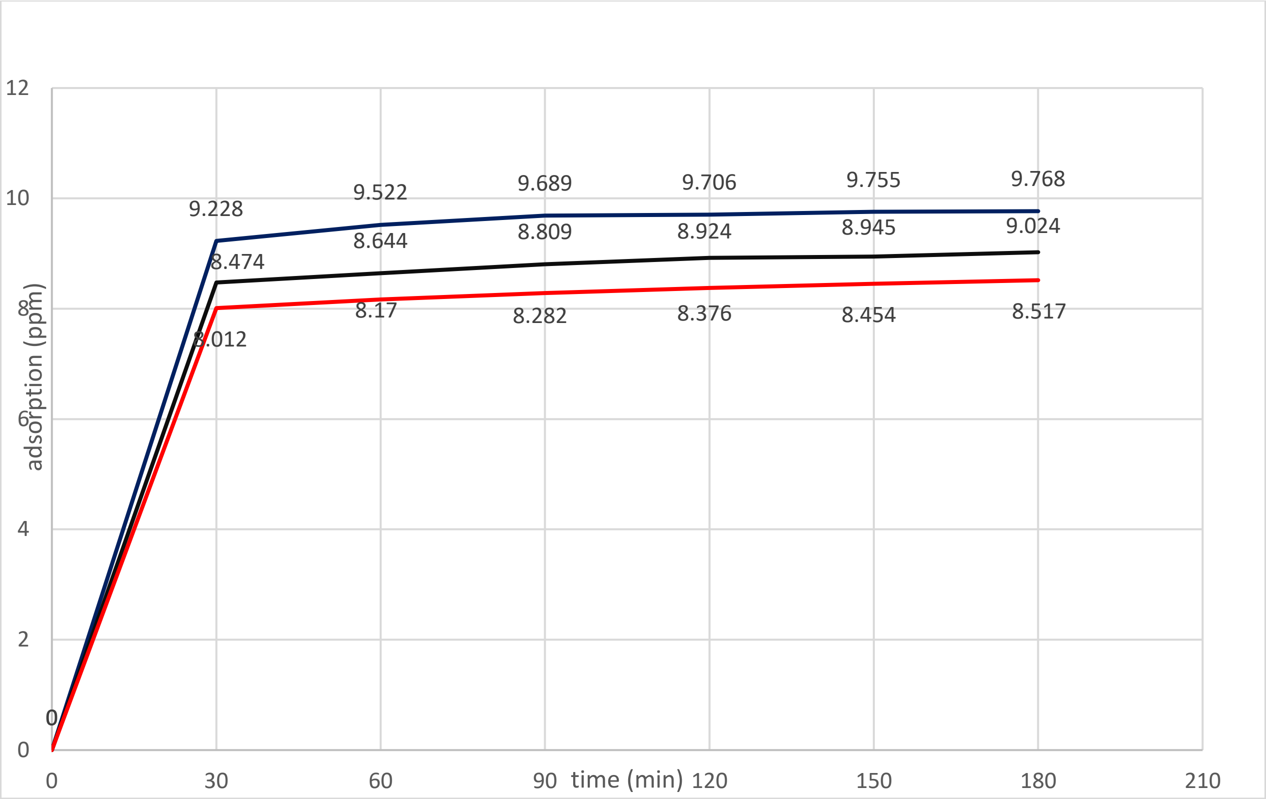

Figure 7: Effect of Time on the adsorption of cadmium from different volume of cadmium stock solution(100ml,200ml,300ml). Blue, black and red represent for 100ml, 200ml and 300ml respectively.

Analysing the dates it is observed that with the increase of time the adsorption of cadmium ions from stock solution increased. In case of 100 ml of 10mg/l cadmium stock solution treated with 50mg $Mg(OH)_2$, the concentration of cadmium in the solution reduce 10mg/l to 0.232 mg/l from 0 minute to 180 minute respectively.

Same process for 200ml and 300ml cadmium stock solution , the concentration of cadmium in the solution reduce from 10mg/l to .976 mg/l and 10mg/l to 1.483 mg/l respectively.

5. Conclusions

Magnesium hydroxide with flower like morphology is obtained by precipitation with the use of magnesium salt and ammonium hydroxide as precipitation agent with a non-ionic compound from the group of poly ethylene glycols. With the use of magnesium sulphate and PEG 400 (modifier) obtained magnesium hydroxide BET surface area (m^2/g) more as compared to used other magnesium salt. The magnesium hydroxide nanostructure reduce cadmium concentration as high as 10 mg/l to as low as 0.201 mg/l. The amount of magnesium hydroxide and the contact time of magnesium hydroxide with the solution is important parameter, with increase amount of magnesium hydroxide adsorption is increased and also adsorption is increased with contact time. Thus magnesium hydroxide powders with highest surface areas and well pore size is a strong material for heavy metal removal from waste water.