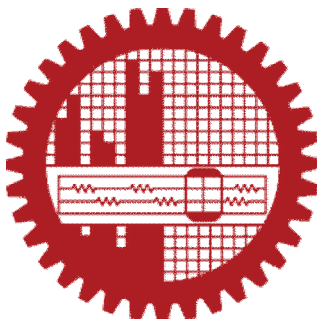


**PREPARATION, CHARACTERIZATION AND STUDIES OF THE ADSORBING
EFFICIENCY OF THE IRON OXIDE-SILICA NANOCOMPOSITE MATERIAL**

**A dissertation submitted in partial fulfillment of the requirements for the degree of
M. Phil. in Chemistry**

By

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DHAKA. Bangladesh.
August 2014.**

CANDIDATE'S DECLARATION

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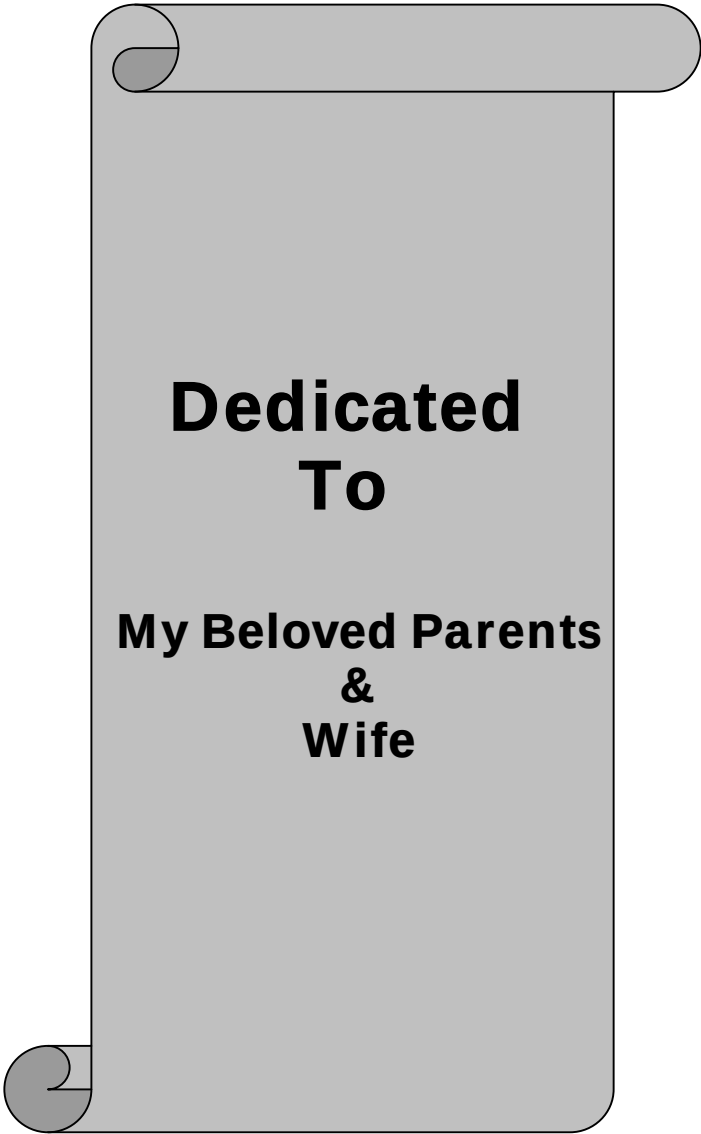
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**Dedicated
To**

**My Beloved Parents
&
Wife**

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Abstract

Composite material is a material composed of two or more distinct phases (matrix phase and dispersed phase) and having bulk properties significantly different from those of any of the constituents. Nanocomposites are composites in which at least one of the phases shows dimensions in the nanometer range ($1\text{ nm} = 10^{-9}\text{m}$). In the present study a novel method for preparing $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite materials is presented. Iron (III) oxide was prepared by electrochemical method. SiO_2 was prepared by basic hydrolysis of the tetraethylorthosilicate (TEOS).

This study shows the influence of silica on the structure, size, and distribution of the Fe_2O_3 particles in the $\text{Fe}_2\text{O}_3\text{-SiO}_2$ systems. The structural characterization of the synthesized materials was performed by X-ray diffraction, FT-IR, Scanning Electron Microscopy (SEM), EDS and DTA/TGA. The present study introduces a good alternative method for Cr (VI) removal from aqueous solutions by adsorption, allowing the development of newer, lower operational cost, and more efficient technology than other processes already in use. Adsorption was found to be dependent on pH and initial concentration of Cr(VI) solution. Results of adsorption studies suggest that pristine iron oxide and silicon (IV) oxide removes 72.10% and 24.73% respectively. The iron oxide – silicon (IV) oxide nanocomposite, prepared in this work, removes 93.88% Cr(IV) from aqueous solution. Therefore, it can be concluded that iron oxide–silicon (IV) oxide nanocomposite is a potential adsorbent for adsorption of Cr(VI) from aqueous solution. Studies of the sorption kinetics show that equilibrium adsorption was attained in 20 minutes depending on other experimental conditions. The kinetic data justified Lagergren first-order kinetic equation. Adsorption isotherm study showed that the results fulfilled the Langmuir Model of adsorption isotherm.

Chapter 1

INTRODUCTION

1.1 Composite Material

1.1.1 Definition

Composite material is a type of materials made from two or more different materials having very different properties. The two materials work together to give the composite unique properties.

In another word, composite material is a material composed of two or more distinct phases (matrix phase and dispersed phase) and having bulk properties significantly different from those of any of the constituents ¹. The primary phase, having a continuous character, is called matrix. It holds the dispersed phase and shares a load with it. The second phase (or phases) is embedded in the matrix in a discontinuous form is called dispersed phase, which is usually stronger than the matrix, therefore it is sometimes called reinforcing phase.

Composites are a unique class of materials made from two or more distinct materials that when combined are better (stronger, tougher, and/or more durable) than each would be separately. The different materials work together to give the composite unique properties, but within the composite you can easily tell the different materials apart – they do not dissolve or blend into each other.

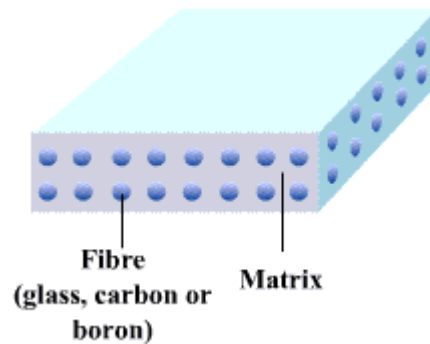


Figure 1.1: Basic construction of a composite material

In composite materials, the components can be physically identified and exhibit an interface between one another. The most common composite is the fibrous composite consisting of reinforcing fibers embedded in a binder, or matrix materials.

1.1.2 Constituents of a composite

Constituents mean the individual materials that make up composites. Most composites have two constituents: **a binder or matrix**, and a **reinforcement or filler**.

Matrix

The matrix is the component that holds the filler together to form the bulk of the material. It usually consists of various epoxy type polymers but other materials may be used. Matrix keeps the reinforcement in a set place. The binder also protects the reinforcement, which may be brittle or breakable, as in the case of the long glass fibers used in conjunction with plastics to make fiberglass.

Reinforcement

The reinforcements or filler is the material that has been impregnated in the matrix to lend its advantage (usually strength) to the composite. The fillers can be of any material such as carbon fiber, glass bead, sand, or ceramic. Reinforcement improves the overall mechanical properties of the matrix. The reinforcement is usually much stronger and stiffer than the matrix, and gives the composite its good properties.

When designed properly, the new combined material exhibits better surface area than would each individual material. Generally, composite materials have excellent adsorbing ability combined with good porosity, making them versatile in a wide range of situations.

1.1.3 Classification

Actually the production of composites is an attempt to copy nature. Wood is a composite of cellulose fibers cemented together with lignin. This kind of composite is called natural composites. And for man-made composites, there are two classification systems of composite materials. One of them is based on the matrix material (metal, ceramic, and polymer) and the second is based on the material structure ².

Classification based on matrix material: With respect to the matrix constituent composite materials are of three types:

Organic Matrix Composites (OMCs): The term organic matrix composite is generally assumed to include two classes of composites, namely Polymer Matrix Composites (PMCs) and carbon matrix composites commonly referred to as carbon-

carbon composites. Polymer Matrix Composites (PMC's) are the most common. Also known as FRP - Fiber Reinforced Polymers - these materials use a polymer-based resin as the matrix, and a variety of fibers such as glass and carbon as the reinforcement. Polymer Matrix Composites are composed of a matrix from thermoset [Unsaturated Polyester (UP), Epoxiy (EP)] or thermoplastic [Polycarbonate (PC), Polyvinylchloride, Nylon, Polystyrene] and embedded glass, carbon, steel or Kevlar fibers (dispersed phase).

For example “fibreglass”, the first successful modern composites, is one of the polymer matrix composites. It is used for making boat hulls, storage tanks, pipes, and car components.

Metal Matrix Composites (MMCs) : Metal Matrix Composites are composed of a metallic matrix (aluminum, magnesium, iron, cobalt, copper) and a dispersed ceramic (oxides, carbides) or metallic (lead, tungsten, molybdenum) phase. MMC's are increasingly found in the mobile industry.

Ceramic Matrix Composites (CMCs): Ceramic Matrix Composites are composed of a ceramic matrix and embedded fibers of other ceramic material (dispersed phase). Ceramic Matrix Composites are used in very high temperature environments.

1.1.4 Properties of composite materials

Superior and unique mechanical and physical properties can be provided by a composite, because it combines the most desirable properties of its constituents while

suppressing their least desirable properties. The example is, a glass-fiber reinforced plastic combines the high strength of thin glass fibers with the ductility and chemical resistance of plastic; the brightness that the glass fibers have when isolated is not a characteristic of the composite ³.

Some other attractive properties can be shown by the composites, such as high thermal or electrical conductivity and a low coefficient of thermal expansion. Also, depending on how the fibers are oriented or interwoven within the matrix, composites can be fabricated that have structural properties specifically tailored for a particular structural use. The most important distinguishing characteristics of a composite are its geometrical features and the fact that its performance is the collective behaviour of its constituents. A composite material can vary in composition, structure and properties from one point to the next inside the material. Surface, catalytic, photo catalytic and elastic properties are also observed for some of the prepared metal oxide composites.

1.1.5 The importance of composites

Composites have properties, which could not be achieved by either of the constituent materials alone. We can see that composites are becoming more and more important as it can help to improve our quality of life. Composites are put into service in flight vehicles, automobiles, boats, pipelines, buildings, roads, bridges, and dozens of other products. Researchers are finding ways to improve other qualities of composites so they may be strong, lightweight, long-lived, and inexpensive to produce. Different materials are suitable for different applications.

1.1.6 Disadvantages of composite material

Although composite materials have certain advantages over conventional materials, composites also have some disadvantages. The common one is the high manufacturing costs. However, as improved manufacturing techniques are developed, it will become possible to produce composite materials at higher volumes and at a lower cost than is now possible. Most composites use thermoset matrices that can't be reshaped. Some of the associated disadvantages of advanced composites are as follows:

- a). High cost of raw materials and fabrication.
- b). Reuse and disposal may be difficult.

However, proper design and material selection can circumvent many of the above disadvantages.

1.1.7 Nanomaterials

Nowadays nano metal oxide is one of the promising materials for scientists. The applications of nano oxide particles are increasing day by day. The most commonly used transition metal oxides are titania, manganese oxide, zinc oxide, cobalt oxide, nickel oxide, iron oxide etc.

Nanotechnology is expected to be the basis of many of the main technological innovations of the 21st century. Research and development in this field is growing rapidly throughout the world. A major output of this activity is the development of new materials in the nanometer scale, including nanoparticles. A unique aspect of nanotechnology is the

vastly increased ratio of the surface area to volume present in many nanoscale materials which opens new possibilities in surface-based science, such as catalysis. A number of physical phenomena become noticeably pronounced as the size of the system decreases. These include statistical mechanical effects, as well as quantum mechanical effects, for example the “the quantum size effect” where the electronic properties of solids are altered with great reductions in particle size. This effect does not come into play by going from macro dimension. However, it becomes dominant when the nanometer size range is reached.

Materials reduced to the nanoscale can suddenly show very different properties compared to what they exhibit on a macroscale, enabling unique application. For instance, opaque substances become transparent (copper); inert materials become catalyst (platinum); stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold); insulators become conductors (silicon). Materials such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology exhibits at the nanoscale.

A nanoparticle (which historically has included nanopowder, nanocluster and nanocrystal) is a small particle with at least one dimension less than 100 nm. This definition can be fleshed out further in order to remove ambiguity from future nano nomenclature. A nanoparticle is an amorphous or semicrystalline zero dimensional (0D) nano structure with at least one dimension between 10 and 100 nm and a relatively large ($\geq 15\%$) size dispersion ⁴.

1.1.8 Nanocomposites

The definition of nanocomposite material has broadened significantly to encompass a large variety of system such as one-dimensional, two dimensional, three-dimensional and amorphous materials made of distinctly dissimilar components and mixed at the nanometer scale.

Nanocomposite materials formed by metallic or oxide particles dispersed in polymer, ceramic or vitreous matrices have important application in areas such as catalysis and electronics. An interesting class of nanocomposite materials is formed by nanometer sized magnetic particles dispersed in insulating matrix. These nanocrystalline particles have a high surface/volume ratio, leading to magnetic properties different from those of bulk materials. Such properties are also highly dependent on the particle size distribution as well as on the aggregation of particles when compared to different production methods. Sol-gel process has proved to be an efficient method to prepare ultra-fine particles dispersed in different matrices and, particularly, to produce thin film. Through this method, a good control of the sample morphology, texture, structure, and chemical composition can be attained by carefully monitoring the preparation parameters. The use of an inorganic matrix allows narrow dispersion of particle size, and homogeneous distribution⁵.

Nanocomposites are composites in which at least one of the phases shows dimensions in the nanometer range ($1 \text{ nm} = 10^{-9} \text{ m}$)⁶. Nanocomposite materials have emerged as suitable alternatives to overcome limitations of micro composites and monolithic, while posing preparation challenges related to the control of elemental composition and

stoichiometry in the nanocluster phase. They are reported to be the materials of the 21st century in the view of possessing the design uniqueness and property combinations that are not found in conventional composites. The general understanding of these properties is yet to be reached, even though the first inference on them was reported as early as 1992.

The general class of nanocomposite organic/inorganic materials is a fast growing area of research. Significant effort is focused on the ability to obtain control of the nanoscale structures via innovative synthetic approaches. The properties of nano-composite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics.

The inorganic components can be three-dimensional framework systems such as zeolites, two-dimensional layered materials such as clays, metal oxides, metal phosphates, and chalcogenides. Experimental work has generally shown that virtually all types and classes of nanocomposite materials lead to new and improved properties when compared to their macro composite counterparts. Therefore, nanocomposites promise new applications in many fields such as mechanically reinforced lightweight components, non-linear optics, battery cathodes and Ionic, nano-wires, sensors and other systems. The general class of organic/inorganic nanocomposites may also be of relevance to issues of bio-ceramics and biomineralization in which *in-situ* growth and polymerization of biopolymer and inorganic matrix is occurring. Finally, lamellar nanocomposites represent an extreme case of a composite in which interface interactions between the two phases are maximized. Since the remarkable properties of conventional composites are mainly due to interface interactions, the materials dealt with here could provide good model systems in which

such interactions can be studied in detail using conventional bulk sample (as opposed to surface) techniques. Inorganic layered materials exist in great variety. They possess well defined, ordered intra lamellar space potentially accessible by foreign species. This ability enables them to act as matrices or hosts for polymers, yielding interesting hybrid nano-composite materials.

1.1.9 General method of preparation of iron oxide-SiO₂ composite

Nowadays, the attention of many scientists is focused on the development of new methods for synthesis and stabilization of composite materials, especially nanoparticles. Moreover, special attention is paid to monodispersed and stable particles formation. Different metals, metal oxides, sulfides, polymers, core-shell and composite nanoparticles can be prepared using a number of synthetic techniques, which are broadly classified into three categories, namely, physical methods, chemical methods and electro-chemical methods.

Chemical technique involves (i) Chemical vapor deposition (ii) vapor-phase synthesis: (iii) Hydrothermal synthesis (iv) Sol-gel technique (v) Sonochemical technique (vi) Micro emulsion technique and (vii) Wet-chemical Process.

Physical method involves – (i) Laser ablation (ii) Sputtering (iii) Spray route pyrolysis and (iv) Inert Gas condensation.

Nanostructured composites can also be synthesized by electrochemical method. The electrochemical method has been used for the synthesis of an array of nanomaterials such

as metals, inorganic composites, conducting polymer fibers or tubes, nanotubes and nanofibers etc. In this method, nanostructured materials are allowed to deposit on the electrode from different electrolytic solution. Depending on the precursor of the element to be deposited, electrodes of various types were used.^{7,8}

General method of Chemical Synthesis

A widely used chemical process is the oxidative polymerization. Various oxidizing agents, such as potassium dichromate, ammonium persulphate, ferric chloride, hydrogen peroxide etc. are used in these processes. Persulphate is the most commonly used oxidant and its ammonium salt was preferred to the potassium counterpart because of its better solubility in water. A colloidal solution of silica is used for the polymerization. During dispersion polymerization, a monomer, soluble in the reaction medium is converted into polymer, which is insoluble under those conditions. In this approach the silica particles act as colloidal substrate having high surface area the resulting nanocomposite particles are stable colloidal dispersions, which consist of micro aggregates of silica particles “glued” together by the conducting polymer component.

Conventional chemical polymerization techniques have been successfully applied by various research groups for the preparation of sterically stabilized particles of electrically conducting polymers.

In this research, we focused our attention on the preparation of iron oxide –silica composites by Sol-Gel method and we attempted to synthesize the iron oxide-silica composite following the Sol-Gel method. We used tetraethylorthosilicate (TEOS) as the precursor of silicon (IV) oxide and iron oxide was prepared by electrochemical method.

MariaZaharescu et al⁹ prepared iron oxide-silica composite by Sol-Gel method. The reagents employed were tetraethoxysilane (TEOS)(Merck) as a precursor to silicon (IV) oxide and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as a precursor to iron oxide, absolute ethyl alcohol as solvent ammonia as catalyst and water for hydrolysis. They reported that the iron oxide-silica composite was prepared as follows:

- (i) The iron oxide was generated during the Sol-Gel process
- (ii) The SiO_2 matrix was initially obtained and iron oxide was formed by thermal treatment after impregnation of soluble Fe^{2+} salt in the previously processed matrix;
- (iii) Magnetite powder prepared by wet chemical method were mixed with Sol-Gel solution, being embedded into SiO_2 based matrix after gelation.

They characterized the synthesized iron oxide-silica composite by XRD, DTA/TG techniques and reported that materials with high porosity and nano-sized oxides content could be prepared by Sol-Gel method.

Silicon (IV) oxide of iron oxide-silica composite synthesized by Sol-Gel method provides a high surface area, which enables the composite to act as a good sorbent material.

Clapsaddle et al.¹⁰ synthesized silicon oxide in an iron (III) oxide matrix by Sol-Gel method. In the synthesis, iron oxide precursor, iron(III) chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was mixed with a silica precursor, tetraethylorthosilicate(TEOS) in ethanol and gelled using an organic epoxide. The composition of the resulting materials was varied from Fe/Si (mol/mol)=1-5 by adjusting the amount of silica precursor added to the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$

solution. They reported that the synthesis method they presented is general for the synthesis of several other metal oxide/silicon oxide nanocomposite materials.

R. Predoi et al ¹¹ synthesized nanocomposites $\text{Fe}_x\text{O}_y\text{-SiO}_2$, with an iron content of 3 wt. % by the Sol-Gel method starting from tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS) precursors as the SiO_2 sources. This original method produces large quantities of amorphous gels that are thermally treated at 550°C and 1000°C as the final step of the synthesis. The average diameter of iron particles in the nano-composite materials can be controlled by the iron concentration and thermally treatment. The dried gel was treated at increasing temperatures, and the samples were characterized by transmission electron microscopy (TEM), IR-spectroscopy and magnetic measurements. The result indicates that the formation and the stability of the iron oxide phases are strongly affected by the precursors used as the SiO_2 sources.

1.1.10 Application

Composites have acquired a leading position in the development of new materials. Due to some miraculous properties, composites have widen research arena in Chemistry.

The nanocomposite particles are important in two ways. Firstly, the silica component enables facile functionalisation at the particle surface. Secondly, the intense black colour, which is an intrinsic property of the conducting polymer component (in this case polypyrrole), eliminates the need to use an extrinsic dye to achieve the visual agglutination test. In principle, this increases the sensitivity of the test, allowing lower analyte concentrations to be detected.

Nanoporous materials like Zeolites are micro porous, aluminosilicate minerals commonly used as commercial adsorbents. These materials are also known as *molecular sieve* – they contain tiny pores of a precise and uniform size that are useful as adsorbent for gases and liquids. Due to these characteristics, zeolite has found wide applications in adsorption, catalysis, and the removal of heavy metal ions from industrial wastewaters. Composite materials prepared by different method can be used for the removal of different heavy metals from wastewater. Thus we can use composite materials for environmental applications.

1.2 The Sol-Gel Method^{12,13}

The sol-gel process is very long known since the late 1800s. The versatility of the technique has been rediscovered in the early 1970s when glasses were produced without high temperature melting processes. This made possible the organic modification of silicon compounds (ORMOSIL), which cannot withstand high temperatures. The interest in sol-gel processing can be traced back in the mid-1980s with the observation that the hydrolysis of tetraethyl orthosilicate (TEOS) under acidic conditions led to the formation of SiO₂ in the form of fibers and monoliths. Sol-gel research grew to be so important that in the 1990s more than 35,000 papers were published worldwide on the process.^{14,15,16}

Definition

The **sol-gel** process is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials (typically metal oxides) starting from a colloidal solution (*sol*) that acts as the

precursor for an integrated network (or *gel*) of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal salts (such as chlorides, nitrates and acetates), which undergo various forms of hydrolysis and polycondensation reactions.

Process

In this chemical procedure, the 'sol' (or solution) gradually evolves towards the formation of a gel-like diphasic system containing both a liquid phase and solid phase whose morphologies range from discrete particles to continuous polymer networks. In the case of the colloid, the volume fraction of particles (or particle density) may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation.

Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes imposed upon the structural template during this phase of processing.

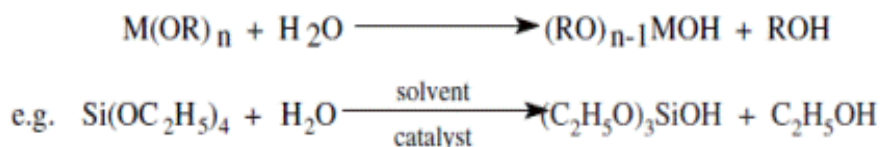
Afterwards, a thermal treatment, or firing process, is often necessary in order to favor further polycondensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth. One of the distinct advantages of using this methodology as opposed to the more traditional processing techniques is that densification is often achieved at a much lower temperature.

The precursor sol can be either deposited on a substrate to form a film (e.g., by dip coating or spin coating), cast into a suitable container with the desired shape (e.g., to obtain monolithic ceramics, glasses, fibers, membranes, aero gels), or used to synthesize powders (e.g., micro spheres, nanospheres). The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. Even small quantities of dopants, such as organic dyes and rare earth elements, can be introduced in the sol and end up uniformly dispersed in the final product. It can be used in ceramics processing and manufacturing as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes. Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio)sensors, medicine (e.g., controlled drug release), reactive material and separation (e.g., chromatography) technology.

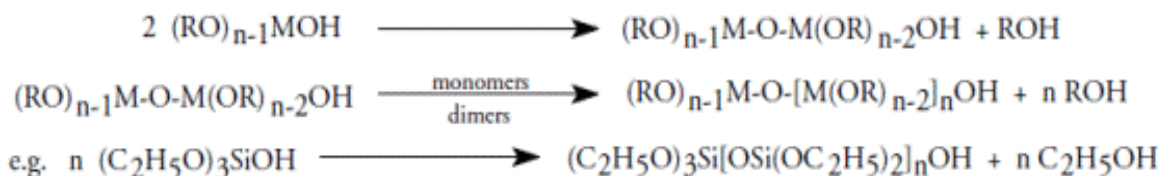
Preparation of metal oxides using sol-gel routes proceeds by three basic steps:

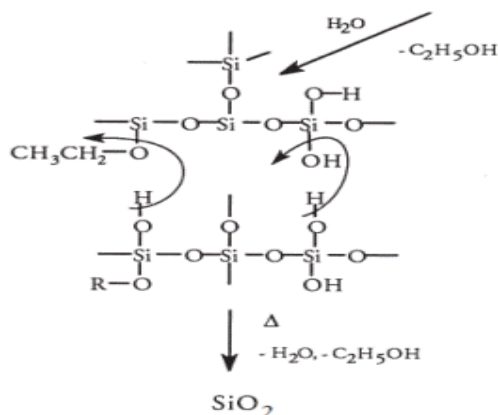
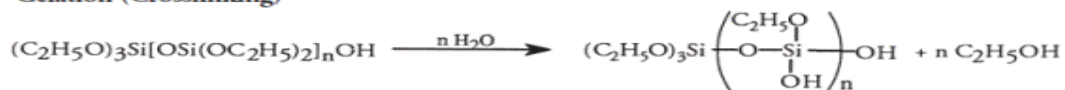
- 1) partial hydrolysis of metal alkoxides to form reactive monomers,
- 2) condensation of these monomers to form colloid-like oligomers (sol formation),
- 3) additional hydrolysis to promote polymerization and cross-linking leading to a three-dimensional matrix (gel formation).

Monomer Formation (Partial Hydrolysis)



Sol Formation (Polycondensation)



Gelation (Crosslinking)**Applications**

The applications for sol gel-derived products are numerous¹⁷

Nanoscale powders: Ultra-fine and uniform ceramic powders can be formed by precipitation. These powders of single and multiple component compositions can be produced on a nanoscale particle size for dental and biomedical applications. Composite powders have been patented for use as agro chemicals and herbicides. Powder abrasives, used in a variety of finishing operations, are made using a sol-gel type process. One of the more important applications of sol-gel processing is to carry out zeolite synthesis.

Advantages

The sol-gel technique offers a low-temperature method for synthesizing materials that are either totally inorganic in nature or both inorganic and organic. The process, which is based on the hydrolysis and condensation reaction of organometallic compounds in

alcoholic solutions, offers many advantages for the fabrication of coatings, including excellent control of the stoichiometry of precursor solutions, ease of compositional modifications, customizable microstructure, ease of introducing various functional groups or encapsulating sensing elements, relatively low annealing temperatures, the possibility of coating deposition on large area substrates, and simple and inexpensive equipment. Within the past several years, a number of developments in precursor solutions, coating processes and equipment have made the sol-gel technique even more widespread.

1.3 Adsorption¹⁸

1.3.1 Definition

The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid resulting in the higher concentration of the molecules on the surface is called Adsorption. The substance thus adsorbed on surface is called Adsorbate and the substance on which it is adsorbed is called Adsorbent.

Alternately, adsorption is the process through which a substance, originally present in one phase, is removed from that phase by *accumulation at the interface* between that phase and a separate (solid) phase. In principle adsorption can occur at any solid fluid interface.

The driving force for adsorption is the reduction in interfacial (surface) tension between the fluid and the solid adsorbent as a result of the adsorption of the adsorbate on the surface of the solid. The most important factors affecting adsorption are:

- *Surface area of adsorbent*: Larger sizes imply a greater adsorption capacity.

- *Particle size of adsorbent*: Smaller particle sizes reduce internal diffusional and mass transfer limitation to the penetration of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly full adsorption capability can be attained).
- *Contact time or residence time*: The longer the time the more complete the adsorption will be. However, the equipment will be larger.
- *Solubility of solute (adsorbate) in liquid (wastewater)*: Substances slightly soluble in water will be more easily removed from water (i.e., adsorbed) than substances with high solubility. Also, non-polar substances will be more easily removed than polar substances since the latter have a greater affinity for water.
- *Affinity of the solute for the adsorbent (carbon)*: The surface of activated carbon is only slightly polar. Hence non-polar substances will be more easily picked up by the carbon than polar ones.
- *Number of carbon atoms*: For substances in the same homologous series a larger number of carbon atoms is generally associated with a lower polarity and hence a greater potential for being adsorbed (e.g., the degree of adsorption increases in the sequence formic-acetic-propionic-butyric acid).
- *Size of the molecule with respect to size of the pores*: Large molecules may be too large to enter small pores. This may reduce adsorption independently of other causes.

- *Degree of ionization of the adsorbate molecule:* More highly ionized molecules are adsorbed to a smaller degree than neutral molecules.
- *pH :* The degree of ionization of a species is affected by the pH (e.g., a weak acid or a weak basis). This, in turn, affects adsorption.
- *Nature of gas being Adsorb:* Higher the critical temp. of gas, greater is the amount of that gas adsorbed.
- *Temperature:* Adsorption decreases with increase in temperature and vice - versa.
- *Pressure:* Adsorption of a gas increases with increase of pressure because on applying pressure gas molecules come close to each other.

1.3.2 Causes of Adsorption

Adsorption arises at the surface of solids as a result of presence of unbalanced forces at the surface. These forces develop either during the crystallization of solids or by virtue of the presence of unpaired electron in d-orbital.

1.3.3 Characteristics of Adsorption

1. It is specific and selective in nature.
2. It is accompanied by decrease in the free energy of the system. When G becomes zero, Adsorption equilibrium is established.
3. Adsorption is spontaneous process therefore change in free energy (G) for the process is negative.

According to Gibb's Helmholtz equation:

$$G = H - TS$$

$G = -Ve$; $H = -Ve$ (it is exothermic process) And S is $-Ve$ because adhering of gas molecules to the surface lowers the randomness.

1.3.4 Types of Adsorption

1.3.4. A Physical Adsorption:

Physisorption, also called physical adsorption, is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption¹⁹. The weak bonding of physisorption is due to the induced dipole moment of a nonpolar adsorbate interacting with its own image charge in the polarizable solid.

Some features which are useful in recognizing physisorption include:

- (a) the phenomenon is a general one and occurs in any solid/fluid system, although certain specific molecular interactions may occur, arising from particular geometrical or electronic properties of the adsorbent and/or adsorptive;
- (b) evidence for the perturbation of the electronic states of adsorbent and adsorbate is minimal;
- (c) the adsorbed species are chemically identical with those in the fluid phase, so that the chemical nature of the fluid is not altered by adsorption and subsequent desorption;
- (d) the energy of interaction between the molecules of adsorbate and the adsorbent is of the same order of magnitude as, but is usually greater than, the energy of condensation of the adsorptive;

- (e) the elementary step in physical adsorption from a gas phase does not involve an activation energy. Slow, temperature dependent, equilibration may however result from rate-determining transport processes;
- (f) in physical adsorption, equilibrium is established between the adsorbate and the fluid phase. In solid/gas systems at not too high pressures the extent of physical adsorption increases with increase in gas pressure and usually decreases with increasing temperature. In the case of systems showing hysteresis the equilibrium may be metastable;
- (g) under appropriate conditions of pressure and temperature, molecules from the gas phase can be adsorbed in excess of those in direct contact with the surface (multilayer adsorption or filling of micro pores).

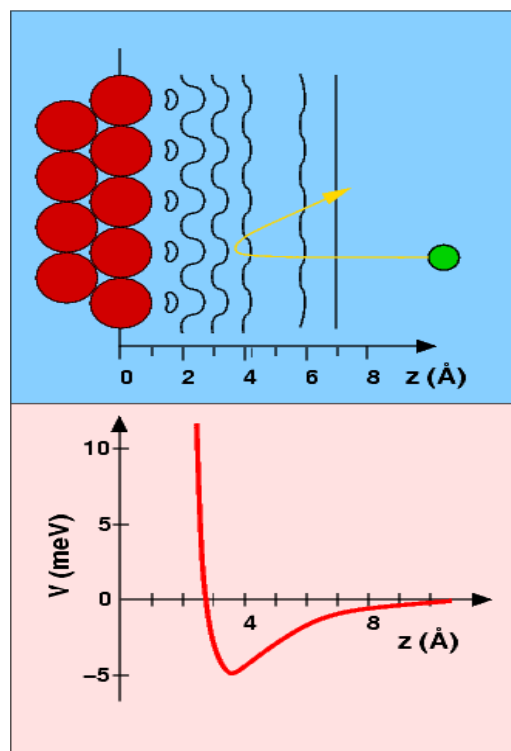


Figure 1.2: Example of Physisorption: He-Metal interaction^{18(a)}

1.3.4.B Chemical Adsorption:

Chemisorption is a sub-class of adsorption, driven by a chemical reaction occurring at the exposed surface. A new chemical species is generated at the adsorbent surface (e.g. corrosion, metallic oxidation). The strong interaction between the adsorbate and the substrate surface creates new types of electronic bonds - ionic or covalent, depending on the reactive chemical species involved²⁰. It is characterised by:

- An activation energy for the chemical reaction that takes place only in a monolayer
- A high enthalpy change/ temperature gain, indicating an exothermic chemical reaction: $-20 \text{ kJ/mol} > \Delta H > -200 \text{ kJ/mol}$

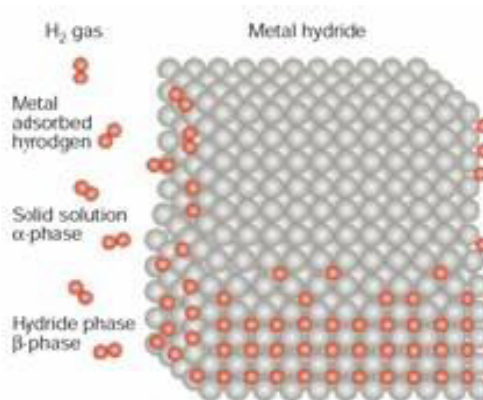


Figure 1.3: Illustration of Chemisorption^{18(a)}

Due to specificity, the nature of chemisorption can greatly differ from system to system, depending on the chemical identity and the surface structure. When a gas is held on the surface of solid by forces similar to those of a chemical bond, the type of

adsorption is called chemical adsorption or chemisorptions. It is also known as Langmuir adsorption.

1.3.5 Adsorption on solid liquid interface

There is a competition between the solute and solvent molecules for adsorption in the case of adsorption from solution. If the solute is adsorbed more than the solvent, i.e., the concentration of solute is less in the bulk, the adsorption is termed as positive adsorption. But if it is more in the bulk than in the interface, then negative adsorption results.

If the solute is a strong electrolyte, the cations and the anions are not likely to adsorb equally, particularly at low concentration. In general one of the ions depending on the nature of the adsorbent is preferentially adsorbed and the surface will acquire electric charge accordingly.

The extent of adsorption is greatly influenced by the lyophobicity of compound. The higher is the solvophobicity greater is the adsorption and vice versa. Adsorption from solution is also influenced by the pH of the solution. The change of ionic strength of the medium also alters the mode of adsorption.

In case of adsorption from solution, the effects of solvent on solution can not be neglected. Especially, when the surface is polar. For very dilute solutions and for low solubility of solute, the measurement of change in concentration of solution resulting from adsorption gives a very responsible isotherm for solute.

1.3.6 Factors affecting adsorption

i) Temperature: The level of adsorption at any particular concentration decreases with the increase in temperature; that is the overall process is exothermic. At higher temperature the adsorbed molecules have greater vibrational energies and therefore, more likely to desorb from the surface.

ii) Nature of the solvent: The solvent has an important effect, since it competes with the surface of the adsorbent in attracting the solute. There are three different ways to describe the influence of solvent on adsorption behavior of the solute (a) its interaction with the solute in solution, (b) its interaction with the adsorbed layer, and (c) its interaction with the solute in the adsorbed layer. However, when the solvent is water, it is worthless to consider the solvent effect.

iii) Particle and pore size: The adsorption efficiency increases as mean diameter of the particle decreases. Large surface area is available for adsorption with the small particles. Another reason is the reduced diffusive path length of the interior of small adsorbent particles and the adsorbate particles require less energy of jump from one active site to another, resulting in higher uptake by the adsorbent.

iv) pH of the solution: The effect of pH is extremely important when the adsorbing species are capable of ionizing in response to prevailing pH. It is well known that substances adsorb poorly when they are ionized. When the pH is such that an adsorbable compound exists in ionic form, adjacent molecules of the adsorbed species on the adsorbent surface will repel each other to a significant degree, because they carry the

same electrical charges. Thus the adsorbing species cannot be packed together very densely on the surface. This is the common observation that non-ionized forms of acidic and basic compounds adsorb much better than their ionized counterparts. The acidic species thus adsorb better at low pH and basic species adsorb better at high pH.

1.3.7 Adsorption equilibrium

The adsorbed solute tends to desorb into the solution during the adsorption from solution as the adsorption continues. At one stage, equal amount of solute is adsorbed and desorbed simultaneously. Eventually, the rate of adsorption and the rate of desorption will attain an equilibrium. This is called adsorption equilibrium and the corresponding time at which such equilibrium is achieved is known as the equilibrium time, t_e . The knowledge of equilibrium time is necessary for adsorption which controls the adsorption capacity.

The position of equilibrium is the characteristics of the following factors:

a) the entire system, b) the adsorbate, c) the adsorbent, d) the solvent, e) temperature, f) pH and g) ionic strength.

To investigate the mechanism of adsorption, the study of amount adsorbed at constant temperature using different concentration of adsorbate is mostly chosen. A number of mathematical expressions have been developed to give quantitative relationship between the amount adsorbed with equilibrium concentration of the solution. The amount adsorbed from solution at equilibrium is a function of temperature and equilibrium concentration of adsorbate, i.e. $x/m = f(C_e T)$

where, x/m = mass of adsorbate adsorbed per gram of adsorbent in mol g^{-1}

C_e = equilibrium concentration (M) of the solution; T = Absolute temperature (K)

1.3.8 Adsorption Isotherm¹⁸⁻²³

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. In the process of adsorption, adsorbate gets adsorbed on adsorbent.

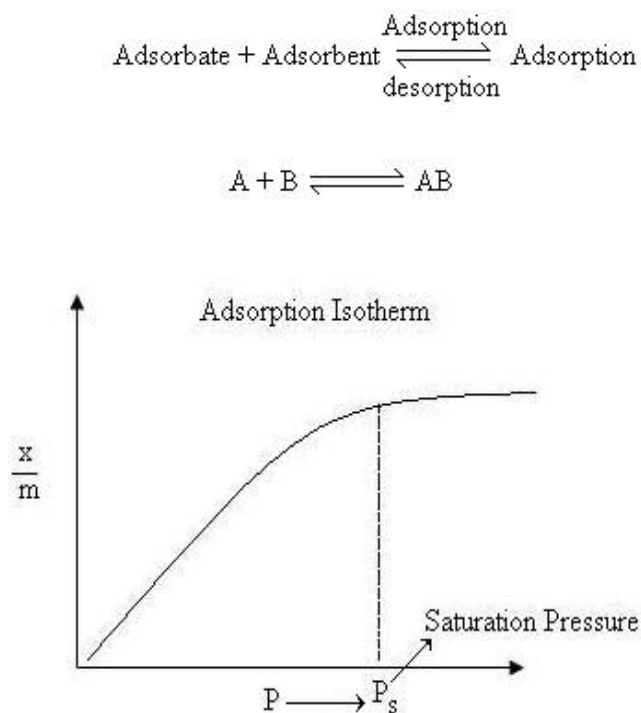


Figure 1.4: Basic Adsorption Isotherm^{18(b)}

1.3.8.A Freundlich Adsorption Isotherm

In 1909, Freundlich gave an empirical expression representing the isothermal variation of Adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure.

$$\frac{x}{m} = k_f P^{\frac{1}{n}}$$

This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation.

Where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p and k , n are constants whose values depend upon adsorbent and gas at particular temperature.

Explanation of Freundlich Adsorption equation:

At low pressure, extent of adsorption is directly proportional to pressure (raised to power one).

$$\frac{x}{m} \propto P^1$$

At high pressure, extent of adsorption is independent of pressure (raised to power zero).

$$\frac{x}{m} \propto P^0$$

Therefore at intermediate value of pressure, adsorption is directly proportional to pressure raised to power $1/n$. Here n is a variable whose value is greater than one.

$$\therefore \frac{x}{m} \propto P^{\frac{1}{n}}$$

Using constant of proportionality, k , also known as adsorption constant we get

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

The above equation is known as Freundlich adsorption equation.

Plotting of Freundlich Adsorption Isotherm:

As per Freundlich adsorption equation

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

Taking log both sides of equation, we get, $\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n} \log p$

The equation above equation is comparable with comparable with equation of straight line, $y = m x + c$ where, m represents slope of the line and c represents intercept on y axis.

Plotting a graph between $\log(x/m)$ and $\log p$, we will get a straight line with value of slope equal to $1/n$ and $\log k$ as y-axis intercept.

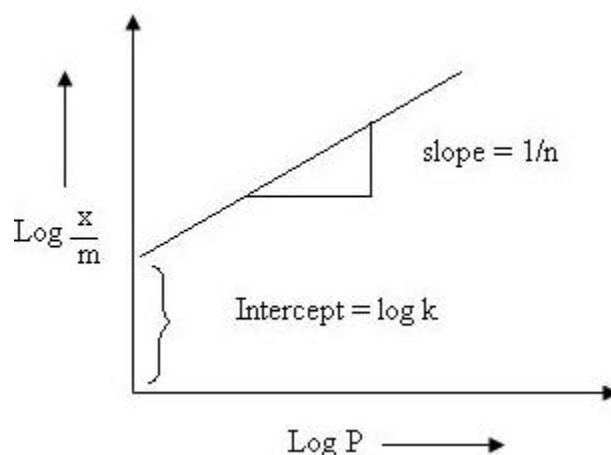


Figure 1.5: $\log(x/m)$ vs. $\log p$ graph^{18(b)}

The Freundlich Adsorption Isotherm is mathematically expressed as

$$x/m = K p^{1/n}$$

It is also written as

$$\log(x/m) = \log k + (1/n) \log p$$

Or $x/m = K c^{1/n}$

It is also written as

$$\log(x/m) = \log k + (1/n) \log c$$

Where, x = mass of adsorbate ; m = mass of adsorbent ; p = Equilibrium pressure of adsorbate ; c = Equilibrium concentration of adsorbate in solution.

K and n are constants for a given adsorbate and adsorbent at a particular temperature.

At high pressure $1/n = 0$ Hence extent of adsorption is independent of pressure.

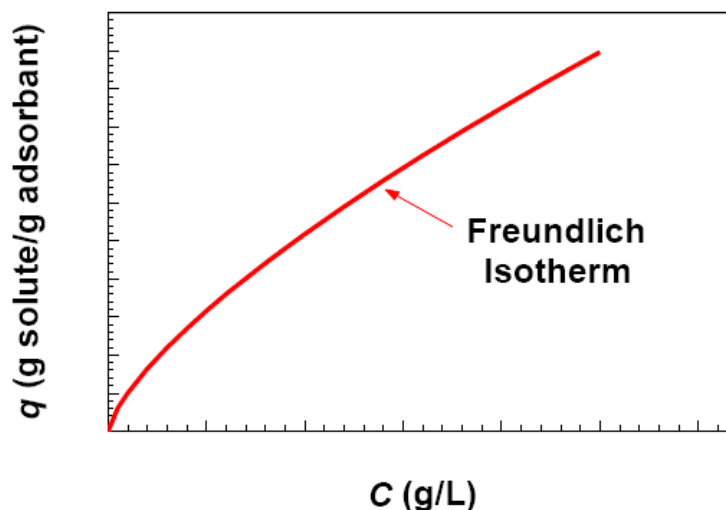


Figure 1.6: Example of the Freundlich isotherm, showing the amount adsorbed, q , as a function of equilibrium concentration in the solution, c (e.g., in g/L)^{18(c)}.

Limitation of Freundlich Adsorption Isotherm:

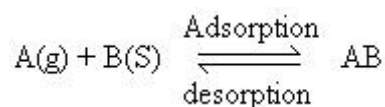
Experimentally it was determined that extent of adsorption varies directly with pressure till saturation pressure P_s is reached. Beyond that point rate of adsorption saturates even after applying higher pressure. Thus Freundlich Adsorption Isotherm failed at higher pressure.

1.3.8.B Langmuir Adsorption Isotherm

In 1916, Irving Langmuir published an isotherm for gases adsorbed on solids, which retained his name. It is an empirical isotherm derived from a proposed kinetic mechanism. This isotherm was based on five assumptions:

1. The surface containing the adsorbing sites is perfectly flat plane with no corrugations (assume the surface is homogeneous).

2. The adsorbing gas adsorbs into an immobile state.
3. All sites are equivalent.
4. Each site can hold at most one molecule of A (mono-layer coverage only).
5. There are no interactions between adsorbate molecules on adjacent sites.



Where A(g) is unadsorbed gaseous molecule, B(s) is unoccupied metal surface and AB is Adsorbed gaseous molecule.

Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

$$\theta = \frac{KP}{1 + KP}$$

Where θ the number of sites of the surface which are covered with gaseous molecule, P represents pressure and K is the equilibrium constant for distribution of adsorbate between the surface and the gas phase. At lower pressure, KP is so small, that factor (1+KP) in denominator can almost be ignored. So Langmuir equation reduces to

$$\theta = KP$$

At high pressure KP is so large, that factor (1+KP) in denominator is nearly equal to KP. So Langmuir equation reduces to

$$\theta = \frac{KP}{KP} = 1$$

Langmuir adsorption equation can be written as (for liquid adsorbate)

$$Q = \frac{K_a C}{1 + K_a C}$$

Where, $Q = Q_m$ = for a complete monolayer, K_a = a coefficient; C_e = concentration in the fluid. Taking reciprocals and rearranging:

$$\frac{C_e}{Q} = \frac{1}{K_a Q_m} + \frac{C_e}{Q_m}$$

A plot of C_e/Q versus C_e should indicate a straight line of slope $1/Q_m$ and an intercept of $1/K_a Q_m$. The graph shows data points and lines to both Freundlich and Langmuir equation.

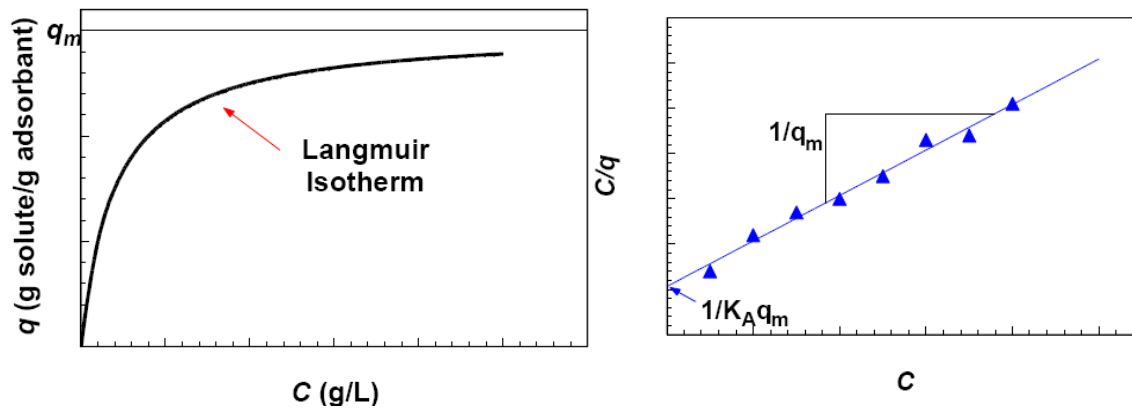


Figure 1.7: (a) Langmuir Isotherm; (b) Determination of parameters in Langmuir isotherm^{18(c)}

Limitations of Langmuir Adsorption Equation

1. The adsorbed gas has to behave ideally in the vapor phase. This condition can be fulfilled at low pressure conditions only. Thus Langmuir Equation is valid under low pressure only.
2. Langmuir Equation assumes that adsorption is monolayer. But, monolayer formation is possible only under low pressure condition. Under high pressure condition the assumption breaks down as gas molecules attract more and more molecules towards each other. *BET theory* proposed by Brunauer, Emmett and Teller explained more realistic multilayer adsorption process.
3. Another assumption was that all the sites on the solid surface are equal in size and shape and have equal affinity for adsorbate molecules i.e. the surface of solid is homogeneous. But we all know that in real solid surfaces are heterogeneous.
4. Langmuir Equation assumed that molecules do not interact with each other. This is impossible as weak force of attraction exists even between molecules of same type.
5. The adsorbed molecules have to be localized i.e. decrease in randomness is zero ($\Delta S = 0$). This is not possible because on adsorption liquefaction of gases takes place, which results into decrease in randomness but the value is not zero.

1.3.8.C. BET adsorption Isotherm

In 1938, Brunauer, Emmett and Teller²² derived the first isotherm for multilayer adsorption. It assumes a random distribution of sites that are empty or that are covered with by one monolayer, two layers and so on, as illustrated alongside.

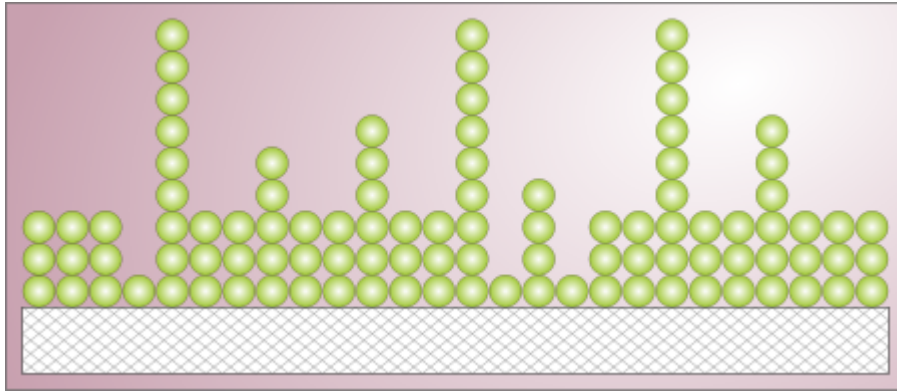


Figure 1.8: Brunauer's model of multilayer adsorption, that is, a random distribution of sites covered by one, two, three, etc., adsorbate molecules.

The BET equation is given as

$$V_{total} = \frac{V_{mono} C \left(\frac{P}{P_0} \right)}{\left(1 - \frac{P}{P_0} \right) \left(1 + C \left(\frac{P}{P_0} \right) - \frac{P}{P_0} \right)}$$

The another form of BET equation is

$$\frac{P}{V_{total}(P - P_0)} = \frac{1}{V_{mono} C} + \frac{C - 1}{V_{mono} C} \left(\frac{P}{P_0} \right)$$

Where V_{mono} be the adsorbed volume of gas at high pressure conditions so as to cover the surface with a unilayer of gaseous molecules,

$$\frac{K_1}{K_L}$$

the ratio is designated C. K_1 is the equilibrium constant when single molecule adsorbed per vacant site and K_L is the equilibrium constant to the saturated vapor liquid equilibrium.

It is important that many unusual adsorption isotherms are fitted well by the BET equation. This is to be expected when there are three coefficients to manipulate.

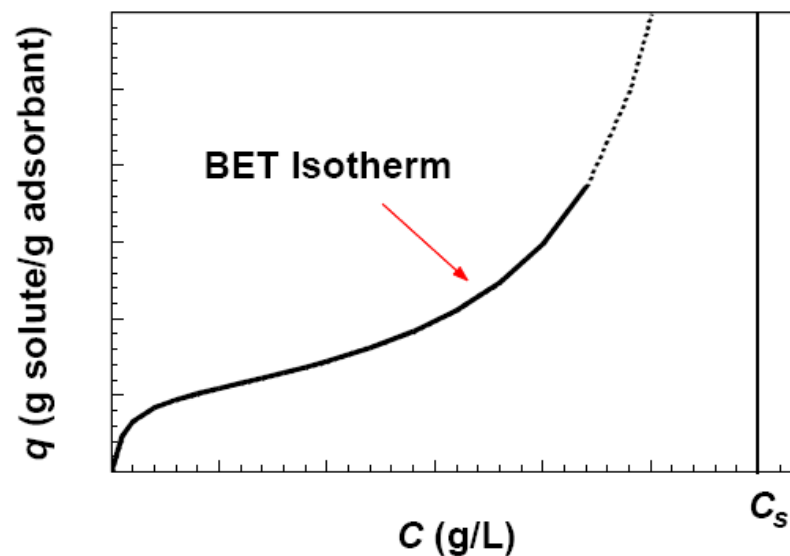


Figure 1.9 : BET isotherm ^{18(c)}

1.3.8.D. Type of Adsorption Isotherm

Five different types of adsorption isotherm and their characteristics are explained below.

Type I Adsorption Isotherm

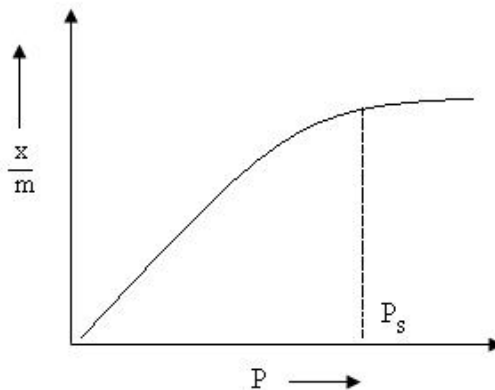


Figure 1.10: Type I Adsorption Isotherm^{18(b)}

- The above graph depicts Monolayer adsorption and can be easily explained using Langmuir Adsorption Isotherm.
- If BET equation, when $P/P_0 \ll 1$ and $c \gg 1$, then it leads to monolayer formation and Type I Adsorption Isotherm is obtained.
- Examples of Type-I adsorption are Adsorption of Nitrogen (N_2) or Hydrogen (H_2) on charcoal at temperature near to -180°C .

Type II Adsorption Isotherm

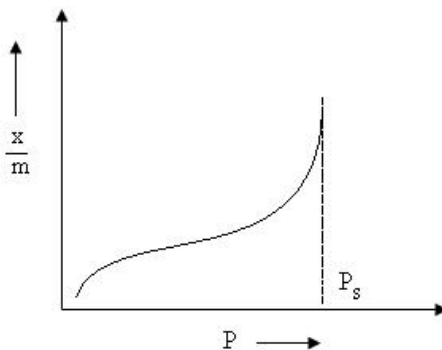


Figure 1.11: Type II Adsorption Isotherm^{18(b)}

- Type II Adsorption Isotherm shows large deviation from Langmuir model of adsorption.
- The intermediate flat region in the isotherm corresponds to monolayer formation.
- In BET equation, value of C has to be very large in comparison to 1.

- $\Delta H_{\text{des}}^0 > \Delta H_{\text{ads}}^0$

- Examples of Type-II adsorption are Nitrogen (N_2 (g)) adsorbed at -195°C on Iron (Fe) catalyst and Nitrogen (N_2 (g)) adsorbed at -195°C on silica gel.

Type III Adsorption Isotherm

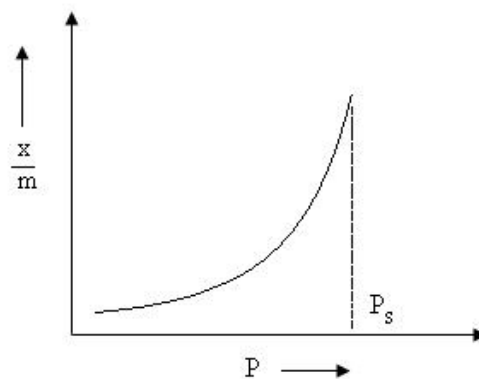


Figure 1.12: Type III Adsorption Isotherm^{18(b)}

- Type III Adsorption Isotherm also shows large deviation from Langmuir model.
- In BET equation value if $C \ll 1$ Type III Adsorption Isotherm obtained.
- This isotherm explains the formation of multilayer.
- There is no flattish portion in the curve which indicates that monolayer formation is missing.
- Examples of Type III Adsorption Isotherm are Bromine (Br_2) at 79°C on silica gel or Iodine (I_2) at 79°C on silica gel.

Type IV Adsorption Isotherm

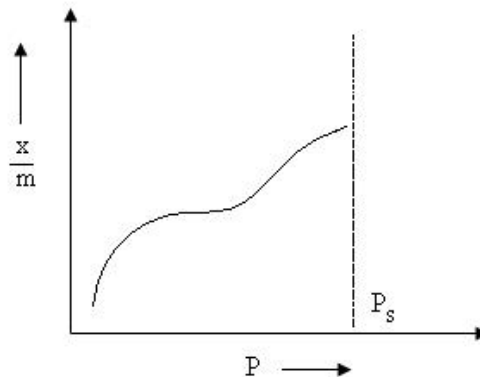


Figure 1.13: Type IV Adsorption Isotherm^{18(b)}

- At lower pressure region of graph is quite similar to Type II. This explains formation of monolayer followed by multilayer.
- The saturation level reaches at a pressure below the saturation vapor pressure. This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at pressure below the saturation pressure (P_s) of the gas.
- Examples of Type IV Adsorption Isotherm are of adsorption of Benzene on Iron Oxide (Fe_2O_3) at 50°C and adsorption of Benzene on silica gel at 50°C .

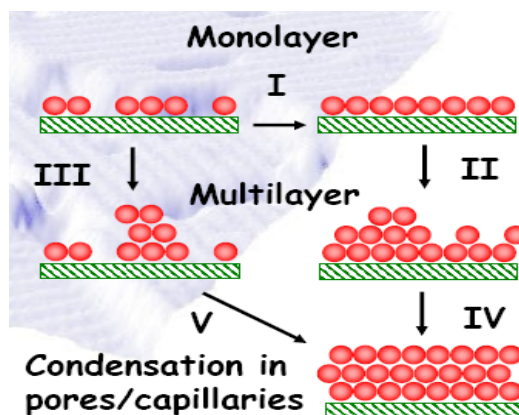


Figure 1.14: Nature of adsorption isotherm^{18(f)}

Type V Adsorption Isotherm

- Explanation of Type V graph is similar to Type IV.
- Example of Type V Adsorption Isotherm is adsorption of Water (vapors) at 100°C on charcoal.

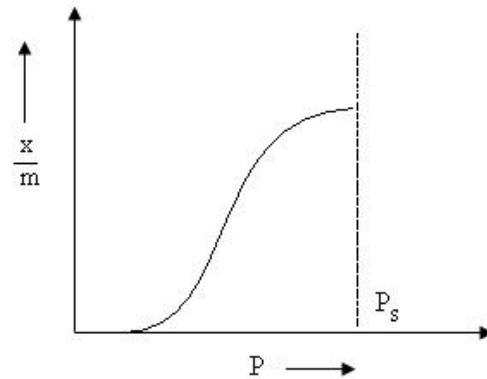


Figure 1.15: Type V Adsorption Isotherm^{18(b)}

1.3.9 Application of Adsorption

1. In preserving vacuum: In Dewar flasks activated charcoal is placed between the walls of the flask so that any gas which enter in to the annular space either due to glass imperfection or diffusion through glass is adsorbed.
2. In gas masks: All gas masks are devices containing suitable adsorbent so that the poisonous gases present in the atmosphere are preferentially absorbed and the air for breathing is purified.
3. In clarification of sugar: Sugar is decolorized by treating sugar solution with charcoal powder. The later adsorbs the undesirable colours present.
4. In softening of hard water: The use of ion exchangers for softening of hard water is based upon the principle of competing adsorption just as in chromatography.
5. In removing moisture from air in the storage of delicate instruments: Such instruments which may be harmed by contact with the moist air, are kept out of contact with moisture using silica gel.

6. In Adsorption indicator: Various dyes, which owe their use to adsorption, have been introduced as indicator particularly in precipitation titration. For example, KBr is easily titrated with AgNO_3 using eosin as indicator.

1.3.10 Adsorption kinetics-the rate of adsorption²⁴

The rate of adsorption, R_{ads} , of a molecule onto a surface can be expressed in the same manner as any kinetic process. For example, when it is expressed in terms of the partial pressure of the molecule in the gas phase above the surface:

$$R_{\text{ads}} = k' P^x;$$

Where x = kinetic order; k' = rate constant; P = partial pressure

If the rate constant is expressed in an Arrhenius form, then we obtain a kinetic equation of the form: $R_{\text{ads}} = A \exp (-E_a / RT) \cdot P^x$

Where E_a is the *activation energy for adsorption*, and A the *pre-exponential (frequency) factor*.

It is much more informative, however, to consider the factors controlling this process at the molecular level.

The rate of adsorption is governed by

1. the rate of arrival of molecules at the surface
2. the proportion of incident molecules which undergo adsorption

i.e. we can express the rate of adsorption (per unit area of surface) as a product of the incident molecular flux, F , and the sticking probability, S .

$$R_{\text{ads}} = S \cdot F \quad [\text{molecules m}^{-2} \text{ s}^{-1}]$$

The flux of incident molecules is given by the Hertz-Knudsen equation

$$\text{Flux, } F = P / (2\pi mkT)^{1/2} \quad [\text{molecules m}^{-2} \text{ s}^{-1}]$$

Where, P = gas pressure [N m^{-2}]; m = mass of one molecule [kg]; T = temperature [K]

The sticking probability is clearly a property of the adsorbate / substrate system under consideration but must lie in the range $0 < S < 1$; it may depend upon various factors - foremost amongst these being the existing coverage of adsorbed species (θ) and the presence of any activation barrier to adsorption. In general, therefore,

$$S = f(\theta \exp(-E_a / RT)).$$

where, once again, E_a is the activation energy for adsorption and $f(\theta)$ is some, as yet undetermined, function of the existing surface coverage of adsorbed species.

Combining the equations for S and F yields the following expression for the rate of adsorption:

$$R = \frac{f(\theta) \cdot P}{\sqrt{2\pi mkT}} \exp(-E_a / RT)$$

The above equation indicates that the rate of adsorption is expected to be first order with regard to the partial pressure of the molecule in the gas phase above the surface.

It should be recognised that the activation energy for adsorption may itself be dependent upon the surface coverage, i.e. $E_a = E(\theta)$.

If it is further assumed that the sticking probability is directly proportional to the concentration of vacant surface sites (which would be a reasonable first approximation for non-dissociative adsorption) then $f(\theta)$ is proportional to $(1-\theta)$; where, in this instance, θ is the fraction of sites which are occupied (i.e. the Langmuir definition of surface coverage).

1.4 Characterization techniques

1.4.1 Principle of FT-IR²⁵

Infrared spectroscopy is an important technique in organic chemistry. It is an easy way to identify the presence of certain functional groups in a molecule. Also, one can use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities.

FT-IR spectroscopy has been a workhorse technique for materials analysis in the lab for over 70 years. An IR spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the same IR spectrum. Therefore, IR spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With intuitive software algorithms, infrared is an excellent tool for quantitative analysis.

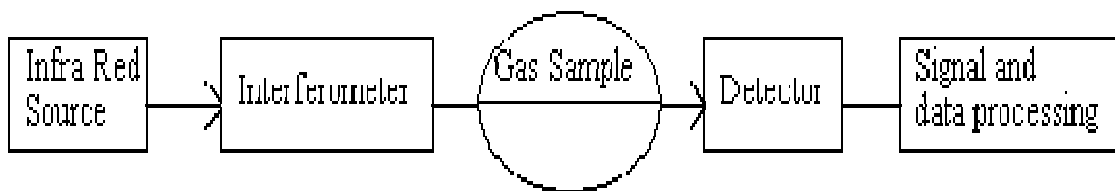


Figure 1.16: Basic components of FT-IR^{25(a)}

The basic components of an FTIR are shown schematically in **Figure 1.15**. The infrared source emits a broad band of different wavelength of infrared radiation. The IR radiation goes through an interferometer that modulates the infrared radiation. The interferometer performs an optical inverse Fourier transform on the entering IR radiation. The modulated IR beam passes through the gas sample where it is absorbed to various extents at different wavelengths by the various molecules present. Finally the intensity of the IR beam is detected by a detector, which is a liquid-nitrogen cooled MCT (Mercury-Cadmium-Telluride) detector in the case of the Temet GASMET FTIR CR-series. The detected signal is digitised and Fourier transformed by the computer to get the IR spectrum of the sample gas.

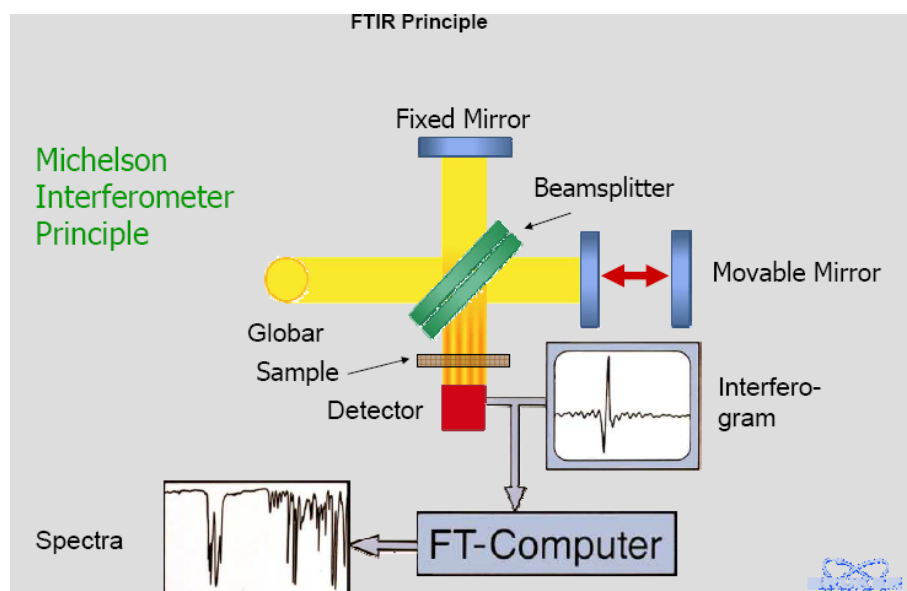


Figure 1.17: Michelson Interferometer

The unique part of an FTIR spectrometer is the interferometer. A Michelson type plane mirror interferometer is displayed in **Figure 1.16**. Infrared radiation from the source is collected and collimated (made parallel) before it strikes the beam splitter. The beam splitter ideally transmits one half of the radiation, and reflects the other half. Both transmitted and reflected beams strike mirrors, which reflect the two beams back to the beam splitter. Thus, one half of the infrared radiation that finally goes to the sample gas has first been reflected from the beam splitter to the *moving* mirror, and then back to the beam splitter. The other half of the infrared radiation going to the sample has first gone through the beam splitter and then reflected from the *fixed* mirror back to the beam splitter. When these two optical paths are reunited, interference occurs at the beam splitter because of the optical path difference caused by the scanning of the moving mirror.

The optical path length difference between the two optical paths of a Michelson interferometer is two times the displacement of the moving mirror. The interference signal measured by the detector as a function of the optical path length difference is called the interferogram. A typical interferogram produced by the interferometer is shown in **Figure 1.17**. The graph shows the intensity of the infrared radiation as a function of the displacement of the moving mirror. At the peak position, the optical path length is exactly the same for the radiation that comes from the moving mirror as it is for the radiation that comes from the fixed mirror.

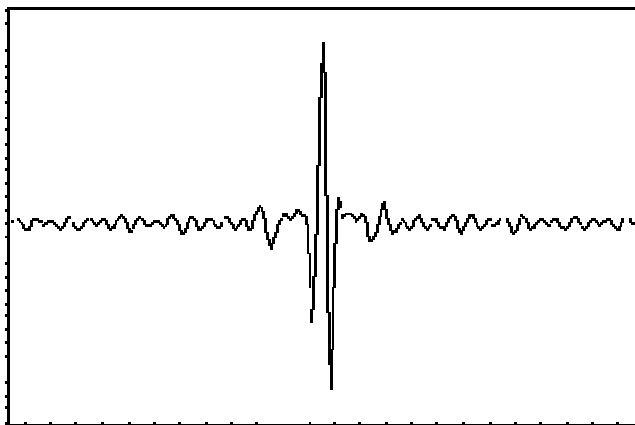


Figure 1.18: A typical interferogram^{25(a)}

The spectrum can be computed from the interferogram by performing a Fourier transform. A mathematical function called a Fourier transform allows us to convert an intensity-vs.-time spectrum into an intensity-vs.-frequency spectrum.

The Fourier transform:

$$A(r) = \sum X(k) \exp\left(-2\pi \frac{ir k}{N}\right)$$

$A(r)$ and $X(k)$ are the frequency domain and time domain points, respectively, for a spectrum of N points.

1.4.2 Principle of X-ray Diffractometer (XRD)²⁶

X-ray diffraction (XRD) is one of the most powerful technique for qualitative and quantitative analysis of crystalline compounds. The technique provides information that cannot be obtained any other way. The information obtained includes types and nature of crystalline phases present, structural make-up of phases, degree of crystallinity, amount of amorphous content, micro strain & size and orientation of crystallites.

When a material (sample) is irradiated with a parallel beam of monochromatic X-rays, the atomic lattice of the sample acts as a three dimensional diffraction grating causing the X-ray beam to be diffracted to specific angles. The diffraction pattern, that includes position (angles) and intensities of the diffracted beam, provides several information about the sample and are discussed below:

- Angles are used to calculate the interplanar atomic spacing (d- spacing). Because every crystalline material will give a characteristic diffraction pattern and can act as a unique 'fingerprint', the position (d) and intensity (I) information are used to identify the type of material by comparing them with patterns for over 80,000 data entries in the database, compiled by the Joint Committee for Diffraction Standards (JCDS). By this method, identification of any crystalline compounds, even in a complex sample, can be made.
- The position (d) of diffracted peaks also provides information about how the atoms are arranged within the crystalline compound (unit cell size or lattice parameter). The intensity information is used to assess the type and nature of atoms. Determination of lattice parameter helps understand extent of solid solution (complete or partial substitution of one element for another, as in some alloys) in a sample.
- Width of the diffracted peaks is used to determine crystallite size and micro-strain in the sample.
- The 'd' and 'I' from a phase can also be used to quantitatively estimate the amount of that phase in a multi-component mixture.

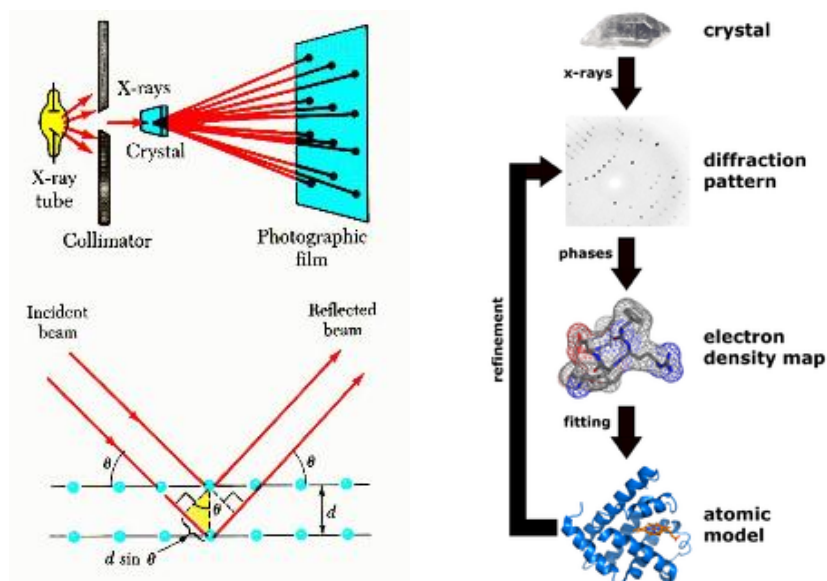


Figure1.19: Workflow for solving the structure of a molecule by X-ray crystallography²⁶.

As mentioned earlier, XRD can be used not only for qualitative identification but also for quantitative estimation of various crystalline phases. This is one of the important advantage of the important advantage of X-ray diffraction technique. Several methods have been proposed and successfully used to quantify crystalline phases in mixtures. They include external standard methods, the reference-intensity-ratio (RIR) method, chemical methods and the whole pattern fitting Rietveld method. Of the available methods, the Rietveld method is probably the most accurate and reliable method. The Rietveld method is a whole-pattern fitting least squares refinement technique and has been successfully used for quantification and characterization of inorganic and organic compounds. It has also been used for crystal structure refinement, to determine size and strain of crystallites.

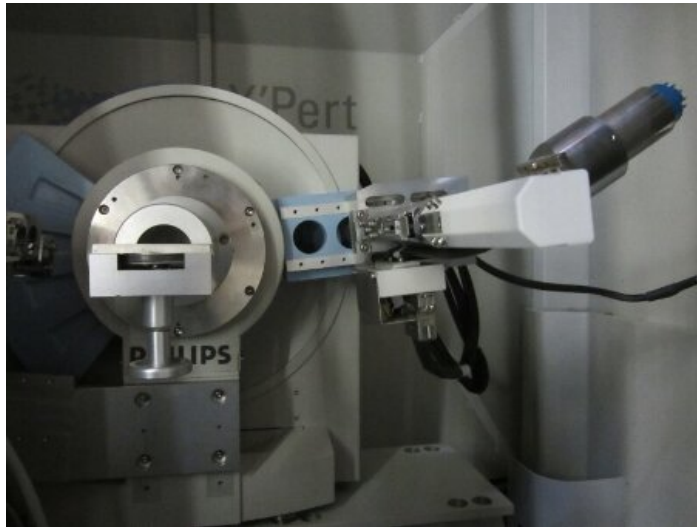


Figure1.20: X-ray diffractometer

1.4.3 Principle of Scanning Electron Microscope (SEM) ²⁷

A typical SEM instrument, showing the electron column, sample chamber, EDS detector, electronics console, and visual display monitors. The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is

especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD).

The scanning electron microscope (SEM) enables the investigation of specimens with a resolution down to the nanometer scale. Here an electron beam is generated by an electron cathode and the electromagnetic lenses of the column and finally swept across the surface of a sample (**Fig.1.20**). The path of the beam describes a raster which is correlated to a raster of gray level pixels on a screen. As a consequence the magnification is simply computed by the ratio of the image width of the output medium divided by the field width of the scanned area.



Figure 1.21: Scanning electron microscope

The main signals which are generated by the interaction of the primary electrons (PE) of the electron beam and the specimen's bulk are secondary electrons (SE) and backscattered electrons (BSE) and furthermore X rays. They come from an interaction volume in the specimen which differs in diameter according to different energies of the primary electrons (typically between 200 eV and 30 keV). The SE come from a small layer on the surface and yield the best resolution, which can be realized with a scanning electron microscope. The well known topographical contrast delivers micrographs which resemble on conventional light optical images.

The BSE come from deeper regions of the investigated material thus giving a lower resolution. The typical compositional contrast gives material specific information since the signal is brighter for regions of a higher middle atomic number of the investigated area. As a byproduct of the image giving signals X-rays are produced. They result from ionization processes of inner shells of the atom leading to electromagnetic radiation. The characteristic X-rays give information about the chemical composition of the material. The methods energy dispersive X-ray spectroscopy (EDS) and wavelength dispersive X-ray spectroscopy (WDS) enable the detection of chemical elements from Boron to Uranium in a qualitative and even quantitative manner. They differ in the energy resolution (the energy values are correlated to the line energy of a special chemical element) in the processing and in time of measurement.

In the conventional scanning electron microscope, which operates in high vacuum, the specimen has to be electrically conductive or has to be coated with a conductive layer (e.g. Carbon, Gold etc.).

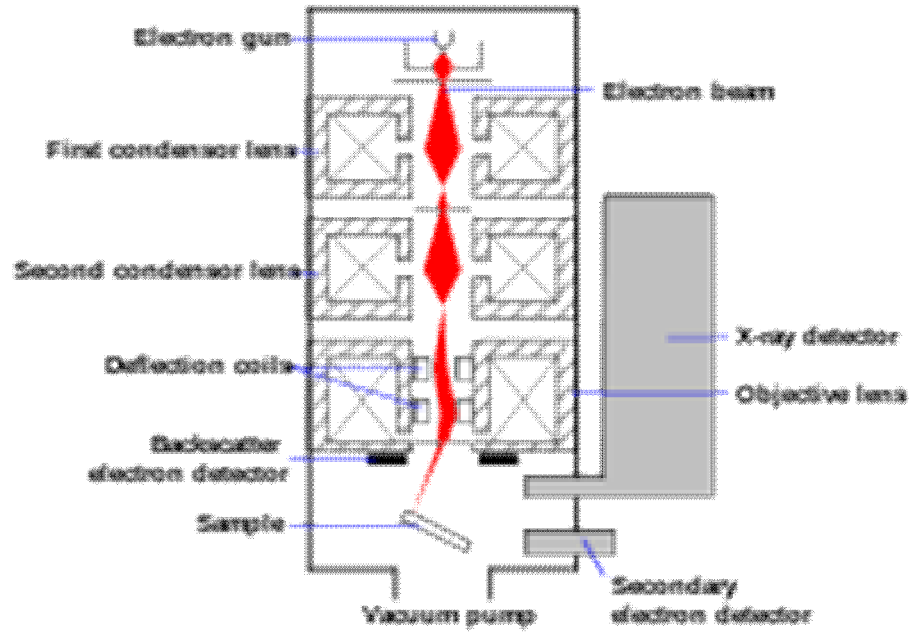


Figure1.22: Schematic diagram of a SEM

Essential components of all SEMs include the following:

- Electron Source ("Gun")
- Electron Lenses
- Sample Stage
- Detectors for all signals of interest
- Display / Data output devices
- Infrastructure Requirements:
 - o Power Supply
 - o Vacuum System
 - o Cooling system
 - o Vibration-free floor
 - o Room free of ambient magnetic and electric fields

SEMs always have at least one detector (usually a secondary electron detector), and most have additional detectors. The specific capabilities of a particular instrument are critically dependent on which detectors it accommodates.

1.4.4 Principle of Differential Thermal Analysis (DTA) ²⁸

Both Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) are concerned with the measurement of energy changes in materials. They are thus the most generally applicable of all thermal analysis methods, since every physical or chemical change involves a change in energy.

DTA is the older technique. The principle of the "classical" arrangement is readily explained with reference to the following figures.

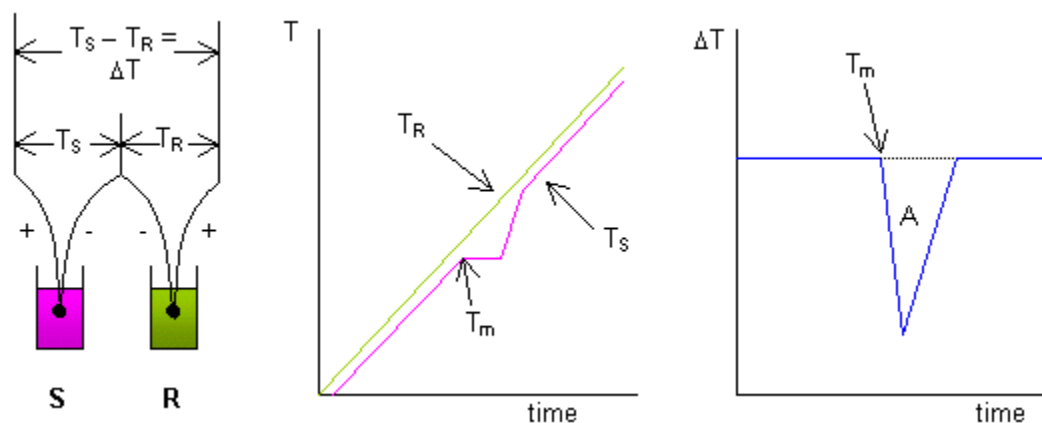


Figure 1.23: Illustration of principles of DTA ²⁸ (a)

S and **R** are containers holding the Sample and an inert Reference material. In these are thermocouples measuring their respective temperatures. By connecting the thermocouples in opposition, the difference in temperature (ΔT) is also measured. If

S and **R** are heated at the same rate, by placing them in the same furnace, their temperatures will rise as in the middle figure. T_R rises steadily, as the reference material is chosen to have no physical or chemical transitions. T_S also rises steadily in the absence of any transitions, but if for instance the sample melts, its temperature will lag behind T_R as it absorbs the heat energy necessary for melting. When melting is complete, steady heating is resumed. The right-hand figure shows the DTA curve - a plot of ΔT against time, or more usually, sample temperature. The curve shows an endothermic (heat-absorbing) peak. If an exothermic (heat-producing) event had occurred, the curve would show a peak in the opposite direction. The area **A** on the curve is proportional to the heat of the reaction:

$$\Delta H = K.A = K \int \Delta T . dt$$

The constant **K** comprises many factors, including the thermal properties of the sample, and varies with temperature. The generation of quantitative data using the "classical" arrangement above is laborious.

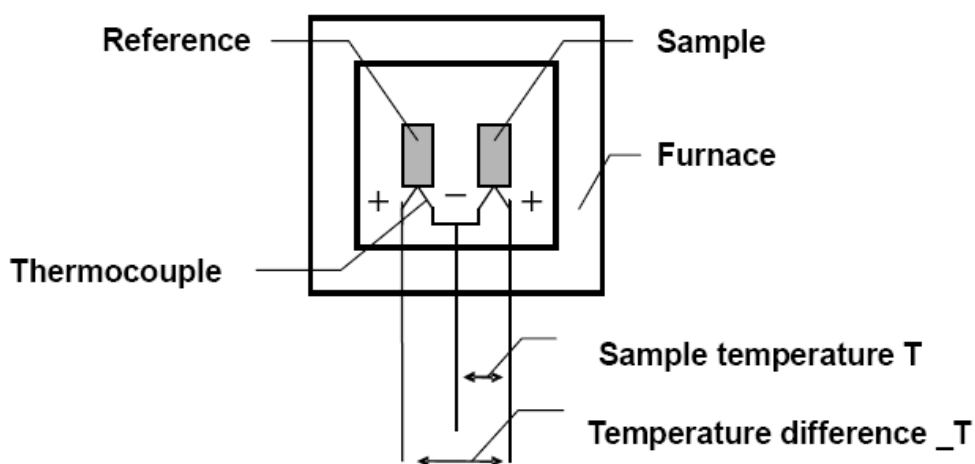


Figure 1.24: DTA device structure^{28(c)}

Nowadays the thermocouples are rarely, if ever in the sample itself, but are placed below the container, which has the effect of reducing the influence of sample properties on the area of the DTA peak. With such designs, it is easier to determine the variation in K with temperature, and quantitative data are more readily obtained. DTA instruments are still valuable, particularly at higher temperatures ($>1000^{\circ}\text{C}$), or in aggressive environments.

1.4.5 Principle of Thermo gravimetric Analysis (TGA)

The diagram shows the configuration of a device that conducts TG and DTA measurements simultaneously with a horizontal scale in a differential structure. The respective balance beams for the sample and the reference are placed in the furnace, mass is measured with drive coils sensitivity-calibrated for the sample and the reference independently, and the difference in mass is output as TG signal.

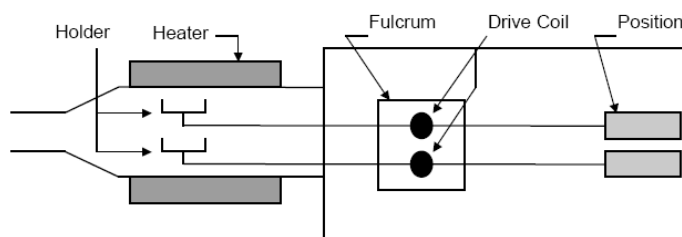


Figure 1.25: Horizontal Differential TG-DTA Device Structure^{28(c)}

By conducting mass measurements differentially, effects of beam expansion, convection and effects of buoyancy are cancelled and high sensitivity thermal mass measurement is achieved. By measuring with independent drive coils for the sample and reference, TG baseline drift (baseline movement due to temperature change) can be adjusted easily and electrically. Also, thermocouple is placed directly below the respective holders for the sample and reference, measuring sample temperature while outputting DTA signal simultaneously.

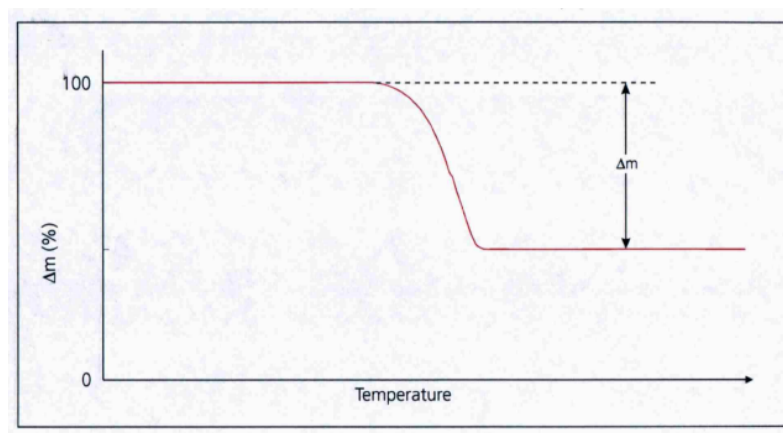


Figure 1.26: Step of weight loss with increasing temperature^{28 (b)}

In this technique changes in the mass of a sample are studied while the sample is subjected to a controlled temperature program. Most often a linear increase in temperature is followed but isothermal studies can be carried out, when changes in sample mass with time are noted. TGA is inherently quantitative, and therefore an extremely powerful thermal technique, but gives no direct chemical information. The ability to analyze the volatile products during a weight loss is of great value.

Careful calibration for temperature is important, especially for kinetic studies. Various means are available for temperature calibration, which is not a trivial matter, though reproducibility is often more important than absolute accuracy. Weight calibration is readily achieved using standard weights.

1.4.6 Principle of Atomic Absorption Spectrophotometer (AAS)

Atomic absorption spectroscopy (AAS) is a spectro-analytical procedure for the qualitative and quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. In analytical chemistry the

technique is used for determining the concentration of a particular element (the analyte) in a sample to be analyzed. AAS can be used to determine over 70 different elements in solution or directly in solid samples. Atomic absorption spectrometry was first used as an analytical technique, and the underlying principles were established in the second half of the 19th century by Robert Wilhelm Bunsen and Gustav Robert Kirchhoff, both professors at the University of Heidelberg, Germany. The modern form of AAS was largely developed during the 1950s by a team of Australian Chemists. They were led by Sir Alan Walsh at the CSIRO (Commonwealth Scientific and Industrial Research Organization), Division of Chemical Physics, in Melbourne, Australia.

The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and relies therefore on Beer-Lambert Law. In short, the electrons of the atoms in the atomizer can be promoted to higher orbitals (excited state) for a short period of time (nanoseconds) by absorbing a defined quantity of energy (radiation of a given wavelength). This amount of energy, i.e., wavelength, is specific to a particular electron transition in a particular element. In general, each wavelength corresponds to only one element, and the width of an absorption line is only of the order of a few picometers (pm), which gives the technique its elemental selectivity. The radiation flux without a sample and with a sample in the atomizer is measured using a detector, and the ratio between the two values (the absorbance) is converted to analyte concentration or mass using Beer-Lambert Law.

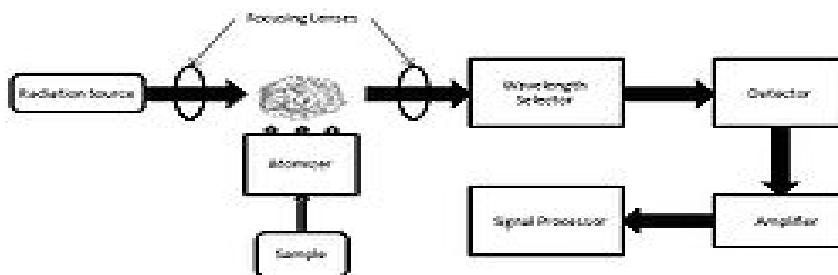


Figure 1.27: Atomic absorption spectrometer block diagram

The basic instrument for atomic absorption requires a light source, an atom source, a monochromator to isolate the specific wavelength of light, a detector, some electronics to treat the signal, and a data display. The light source is usually a hollow cathode lamp.



Figure 1.28: Atomic absorption spectrophotometer

Atomic spectroscopy has experienced remarkable growth and diversity in the past few years, making it more difficult for analysts to keep up with developments in the field. Atomic spectroscopy is not one but three techniques: 1) atomic absorption, 2) atomic emission, and 3) atomic fluorescence. The first two are the most common and widely

used techniques. The linear relationship between the amount of light absorbed or emitted and the amount of species of interest is called the Beer-Lambert Law. It can be used to find unknown concentrations by measuring the light emitted or absorbed.

1.5 Review of Background Literature

A review of the current developments in the area removal efficiency of composite materials prepared by different method is represented in this section. Present research is focused on the treatment of wastewater containing chromium (VI) with silica coated iron oxide composite material prepared by different methods and hence a detailed review is presented on core-shell (coated) composites. Review of the literature reveals that considerable volume of research have been carried out to develop coated composites and their applications on waste water treatment for removal of hexavalent chromium ..

Gang et al.²⁶ studied removal of Cr(VI) by modified poly(4-vinyl pyridine) (PVP)-coated silica gel. Their research involved the synthesizing of a reactive polymer, long alkyl quarternized poly (4-vinyl pyridine) (PVP) and coating it on the surface of silica gel to produce a granular sorbent. The sorbent was used to remove Cr(VI) from water. Batch experiments were conducted to determine the kinetics, sorption isotherm, pH effects and influence of other ions on the chromium adsorption onto the coated silica gel. The research demonstrated that the synthesized PVP-coated silica gel (referred to as coated gel) could successfully remove Cr(VI) from solution. The adsorption of Cr(VI) by the coated gel was strongly influenced by the pH. The maximum sorption occurred at about

pH 4.5-5.5 under the test conditions. The removal efficiency was 100% when the initial Cr(VI) concentration was 2.5 mg/L using 2.5 g/L of coated gel at pH 5.0. The concentration of Cr(VI) had a pronounced effect on the rate of sorption. They also reported that compared to ion exchange, the sorption kinetics of Cr(VI) were fast and equilibrium sorption data fitted the Langmuir isotherm model.

Albino et al (2006)⁴² reported that aniline formaldehyde condensate (AFC) coated silica gel for removal of Cr(VI) from wastewater by considering the effects of various parameters like reaction pH, dose of AFC coated silica gel, initial Cr(VI) concentration and aniline to formaldehyde ratio in AFC synthesis. The optimum pH for total chromium [Cr(VI) and Cr(III)] adsorption was observed as 3. Total chromium adsorption was second order and equilibrium was achieved within 90–120 min. Aniline to formaldehyde ratio of 1.6:1 during AFC synthesis was ideal for chromium removal. Total chromium adsorption followed Freundlich's isotherm with adsorption capacity of 65 mg/g at initial Cr(VI) 200 mg/L. Total chromium removal was explained as combinations of electrostatic attraction of acid chromate ion by protonated AFC, reduction of Cr(VI) to Cr(III) and bond formation of Cr(III) with nitrogen atom of AFC. Almost 40–84% of adsorbed chromium was recovered during desorption by NaOH, EDTA and mineral acids.

Sangkorn Kongjao et al (2007)⁴³ studied removal of chromium from tannery wastewater by electro precipitation technique in a batch electrochemical membrane reactor. This reactor, having a total capacity of 1 liter, was separated into two compartments (anodic and cathode compartments) by using an anionic membrane. A

stainless steel sheet with the square holes having total surface area of 0.0215 m^2 and a Ti/RuO₂ grid was used as the cathode and anode, respectively. The results indicated that the optimum condition for removal of chromium from tannery wastewater was found at the current density of 60.5 A/m^2 at initial pH of 4.5. At this condition, more than 98% of chromium was removed within 60 min. Some organic pollutants contained in wastewater such as oil and grease, color and the level of biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total kjeldahl nitrogen (TKN) were also markedly reduced.

Bailey et al.⁴⁴ prepared a new adsorbent media consisting of iron oxide coated onto sand surface. The oxide coating was made by adding a solution of ferric salt and base to a mixture of sand and applying various heating protocols. Depending on solution pH, the media can be made to adsorb either cationic or anionic elements. In the work, the media was used to collect hexavalent chromium from a synthetic waste stream. The effluent contained 20 mg/L Cr(VI) , and better than 99% removal was achieved consistently. The chromium (VI) removed by sorption to the sand was concentrated at least forty fold using a relatively low pH regeneration process. Regeneration at pH 9.5 was slower than when a $1.0 \text{ mol dm}^{-3} \text{ NaOH}$ solution was used, but the media appears to have a longer working life when the less alkaline solution was employed.

Borai et. al. (2007)⁴⁵ studied the removal of chromium species from wastewater by using mixed silica and alumina hosted carboxylate oxide. The experimental work was developed to improve the physical and chemical characteristics of the prepared mesoporous SiO₂–Al₂O₃ mixed oxides via a sol–gel process. The effective key parameter

on the properties of the materials was achieved by the addition of carboxylate functional group such as Alph-hydroxyl isobutyric acid (AHIBA) during the gelation process and prior the calcinations step. Better performance of these carboxylate resins were attributed to the complexing ability of the carboxylate groups toward polyvalent chromium species which was added to the normal sorption properties of the oxides. Introduction of Al and Si salts together to form mixed oxide modified the way of their substitution in the hosting resin than when they were separately added. The data revealed that mesoporous materials with very narrow pore diameter distribution (micron-sized) and high surface area were obtained. The surface areas and pore size distributions were mainly depend on SiO_2 content. Systematic investigations were carried out on the set of the prepared mixed oxides with different porosity, cross-linking degree and exchange loading to find out the best sorbent for chromium removal.

A fast and efficient method for the removal of hexavalent chromium from aqueous solutions was studied by **Mansoor Anbia et. Al. (2011)** ⁴⁶. In this study, removal of chromium (VI) from aqueous solution by as synthesized MCM-48 adsorbent was studied. Cetyltrimethylammonium bromide (CTAB) was used as a cationic template for the synthesis of MCM-48. The extent of adsorption was investigated as a function of solution pH, agitation speed, contact time, adsorbent and adsorbate concentrations, reaction temperature and supporting electrolyte (sodium chloride). Langmuir and Freundlich isotherms were used to model the adsorption equilibrium data. The adsorption of Cr (VI) was found to be maximum at pH values in the range of 1–3. The yielded maximum adsorption capacity of

153.8 mg/g at initial concentration of 800 (mg/L) was well predicted by the Langmuir isotherm. Compared to the various adsorbents reported in the literature, the surfactant-containing material prepared in this study showed promise for practical applications.

The adsorption of chromium compounds from solutions by a composite of polyaniline/poly ethylene glycol (PANi/PEG) was investigated by **Samani et al. (2010)**⁴⁷. Experiments were conducted in batch mode under various operational conditions including agitation time, solution pH, PANi/PEG dose and initial concentration of chromium salts. Results showed that concentration of PEG at synthesizing stage has a significant effect on the capacity of produced composite for removal of chromium. Morphologically, PANi/PEG composite was closely dependent on the concentration of PEG. Maximum removal of hexavalent chromium was experienced when 2g/L of PEG was used in synthesis of PANi/PEG. Removal of hexavalent chromium by PANi/PEG composite included surface adsorption and reduction reaction. The optimum pH was 5 and the equilibrium time for hexavalent chromium removal was about 30 min. Investigation of the isothermal characteristics showed that chromium adsorption by PANi/PEG composite was in high accordance with Langmuir's isotherm.

Gupta, V.K., et. al (2011)⁴⁸ showed the chromium removal process by using multiwall carbon nanotubes (MWCNTs) /nano-iron oxide composites. The process involves combination of the magnetic properties of iron oxide with adsorption properties of carbon nanotubes. In the study, the adsorption features of (MWCNTs) with the

magnetic properties of iron oxides have been combined in a composite to produce a magnetic adsorbent. Composites of MWCNT/nano-iron oxide were prepared, and were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and Fourier transform infrared spectroscopy (FTIR). XRD suggests that the magnetic phase formed was maghemite and/or magnetite. FESEM image shows nano-iron oxides attached to a network of MWCNTs. The adsorption capability of the composites was tested in batch and fixed bed modes. The composites have demonstrated a superior adsorption capability to that of activated carbon. The results also showed that the adsorptions of Cr(III) on the composites was strongly dependent on contact time, agitation speed and pH, in the batch mode; and on flow rate and the bed thickness in the fixed bed mode. Along with the high surface area of the MWCNT's, the advantage of the magnetic composite was that it can be used as adsorbent for contaminants in water and can be subsequently controlled and removed from the medium by a simple magnetic process.

Synthesis, characterization and studies of the efficiency of chromium removal from wastewater by hydrotalcite-like compounds (HLC) with $Mg/Al = 2$ was studied by **N. Gutiérrez et. al (2009)**⁵¹. Hydrotalcite-like compounds are also known as layered double hydroxides. The general formula of HLC can be expressed as $[M(II)_1xM(III)_x(OH)_2]_x^+ A_n^-$ $x=n$; where M(II) was a divalent metal ion, M(III) was a trivalent metal and A was an anion that occupy the interlayer region of these crystalline materials. These anions were exchanged according to the affinity scale reported by Miyata. The hydrotalcite-like compounds were commonly prepared by co-precipitation of

metallic salts in alkaline medium at constant pH . With the purpose of modifying the textural properties of the HLC, these substances were synthesized by the sol - gel method. In the study, HLC with $Mg/Al = 2$ were synthesized by the sol-gel method, with the purpose of modifying their thermal and textural properties and determine their sorption capacity for Cr (VI). Additionally, the HLC was heated at $350\pm C$ and the product was also used as a sorbent for Chromium (VI). The maximum chromium (VI) uptake by hydrotalcite-like compounds and its heated product were 100 and 125 mg of Cr (VI)/g, respectively.

Sharma Y.C., et al (2009)⁵² showed the chromium removal efficiency by using the adsorbent, iron nanoparticle. Nanoparticles of iron were prepared by sol–gel method. The characterisation of the nanoparticles was carried out by XRD and TEM analysis. Batch experiments were adopted for the adsorption of Cr(VI) from its solutions. The effect of different important parameters such as contact time and initial concentration, pH, adsorbent dose, and temperature on removal of chromium was studied. The removal of chromium increased from 88. 5% to 99.05% by decreasing its initial concentration from 15 to 5mgL^{-1} at optimum conditions. Removal of Cr(VI) was found to be highly pH dependent and a maximum removal (100%) was obtained at pH 2.0. The process of removal was governed by first and pseudo-second-order kinetic equations and their rate constants were determined. The process of removal was also governed by intra particle diffusion. Values of the thermodynamic parameters viz. ΔG° , ΔH° , and ΔS° at different temperatures were determined. Adsorption results indicate that nano iron particles can be effective for the removal of chromium from aqueous solutions.

A. P. Carnizello et al (2009)⁵³ showed Takovite–Aluminosilicate Nanocomposite as Adsorbent for Removal of Cr(III) and Pb(II) from Aqueous Solutions. This work reports on the application of a takovite–aluminosilicate nanocomposite, synthesized by a co-precipitation procedure, as adsorbent for the removal of Cr(III) and Pb(II) from aqueous solutions. Experimental studies to determine the maximum fixation capacities, the adsorption isotherms, and the affinity order of the adsorption process were carried out. The sorption of Pb(II) ions was fast, and the equilibrium was reached within 20 min, while 180 min was necessary for the equilibrium to be reached in the case of Cr(III) ions. The adsorption kinetics of cations was studied in terms of pseudo-first-order and pseudo-second-order kinetics. The Freundlich and Sips isotherm models have also been applied to the equilibrium adsorption data. The takovite–aluminosilicate nanocomposite material had excellent textural properties and was used as an efficient adsorbent of Cr(III) and Pb(II) cations.

Removal of Chromium (VI) from water by using Lanthanum based Hybrid Materials was studied by **Langkam, Johny (2011)**⁵⁴. Cr (VI) was removed from water by a synthesized Lanthanum based hybrid material as adsorbent. The removal of fluoride was 98.50 % at optimum condition from the synthetic solution having initial Cr(VI) concentration of 100 mg/L. The extend of adsorption was investigated as a function of solution pH, contact time, adsorbent concentration, reaction temperature. Langmuir and Freundlich isotherm were used to construct the adsorption equilibrium data.

Application of Cellulose-Clay Composite Biosorbent toward the Effective Adsorption and Removal of Chromium from Industrial Wastewater was studied by **Santhana et al**

(2012)⁵⁵. An effective methodology for the detoxification of chromium using cellulose-montmorillonite composite material as the adsorbent was reported here. The interaction of surfactant modified sodium montmorillonite (NaMMT) with cellulose biopolymer was followed by the subsequent adsorption of Cr(VI) from aqueous solution as bichromate anion onto the surface of the biocomposite material. The composite adsorbent was characterized comprehensively using Fourier transform infrared spectroscopy (FT-IR), Energy dispersive X-ray spectrometry (EDX), X-ray diffraction (XRD) and Branauer-Emmett-Teller (BET) isotherm studies. The material exhibited a maximum adsorption capacity of 22.2 mg g⁻¹ in accordance with the Langmuir isotherm model. The mesoporous nature of the material was ascertained from the nitrogen adsorption isotherm study and the adsorption process was in accordance with second order kinetics. The spontaneity of the adsorption process could be confirmed from the study of the adsorption thermodynamics. The composite material could be regenerated using sodium hydroxide as the eluent. The adsorbent could be reused with quantitative recovery for 10 adsorption-desorption cycles. An aqueous phase feed volume of 400 mL could be quantitatively treated by column method at 100 mg L⁻¹ concentration of Cr(VI) with a preconcentration factor of 50. The applicability of the method was demonstrated in the quantitative removal of total chromium from a chrome tannery effluent sample

Ting and Zexaing⁶² successfully fabricated Metal oxide nanostructures (CuO, Co₃O₄, ZnO and α -Fe₂O₃) by a simple and efficient method: heating the appropriate metals in air at low temperatures ranging from 200 to 400°C. The chemical composition,

morphology and crystallinity of the nanostructures have been characterized by micro Raman spectroscopy, X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Systematic synthesis of mixed-metal oxides in NiO-Co₃O₄, NiO-MoO₃, and NiOCuO systems via liquid-feed flame spray pyrolysis (LF-FSP) was studied by **AZURDIA Jose A., MCCRUM Andrew and LAINE Richard M.**⁶³ The LFFSP

process is a general aerosol combustion synthesis route to a wide range of lightly agglomerated oxide nanopowders. The materials reported here were produced by aerosolizing ethanol solutions of propionate and ammonium molybdate precursors synthesized by reacting the metal nitrate with propionic acid. Mixed metal oxide system produced via the sol-gel method are of particular interest also because the opportunity exists for generating materials intermixed at atomic level. Such systems have the potential for exhibiting chemical properties that differ notably from those of the corresponding single component oxides. Synthesis and characterization of several mixed metal oxides with unique properties has been reported in the literature⁶⁴⁻⁶⁶.

Michael J. Hudson et al have performed an excellent piece of work⁸⁰ on the preparation and characterization of mesoporous, high-surface-area zirconium(IV) oxide. They prepared high-surface-area zirconium(IV) oxide by incorporation of cationic quaternary ammonium surfactants in the hydrous oxide and subsequent calcinations of the inorganic/organic intermediate. The surfactants are incorporated by cation exchange at a pH above the isoelectric point of the hydrous oxide. After calcinations to 723 K and

above, the ordering is a linear function of the chain length. Scaffolding, rather than a templating, mechanism is invoked to explain this ordering. Calcination of the materials to 723–973 K results in the formation of a mesoporous zirconium(IV) oxide. An ingenious piece of research was conducted by **Maria Flytzani-Stephanopoulos**⁸¹ on nanostructured cerium oxide “ecocatalysts”. Various techniques can be used to prepare nanocrystalline cerium oxide. For large scale production, several precipitation and gelation techniques are suitable. Ceria doped with rare-earth oxides or zirconia can be easily prepared by a coprecipitation (CP) method using ammonium carbonate as the precipitant. This involves mixing an aqueous solution of cerium(III) nitrate and other metal nitrates in desired proportions with $(\text{NH}_4)_2\text{CO}_3$ at 60–70°C, keeping a constant pH value of 8, and aging the precipitate at 60–70°C for 1 h. After aging, the precipitate is filtered and washed with distilled water several times, then it is dried at 100–120°C and calcined in air at several hundred degrees Celsius for 10 h at a heating rate of 2°C/min. This method typically produces a well crystallized material with needlelike crystals.

1.6 Objectives with specific aims and possible outcome

Nanocomposite materials, composed of nanometric metal or metal-oxide particles embedded in amorphous matrices, present a variety of interesting magnetic, electric, and catalytic properties. One of the most intriguing questions which is still open is to identify the steps which lead to nanoparticles formation and to clarify how their interaction with

the matrix influences its texture and structure. From the other point of view, how matrix texture and structure influence particle formation and its size and distribution within the matrix.

In view of the formation, characterization and study of the adsorbing efficiency of heavy metal ions from waste water the present study envisages the following:

(1) Preparation of (i) silicon (IV) oxide by hydrolyzing tetraethylorthosilicate (TEOS) in ethanol-water solvent in basic medium ; (ii) iron oxide from iron hydroxide formed by electrochemical method and (iii) iron oxide-silica nanocomposite following Sol-Gel method.

(2) To study the interaction of Cr(VI) in aqueous medium with the synthesized iron-oxide-silicon dioxide nanocomposite and hence to evaluate Cr(VI) removal efficiency of the iron oxide-silicon dioxide nanocomposite from aqueous medium.

The synthesized silicon (IV) oxide, iron oxide and iron oxide-silicon (IV) oxide nanocomposite will be characterized by FT-IR, TGA/DTA, XRD, SEM and EDS.

(3) Sorption efficiency of the synthesized iron oxide-silicon (IV) oxide nanocomposite toward Cr(VI) was studied by investigating the effects of different (i) dosages of adsorbent, (ii) initial concentrations of Cr(VI) solution with contact time and (iii) pH of Cr(VI) solution with contact time. Cr(VI) adsorbed on iron oxide-silicon (IV) oxide nanocomposite was analyzed by FT-IR technique to better understand the interaction of Cr(VI) with iron oxide-silicon (IV) oxide nanocomposite.

Chapter 2

EXPERIMENTAL

2.1 Materials and Chemicals used

2.1.1. Materials used

Adsorbate : Hexavalent chromium . Analytical grade potassium dichromate (VI) (BDH) were used as a precursor to Cr (VI).

Adsorbent : Iron oxide- SiO₂ nanocomposite were prepared in this research work according to the procedures described in section 2.2.3

Solvent used: Double Distilled Water (DDW), pure ethanol (BDH) and analytical grade acetone (BDH).

2.1.2 Chemical reagents used

All the chemical reagents used were of analytical grades. The following chemical reagents were used in this research :

- (i) Tetraethylorthosilicate (TEOS) (Aldrich, Germany)
- (ii) 1,5-Diphenylcarbazide (Farco, China)
- (ii) Sulphuric acid, H₂SO₄ (Merck, Germany)
- (iv) Phosphoric acid, H₃PO₄ (Merck, Germany)
- (v) Acetone (Merck, Germany)
- (vi) Ethanol (Merck, Germany)
- (vii) Ammonium Hydroxide (Merck, India)
- (viii) Potassium dichromate (BDH, England)
- (ix) Sodium Chloride (Merck, India)
- (x) Sodium Hydroxide (Merck, India)

2.1.3 Instruments used

A number of instruments were used to analyze and characterize silicon (IV) oxide, iron oxide and iron oxide- SiO₂ nanocomposite prepared in this research. These includes :

- (i) Scanning Electron Microscope (SEM)*(Model:JEOL JSM-6490LA, Made in Japan)
- (ii) UV-Visible Recording Spectrophotometer (Model: UV-1601 Shimadzu Corporation, Made in Japan)
- (iii) Simultaneous Thermal Analyzer (TGA/DTA)** (Model: SII EXSTAR6000 TG-DTA6300 Seiko Instrument Inc., Made in Japan)
- (iv) X-Ray Diffractometer (XRD)** (Model:X'Pert, Philips, Made in Netherland)
- (v) FT-IR instrument(Model : FTIR -8400/8900,Shimadzu, Made in Japan)
- (vi) Digital Balance (Model: FR-200 , Made in Japan)
- (vii) pH Meter (Model: Ultra basic-10, Denver Instrument, Made in Germany)
- (viii) Centrifuge Machine (Model: Hettich Universal 16A, Made in Germany)
- (ix) Oven (Model: LDO-030E, Daihan Labtech Co. Ltd, Made in Korea)
- (x) Hot plate (Model : MS 300 MTUPS)
- (xi) Pyrex glassware
- (xii) Ultrasonic Steri-cleaner (Model: LU-2, Labnics Equipment, Made in U.S.A.)
- (xiii) Shaker (Heidolph Unimex 1010, Made in Germany)
- (xiv) Atomic Absorption Spectrophotometer (AAS) (Model : PerkinElmer AAnalyst 800 , Made in U.S.A.)
- (xv) Electro coagulator

[* Courtesy of Centre for Advanced Research in Sciences, University of Dhaka.

** Courtesy of BCSIR, Dhaka.]

2.2.0 Preparation of silicon (IV) oxide, iron oxide and Fe₂O₃ -SiO₂ nanocomposite

Silicon (IV) oxide, iron oxide and Fe₂O₃ -SiO₂ nanocomposite were prepared according to the following processes.

2.2.1 Preparation of silicon (IV) oxide

Silicon (IV) oxide was prepared by hydrolysis of tetraethylorthosilicate (TEOS) in ethanol. The ionic equation for the reaction between tetraethylorthosilicate (TEOS) and water in ethanol is:

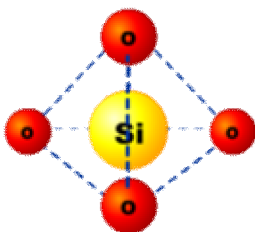


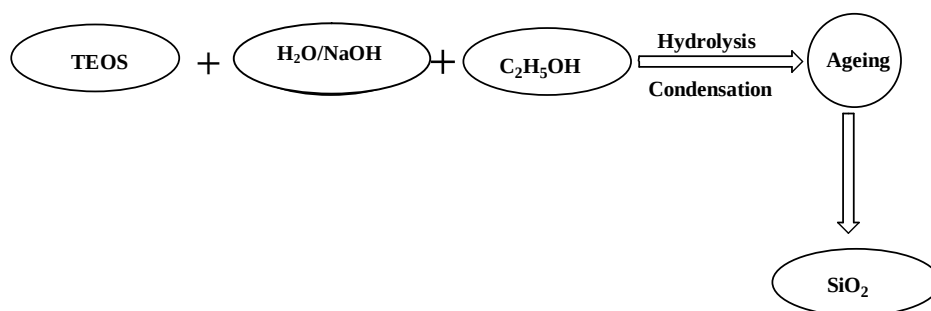
Figure 2.1(a) : Structure of silicon (IV) oxide

A simple one step protocol was used for the preparation of silica, which involves with the hydrolysis and condensation of tetraethylorthosilicate (TEOS) in ethanol : water mixture under basic condition at room temperature. For the preparation of silicon (IV) oxide from TEOS ; TEOS, water and ethanol were mixed at 1.00 : 10.20 : 3.85 molar ratio²⁹. At first 10.60 mL ethanol was taken in a 100 cm³ beaker, and then 10.70 mL of TEOS was added followed by 9.00 mL water containing 0.20 mL molar NaOH. It was then stirred constantly using a thermostated magnetic stirrer at ambient temperature for about one hour. The stirred mixture was then allowed to stand for two days for ageing so that gel formation was completed.



Figure 2.1 (b): Picture of the prepared silicon (IV) oxide

The gel of silicon (IV) oxide was collected as a residue by filtration. Distilled water was poured on the silicon (IV) oxide gel several times to ensure removal of chloride or any other undesirable ions from silicon (IV) oxide because the presence of impurity will cover up the surface and hence the actual surface area will decrease. The gel was dried in an oven at 110°C for 4 hours. Silicon (IV) oxide thus prepared was preserved in a desiccator for characterization. Schematic representation of the process is shown below :



2.2.2 Electrochemical preparation of iron oxide

The electrochemical experiment was carried out in a two-electrode electrochemical cell containing iron as sacrificial electrodes. The experimental set up included the electrode assembly, a DC power supply unit, a voltage stabilizer, a resistance box to regulate the current and a multimeter to read the current values. The electrode assembly consisted of

pairs of iron plates ($7.0\text{ cm} \times 7.0\text{ cm} \times 0.15\text{ cm}$) placed in parallel arrangement. A photograph of the experimental set up is shown in Figure 2.2 (a) which is based on the diagram reported by Mollah et al³⁰:

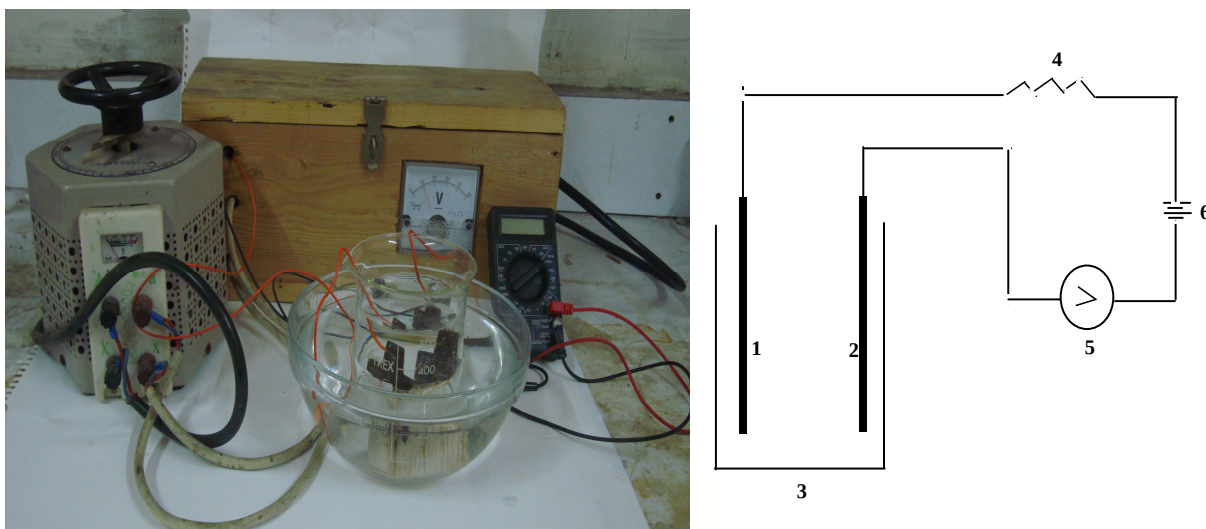


Figure 2.2: (a) Electro-coagulator (b) Schematic diagram of the cell. 1. Anode, 2.Cathode , 3. Pyrex beaker, 4. Variable resistance, 5. Ammeter , 6. D.C. source

500.0 mL of 0.025M aqueous NaCl (99.5%) solution was taken in a 1L beaker and the electrodes were immersed into it. An electrode holder made of ebonite kept the anode and cathode separated by definite distance (2.2 cm). Anode and cathode were fully immersed in the electrolytic solution. Electrolysis was then carried out for about one hour when suspension of oxyhydroxides was generated into the electrolytic solution. Usually a current of 1A was used for electrolysis. At the end of each run, the suspension was kept in open air for 24 hours to settle completely and then filtered through a $2.5\text{ }\mu\text{m}$ pore size membrane filter and the recovered solid was washed with double distilled water until free from chloride. The solid mass was dried in an oven at a temperature of 120°C for 24 hours.

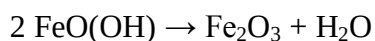


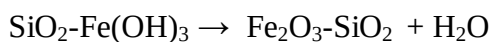


Figure 2.2 (c): Picture of the prepared iron oxide

2.2.3 Preparation of Fe_2O_3 - SiO_2 nanocomposite (1:1) by Sol-Gel method

- (i) Reddish brown precipitate of iron (III) hydroxide was prepared according to the procedure described in **Section 2.2.2**.
- (ii) In a 100 mL beaker TEOS and ethanol were mixed at the molar ratio 1.00 : 3.85 for which 10.70 mL TEOS and 10.60 mL ethanol were used. In a different beaker, 8.80 mL water (1.00:10.20 ratio with TEOS) was taken and reddish brown precipitate of iron (III) oxide prepared according to the process described in **Section 2.2.2** was instantly added into it and was sonicated for about 30 minutes. After that the ethanol solution containing TEOS was added to the beaker containing iron (III) hydroxide. Dilute NaOH solution was added to maintain the pH value of 8.0 and the mixture was sonicated for about 30 minutes. After sonication, the mixture was left for 24 hours at ambient temperature to form $\text{SiO}_2\text{-Fe}(\text{OH})_3$ composite. The composite settled at the bottom of the beaker. The clear solution was discarded carefully using a pipette. Double distilled water was added to the composite and stirred for half an hour and then again left for 2 hours to settle the composite. The clear solution was again discarded carefully using a pipette. This process was repeated several times to ensure

complete removal of chloride and other undesirable ions from the composite. Water from the $\text{Fe}(\text{OH})_3\text{-SiO}_2$ composite was evaporated by gently heating with a low flame and then the composite was heated in the oven at 300°C for 6 hours to convert it into $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite.



The steps are schematically shown in **Figure 2.3**.

The $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1) thus prepared was preserved for characterization and subsequent uses.

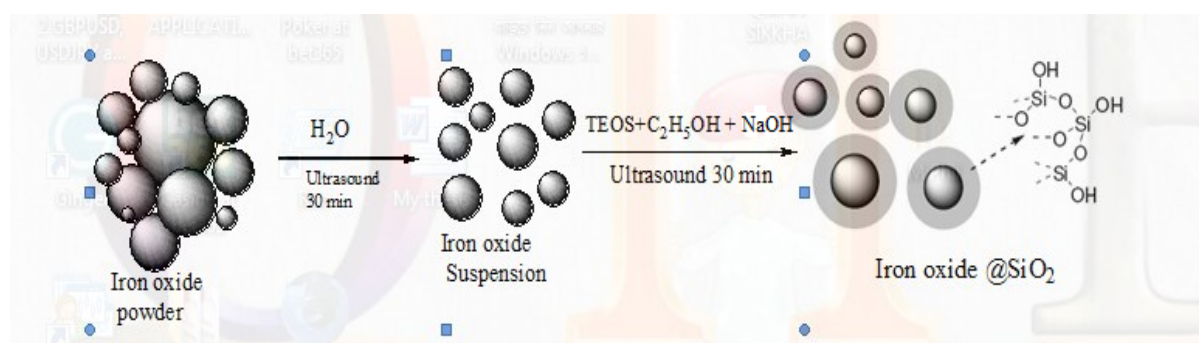


Figure 2.3: Illustration of the silica-coated iron oxide nanocomposite stepwise protocol

2.3.0 Characterization of silicon (IV) oxide, iron oxide and $\text{Fe}_2\text{O}_3 - \text{SiO}_2$ nanocomposite

Silicon (IV) oxide, iron oxide and $\text{Fe}_2\text{O}_3 - \text{SiO}_2$ nanocomposite prepared in this research were characterized by FT-IR, XRD, TGA-DTA and SEM –EDS techniques.

2.3.1 FT-IR spectroscopic investigation of Silicon (IV) oxide, iron oxide, Fe_2O_3 - SiO_2 nanocomposite (1:1) and Fe_2O_3 - SiO_2 nanocomposite (1:1) after adsorption of Cr(VI)

The prepared silicon (IV) oxide, iron oxide, Fe_2O_3 - SiO_2 nanocomposite and Cr(VI) treated (1:1) Fe_2O_3 - SiO_2 nanocomposite were investigated by FT-IR Spectroscopy.

The molecular characterization were carried out by FT-IR spectrophotometer (Model: FT IR -8400/8900) using potassium bromide pellet. The pellets were prepared by mixing 1.00 mg of finely ground dry sample of each compound under investigation and 100.0 mg of spectroscopic grade dry potassium bromide. The mixture was ground thoroughly in an agate mortar and pressed between a pair of dies under a pressure of 8-9 tons using hydraulic press for 5 minutes. The spectra was recorded between 4000-400 cm^{-1} with 2 cm^{-1} resolutions. Usually 32 scans were averaged to record a spectrum. The FT-IR spectra and corresponding absorption bands for silicon (IV) oxide, iron oxide and Fe_2O_3 - SiO_2 nanocomposite are presented in **Figures 3.1, 3.2, 3.3** and **Table 3.1, 3.2, 3.3** respectively in **Section 3.1.1**. The FT-IR spectra for Cr(VI) treated Fe_2O_3 - SiO_2 nanocomposite (1:1) is presented in **Figure 3.4** and **Table 3.4**.

2.3.2 X-Ray Diffraction (XRD) analysis of silicon (IV) oxide, iron oxide and Fe_2O_3 - SiO_2 nanocomposite

The phase composition of prepared silicon (IV) oxide, iron oxide and Fe_2O_3 - SiO_2 nanocomposite were analyzed by an X-ray Diffractometer .

The XRD analysis of the samples were carried out by an X-ray Diffractometer (XRD) (Model : Philips X'pert) with CuK_α radiation ($\lambda = 1.54178 \text{ \AA}$) source with a nickel filter. The samples were grounded to a fine powder and loaded into an aluminum sample holder with dimension $(15 \times 10 \times 2) \text{ mm}^3$ over base line adhesive . Powder specimens were filtered with 400 mesh sieves preceding the x-ray diffraction analysis.

The samples were scanned from 10° to 90° at diffraction angle 2θ in steps of 0.02° and time for each step data collection was 1 second. The XRD machine was fully computer controlled and the data were stored in hard disk memory of the computer for further analysis. All the data of the samples were analyzed using computer to d-values of the fundamental peaks and their intensity. The spacing between the crystal phases d was calculated using Bragg's equation:

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

Where λ is the wavelength of the incident radiation and $\text{Cu (K}_\alpha\text{)}$. The raw materials and hydrated pastes were characterized using the d values of their main fundamental peaks (at least four for each) by comparing the d values and their intensity ratios with the data book of "Selected Power Diffraction Data for Minerals". Phases were identified from their strongest peak of 100% I, where I is the intensity of the peak.

The X-ray Diffraction patterns of silicon (IV) oxide, iron oxide and $\text{Fe}_2\text{O}_3 - \text{SiO}_2$ nanocomposite (1:1) are given in **Section 3.1.2**

2.3.3 Thermo gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

Thermo gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) of the samples were carried out using simultaneous Thermal Analyzer (DTA/ TGA) (Model-SII EXSTAR6000 TG-DTA6300 Seiko Instrument Inc., Japan). Liquid nitrogen gas was used as a stripping gas.

Thermo gravimetric Analysis (TGA): The samples were heated at the rate of $0.5^{\circ}\text{C min}^{-1}$ from ambient to $\approx 1000^{\circ}\text{C}$ and its weight loss were measured using a balance equipped with the analyzer.

Differential Thermal Analysis (DTA): The samples were continuously heated at a constant rate $10^{\circ}\text{C min}^{-1}$ and the temperature difference between inert compound and the sample was recorded. Differences in temperature occur if reactions, which either release (exothermic effect) or consume (endothermic effect) energy take place. These effects were recorded as peaks on the plot of temperature difference against temperature.

The thermograms of Thermo gravimetric Analysis (TGA) / Differential Thermal Analysis (DTA) of silicon (IV) oxide, iron oxide and Fe_2O_3 - SiO_2 nanocomposite (1:1) are shown in **Figures 3.8, 3.9, 3.10** respectively in **Section 3.1.3**.

2.3.4 Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) analysis of silicon (IV) oxide, iron oxide and Fe_2O_3 - SiO_2 nanocomposite

The samples of silicon (IV) oxide, iron oxide and Fe_2O_3 - SiO_2 nanocomposite were analyzed by Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). SEM is a type of electron microscope that creates various images by focusing a high energy beam of electrons onto the surface of the sample and detecting signals from the interaction of the incident electron with the sample's surface. SEM images have greater depth of field (curved surfaces are resolved properly) yielding a characteristic 3D appearance useful for understanding surface structure of a sample. Magnification is of order 10000 X and resolution 10 nm. Analyses were carried out on a JOEL JSM6490LA, (Japan) equipped with germanium detector and diamond window. The samples were mounted using double-sided tape and electrically conducted by coating with metal in AGAR AUTO SOPTTER COATER of the SEM in order to have clear images.

The SEM images of the prepared silicon (IV) oxide, iron oxide and Fe_2O_3 - SiO_2 nanocomposite (1:1) are presented in the **Figures 3.11, 3.13 and 3.15** respectively in **Section 3.1.4**. The EDS spectra of silicon (IV) oxide, iron oxide and Fe_2O_3 - SiO_2 nanocomposite are presented in the **Figures 3.12, 3.14 and 3.16** respectively in **Section 3.1.4**.

2.3.5 UV-Visible Spectrophotometer

For absorption spectroscopic measurements a double UV-Visible spectrophotometer, Model UV-160A (Shimadzu, Japan) was used. The instrument was equipped with a temperature controlled ($\pm 0.1^\circ$) cell component and spectral data processing facility. The sensitivity of the equipment was 0.002 absorbance unit at a signal to noise ratio of 1.0. A quartz cell of path length 1.0 cm was used in this research work.

2.4.0 Interactions of Cr(VI) in aqueous solution with the prepared Fe_2O_3 - SiO_2 nanocomposite

The interactions of Cr(VI) with nanocomposite Fe_2O_3 - SiO_2 have been studied by investigating:

- (i) The effects of different (a) dosages of nanocomposite as a sorbent (b) initial concentrations and shaking time (c) pH of Cr(VI) solution and shaking time on adsorption of Cr(VI) on nanocomposite
- (ii) The adsorption isotherm and the sorption kinetics of Cr(VI) on Fe_2O_3 - SiO_2 nanocomposite as adsorbents.

Experimental procedure for the determination of Cr(VI) by absorption spectroscopy is outlined below.

2.4.1 Preparation of 1,5-Diphenyl Carbazide (DPC) solution

25 cm³ 0.5% solution of 1,5-Diphenyl Carbazide (DPC) was prepared by dissolving 0.125 gm 1,5-Diphenyl Carbazide (DPC) in 100% acetone. Freshly prepared DPC solution was used in each experiment.

2.4.2 Determination of concentration of Cr(VI) from aqueous system

The Concentration of Cr(VI) species in aqueous solution was determined spectrophotometrically according to the method reported earlier³¹.

2.4.3 Preparation of aqueous solution of Cr (VI)

Potassium dichromate (VI) was used as a precursor to (Cr^{6+}). To prepare aqueous solution of Cr(VI), finely powdered $\text{K}_2\text{Cr}_2\text{O}_7$ was heated at 110°C in an oven for 30-45 minutes and allowed to cool in a desiccator. Then 500 cm^3 of 100mgL^{-1} Cr(VI) solution was prepared by dissolving 0.1416 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in double distilled water. Dilute solutions were prepared from this stock solution as per requirements.

2.4.4 Determination of maximum absorption of Cr(VI) -1,5-Diphenyl Carbazide (DPC) complex

100 cm^3 of 1.5 mgL^{-1} Cr(VI) solution was neutralized by 1% NH_4OH solution. In order to keep pH value 2.0 requisite volume of 1:1 H_2SO_4 and 85% H_3PO_4 was added to the solution. 2 mL of 0.5% DPC was added to this solution and the solutions was allowed to stand for about 5-10 minutes for complete complex formation. DPC, which is a highly selective agent for complex formation with Cr (VI), reacts with Cr(VI) to form a red-violet complex. Absorption spectrum (Figure 2.4) at maximum absorbance (λ_{max}) was measured using a quartz cell of path length 1.0 cm by a UV-Visible Spectrophotometer.

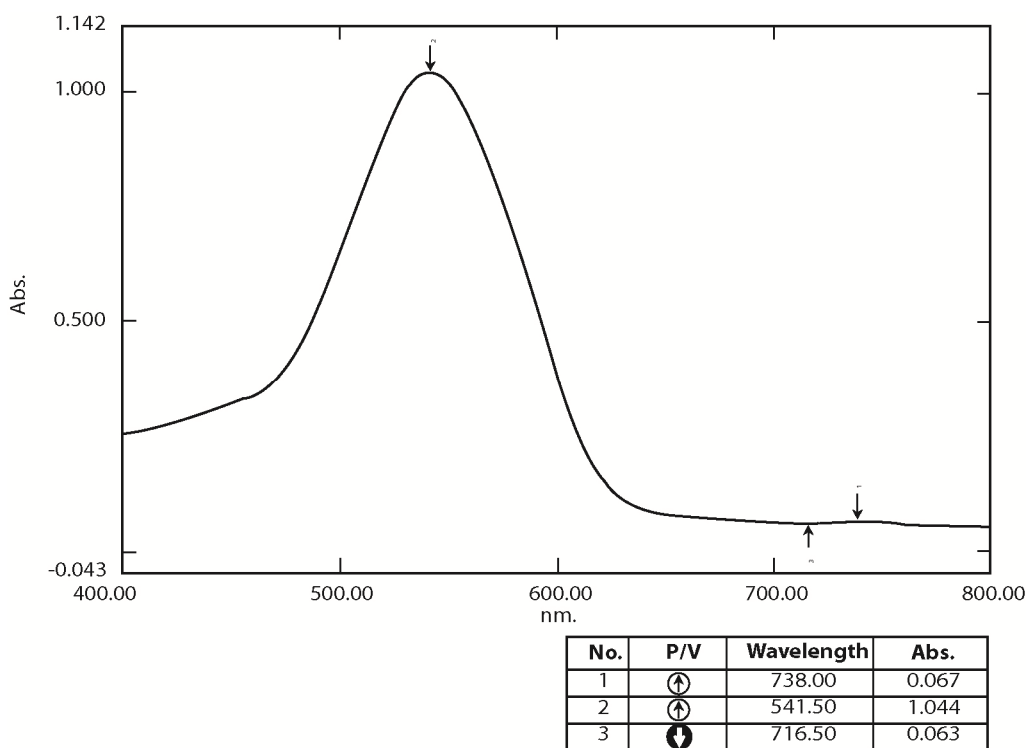


Figure 2.4: Absorption spectrum of Cr(VI)-DPC complex

The spectrum of the complex showed absorption maximum ($\lambda_{\max}$) at 541.50 nm. All experiments in this study for quantitative determination of Cr(VI) was carried out at 541.50 nm.

2.4.5 Construction of calibration curve and determination of molar Absorption Coefficient (ϵ) for Cr(VI) -1,5-Diphenyl Carbazide (DPC) complex

In order to quantitatively determine the concentration of Cr(VI) in aqueous solution, a calibration curve was first constructed. A standard solution of 5.0 mgL^{-1} of Cr(VI) solution was prepared from 100 mgL^{-1} stock solution. A number of standard solutions of concentrations ranging from 0.1 to 1.5 mgL^{-1} were prepared by appropriate dilution of 5.0 mgL^{-1} of Cr(VI) solution with double distilled water. Complex formation of each of these standard solutions with the DPC was carried out according to the same

procedure as described earlier in **Section 2.4.4**. Absorbance of all the solutions were measured at ($\lambda_{\max}$) 541.50 nm using a quartz cell of path length 1.0 cm. The calibration curve was constructed by plotting the absorbance of the Cr(VI) –DPC complex against the corresponding concentrations of Cr(VI). The experimental data and the corresponding plot are shown in the **Table.2.1** is shown in **Figure 2.5**.

Table 2.1 : Calibration curve for Cr(VI) in aqueous solution

Experimental conditions: pH of Cr(VI) solution = 2.0 ± 0.2 ; ($\lambda_{\max}$) of the complex = 541.50 nm, Reference: Double distilled water

Concentration of Cr(VI) solution (mgL^{-1})	Absorbance
0.1	0.0921
0.3	0.2628
0.5	0.4639
0.8	0.7493
1.0	0.8755
1.3	1.1505
1.5	1.28

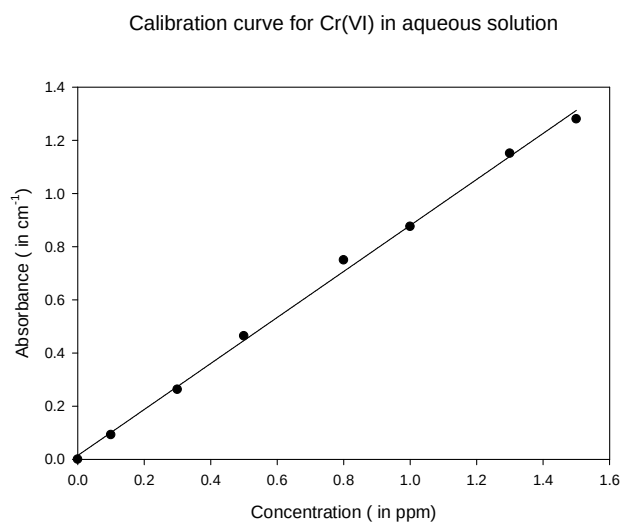


Figure 2.5 Calibration curve for Cr(VI) –DPC complex

The plot is a straight line and it passes through the origin. This nature of the plot suggests the validity of the Beer-Lambert law. The molar absorption coefficient (ϵ) for Cr(VI) –DPC complex at 541.5 nm was determined from the slope of the linear plot (**Figure 2.5**) and it was found to be $0.89 \text{ Lmg}^{-1}\text{cm}^{-1}$.

2.4.6.0 Adsorption studies

Interactions of Cr(VI) with the nanocomposite have been studied by investigating the effects of different parameters such as adsorbent dosage, Cr(VI) concentration, shaking time and pH of the Cr (VI) solution .

2.4.6.1 Investigation of the adsorption efficiency of Cr(VI) in aqueous solution for Fe₂O₃, SiO₂ and Fe₂O₃ - SiO₂ nanocomposite (1:1)

Details of experimental procedures have been described in the **Section 2.4.6.1**. To investigate the effect of adsorption of Cr(VI) from aqueous solution by the iron oxide , silicon (IV) oxide and Fe₂O₃ - SiO₂ nanocomposite (1:1), 0.20 g of sorbent of each type were taken . 100 cm³ of 10 mgL⁻¹ of Cr(VI) solution was freshly prepared from 500cm³ 50 mgL⁻¹ of Cr(VI) solution by appropriate dilution with DDW. pH of 100 cm³ 10 mgL⁻¹ of Cr(VI) solution was carefully adjusted at pH 4.8. 20cm³ of this 10 mgL⁻¹ of Cr(VI) solution was added to different type of the sorbent in a series of reagent bottles. Then the bottles were shaken for 20 minutes by a thermostated mechanical shaker at 250 rpm shaking speed and at temperature (30±0.2) °C. After the stipulated 20 minutes time, the bottles were withdrawn altogether from the shaker and then the supernatant was removed from the sorbent as soon as possible and centrifuged repeatedly until a clear solution was obtained. After that the clear solution was diluted to 10 times of its initial concentration and then the absorbance of the clear solution was measured spectrophotometrically according to the reported procedure⁹⁸.

The experimental data is shown in **Table 3.5 Section 3.2.1**.

2.4.6.2 Investigation of the effect of variation of adsorbent dosage on adsorption of Cr(VI) in aqueous solution for Fe₂O₃ - SiO₂ nanocomposite (1:1)

Details of experimental procedures have been described in the **Section 2.4.6.2**. To investigate the effect of sorbent (Fe₂O₃ - SiO₂ nanocomposite) on Cr(VI) adsorption on Fe₂O₃ - SiO₂ nanocomposite (1:1), different dosages ranging from 0.05 g to 0.30 g of Fe₂O₃ - SiO₂ nanocomposite (1:1) were considered as sorbent. 250 cm³ of 50 mgL⁻¹ of Cr(VI) solution was freshly prepared from 500cm³ 100 mgL⁻¹ of Cr(VI) solution by appropriate dilution with DDW. pH of 250 cm³ 50 mgL⁻¹ of Cr(VI) solution was carefully adjusted at pH 4.8. 25cm³ of this 50mgL⁻¹ of Cr(VI) solution was added to different amounts of the sorbent in a series of reagent bottles. Then the bottles were shaken for 20 minutes by a thermostated mechanical shaker at 250 rpm shaking speed and at temperature (30±0.2°) °C. After the stipulated 20 minutes time, the bottles were withdrawn altogether from the shaker and then the supernatant was removed from the sorbent as soon as possible and centrifuged repeatedly until a clear solution was obtained. The absorbance of the clear solution was measured by using AAS to determine the actual concentration of the Cr(VI) solution after its adsorption on the nanocomposite.

The experimental data and the corresponding plot are shown in **Table 3.6** and **Figure 3.17** respectively in **Section 3.2.2**.

2.4.6.3 Determination of the effect of different initial concentrations of Cr(VI) solution and shaking time on adsorption of Cr(VI) onto Fe₂O₃ -SiO₂ nanocomposite (1:1)

To investigate the effect of different initial concentrations of Cr(VI) solutions toward adsorption on Fe₂O₃ - SiO₂ nanocomposite (1:1), Cr(VI) solution of varied concentration were prepared. 250 cm³ of 40 mgL⁻¹ and 50 mgL⁻¹ of Cr(VI) solution was freshly prepared from 100 mgL⁻¹ of Cr(VI) solution by appropriate dilution with DDW. pH of 250 cm³ 40 mgL⁻¹ and 50 mgL⁻¹ of Cr(VI) solution were carefully adjusted at pH 4.8. 25cm³ of Cr(VI) solution were then added to 0.20 g of the sorbent in a series of reagent bottles. Then the bottles were shaken by a thermostated mechanical shaker at 250 rpm shaking speed and at temperature (30±0.2⁰) °C. After definite interval of time each of the bottles were withdrawn from the shaker. Then the supernatant was removed from the sorbent as soon as possible and centrifuged repeatedly until a clear solution was obtained. The absorbance of the clear solution was measured by using atomic absorption spectrophotometer to determine the actual concentration of the Cr(VI) solution after its adsorption on the composite .

The experimental data and the corresponding plot are shown in **Table 3.7** and **Figure 3.18** respectively in **Section 3.2.3**

2.4.6.4 Determination of the effects of pH of Cr(VI) solution and shaking time on adsorption of Cr(VI) onto Fe₂O₃ / SiO₂ nanocomposite (1:1)

The experiments were carried out at pH 4.80, 3.00 and 8.00 to understand the effect of pH on the adsorption of Cr(VI) on Fe₂O₃ - SiO₂ nanocomposite (1:1). The pH 4.8, 3.0 and 8.0 of 50 mgL⁻¹ of Cr(VI) solution were carefully adjusted by adding freshly prepared 0.1M HCl or 0.1M NaOH solution as required with pH meter. 25cm³ of 50

mgL^{-1} Cr(VI) solution having pH 4.8 was added to 0.20 g of the sorbent in a series of reagent bottles. Then the bottles were shaken by a thermostated mechanical shaker at 250 rpm shaking speed and at temperature $(30 \pm 0.2) ^\circ\text{C}$. After definite interval of time each of the bottles were withdrawn from the shaker. Then the supernatant was removed from the sorbent as soon as possible and centrifuged repeatedly until a clear solution was obtained. The absorbance of the clear solution was measured by using AAS to determine the actual concentration of the Cr(VI) solution after its adsorption on the composite .

The experiments were repeated at pH 3.0 and 8.0. The experimental data and the corresponding plots are shown in **Table 3.8** and **Figure 3.19, 3.20** respectively in **Section 3.2.4**.

2.4.6.5 Adsorption isotherm of Cr(VI) onto Fe_2O_3 - SiO_2 nanocomposite (1:1)

Batch adsorption studies were conducted to determine adsorption isotherm of Cr(VI) adsorption on Fe_2O_3 - SiO_2 nanocomposite (1:1) . 0.20 g of the Fe_2O_3 - SiO_2 nanocomposite (1:1) was taken in a series of reagent bottles . 250 cm^3 of 100 mgL^{-1} of Cr(VI) solutions was freshly prepared in a volumetric flask . Cr(VI) solutions of varying initial concentrations ranging from 10 to 60 mgL^{-1} were freshly prepared by diluting 250 cm^3 of 100 mgL^{-1} of Cr(VI) solution with DDW. The pH of the each dilute Cr(VI) solutions were maintained constant at 4.8 . 25 cm^3 of Cr(VI) solutions of these varying concentrations was added to 0.20 g of the sorbent in a series of reagent bottles. It was previously determined that 20 to 30 minutes time was sufficient to attain equilibrium adsorption . The bottles were, therefore, shaken in a thermostated mechanical shaker for 20-30 minutes. Thereafter, all the bottles were removed from the shaker and then the supernatant was removed from the sorbent as soon as possible

and centrifuged repeatedly until a clear solution was obtained. The absorbance of the clear solution was measured by using AAS to determine the actual concentration of the Cr(VI) solution after its adsorption on the composite .

The amounts of Cr(VI) adsorbed per gram of the composite were calculated from the difference between initial concentration and final concentration of Cr(VI) solution before adsorption and after adsorption. The experimental data and the corresponding plots are shown in **Table 3.9** and **Figure 3.21** respectively in **Section 3.3.1**.

2.4.6.6 Sorption Dynamics

The kinetic study of sorption of Cr(VI) on Fe₂O₃ - SiO₂ nanocomposite (1:1) was carried out by investigating the effect of shaking time on % sorption of Cr (VI) on the Fe₂O₃ - SiO₂ nanocomposite (1:1). In order to study the sorption dynamics, freshly prepared 25cm³ of 50 mgL⁻¹ Cr(VI) solution was added to 0.20 g of the sorbent in a series of reagent bottles. Then the bottles were shaken by a thermostated mechanical shaker at 250 rpm and at temperature (30±0.2) °C for definite interval of shaking time ranging from 5 minutes to 120 minutes. After definite interval of time each of the bottles were withdrawn from the shaker. Then the supernatant was removed from the sorbent as soon as possible and centrifuged repeatedly until a clear solution was obtained. The absorbance of the clear solution was measured by using AAS to determine the actual concentration of the Cr(VI) solution after its adsorption on the composite . The amounts of Cr(VI) adsorbed per gram of the composite at different shaking time were calculated. The experimental data, Lagergren plot for Cr(VI) adsorption and plot for validation of Morris-Weber equation for Cr(VI) adsorption on the composite are shown in **Table 3.11** and **Figure 3.23** and **Figure 3.24** respectively in **Section 3.4.0**.

Chapter 3

RESULTS

&

DISCUSSION

3.0 Results and Discussion

The results and discussion are presented in two parts. Characterization of silicon (IV) oxide, iron oxide and iron oxide - SiO₂ nanocomposite are presented in **Section 3.1.0**. Interaction of Cr(VI) with the nanocomposite are presented in **Section 3.2.0**.

3.1.0 Characterization of silicon (IV) oxide, iron oxide and iron oxide-SiO₂ nanocomposite

Silicon (IV) oxide, iron oxide and iron oxide- SiO₂ nanocomposite were found to be white, brown and light brown respectively.

Silicon (IV) oxide, iron oxide and iron oxide- SiO₂ nanocomposite have been characterized by FT-IR spectroscopy, X-ray Diffraction (XRD), Thermogravimetric Analysis(TGA), Differential Thermal Analysis (DTA) , Energy dispersive X-ray spectroscopy (EDS) and Scanning Electron Microscopy (SEM) techniques .

3.1.1 FT-IR spectroscopic investigation

The silicon (IV) oxide, iron oxide and iron oxide - SiO₂ nanocomposite were investigated by FT-IR spectroscopy for molecular characterization. A sample of Cr (VI) treated nanocomposite (1:1) was also analyzed to elucidate the mechanism of interaction of Cr(VI) with the nanocomposite. The methods of preparation and treatments of samples have been described in **Section 2.3.1**.

FT-IR spectra of silicon (IV) oxide, iron oxide, iron oxide- SiO₂ nanocomposite are shown in **Figures 3.1, 3.2, 3.3** respectively and FT-IR spectra of iron oxide- SiO₂ nanocomposite (1:1) after adsorption of Cr (VI) are shown in **Figure 3.4**.

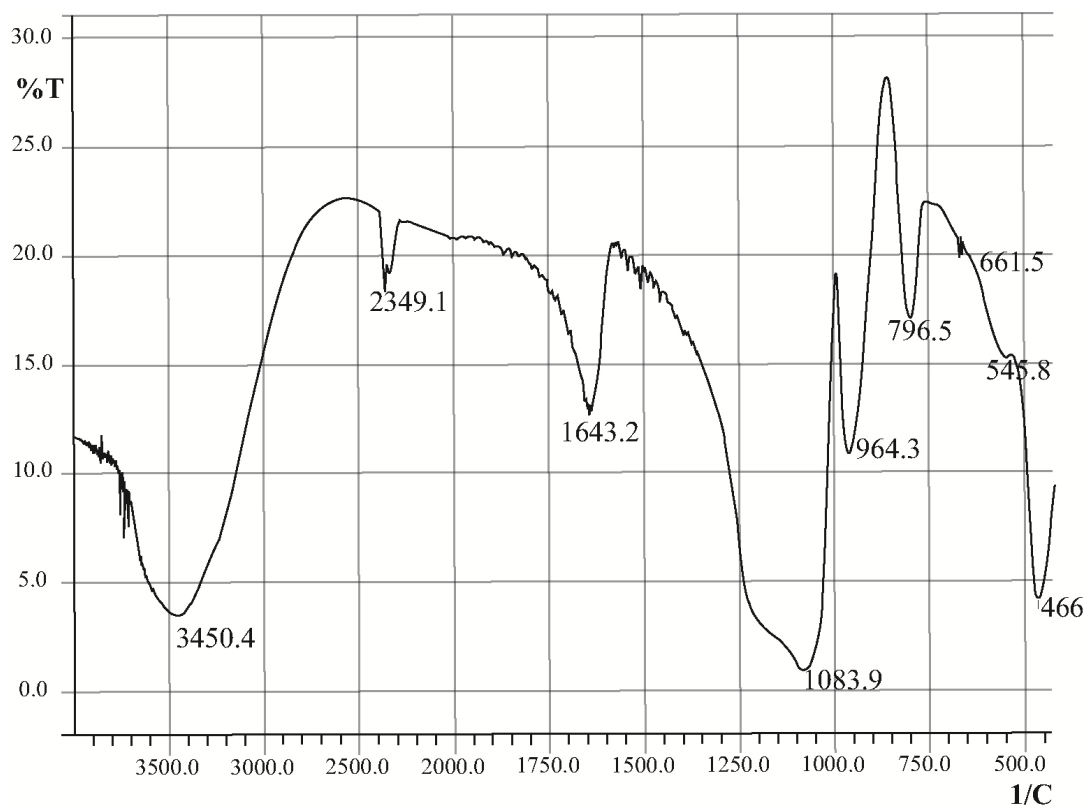


Figure 3.1: FT-IR spectrum of silicon (IV) oxide

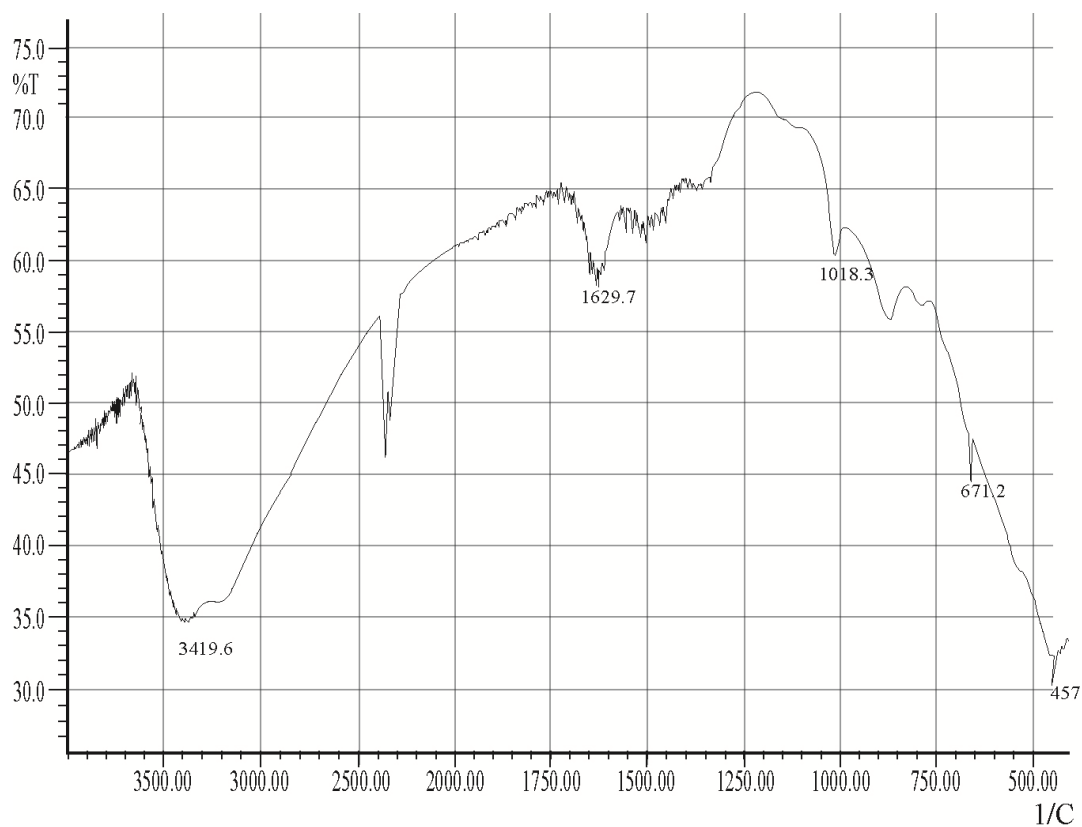


Figure 3.2: FT-IR spectrum of iron (III) oxide

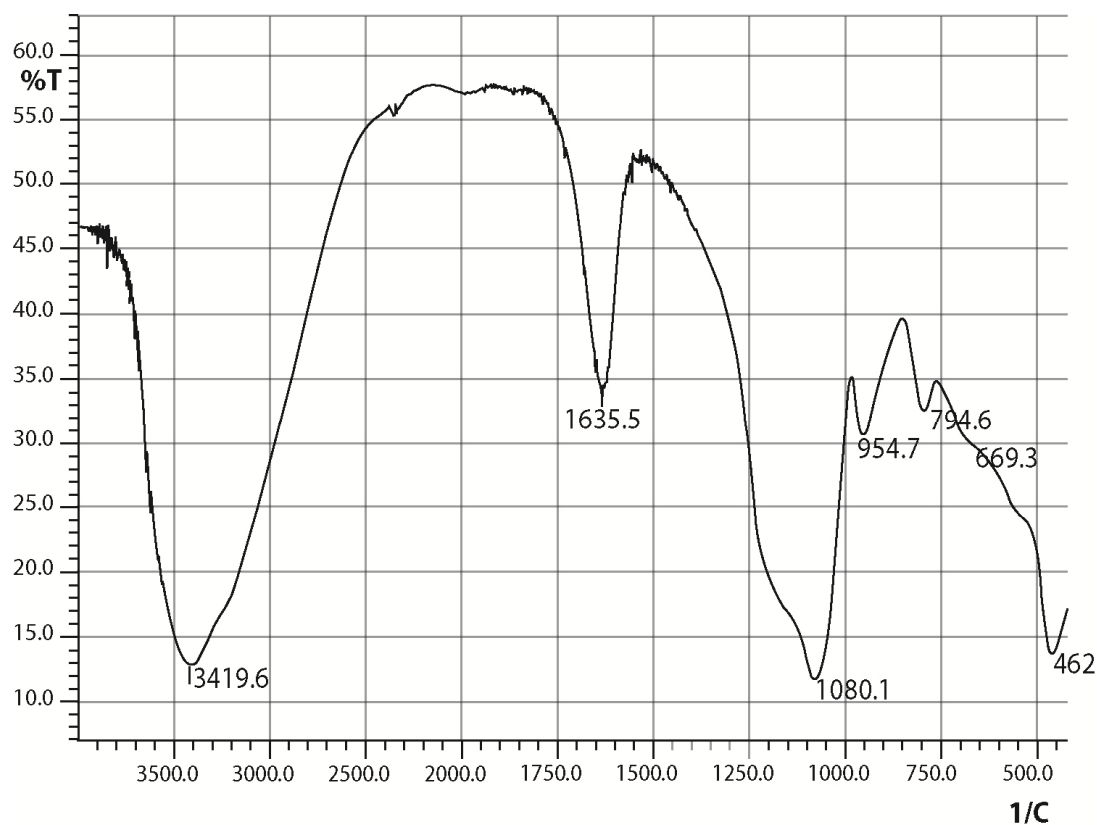


Figure 3.3: FT-IR spectrum of iron oxide- SiO₂ nanocomposite (1:1)

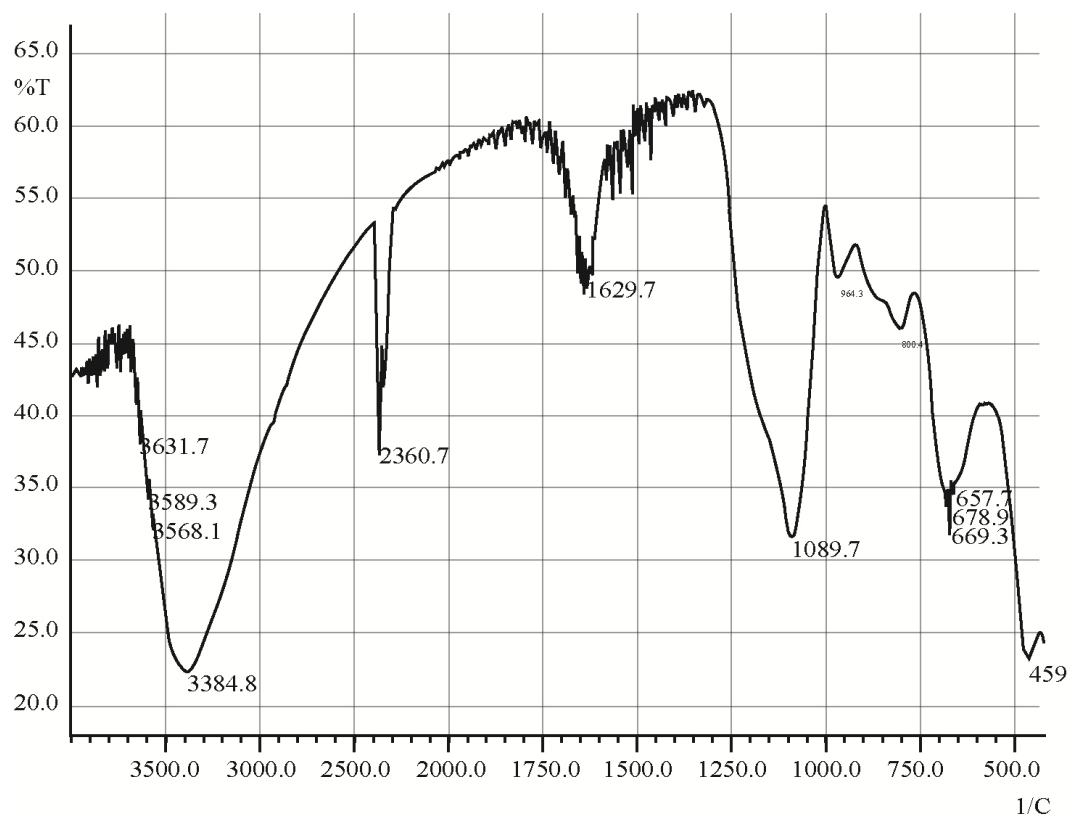


Figure 3.4: FT-IR spectrum of iron oxide-SiO₂ nanocomposite (1:1) after adsorption of Cr(VI)

Characteristics absorption bands of FT-IR analyses of the silicon (IV) oxide and iron oxide are presented in **Table 3.1** and **3.2** along with reported absorption bands of pristine silicon (IV) oxide and iron (III) oxide.

Table 3.1: FT-IR absorption bands of silicon (IV) oxide with band assignments and reported bands of its pristine sample

Probable band assignment	Absorption bands (cm^{-1}) [31]	Experimentally obtained absorption band (cm^{-1})
Si-O-Si bond vibration	450-460	466
Symmetric stretching vibrations of Si-O-Si belonging to ring structures	800-820	797
Asymmetric stretching vibration of Si-O-Si	1000-1260	1084
Combination of vibrations of the SiO_2 network	1640,1870,1960	1643
Due to stretching and bending vibrations of Si-O-H and O-H bonds in surface water molecules	3000-4000	3450

Close examination of **Table 3.1** shows that major absorption bands of the silicon (IV) oxide are in good agreement with the reported values of its authentic sample. Therefore, the FT-IR analysis supports that the sample prepared was silicon (IV) oxide.

Table 3.2: FT-IR absorption bands of iron (III) oxide with band assignments

Name of the iron oxide	Characteristics IR bands (cm^{-1})	References
Hematite	345,470,540	31
Maghemite	400,450,570,590,630	31
Magnetite	400,580	31
Goethite	890,797	31
Lepidocrocite	1026,1161,753	31
Akaganeite	840,640	31
Feroxyhite	1110,920,790,670	31
Hematite Type of iron oxide	3420,1630, 671, 540 and 457	Present experiment

The bands at 457 cm^{-1} and 540 cm^{-1} were assigned to the stretching and torsional vibration modes of the hematite Fe-O bonds in the tetrahedral and octahedral sites respectively, which are in good agreement with the results reported by Mollah M.Y.A³². The absorption bands at 3420 and 1630 cm^{-1} are due to stretching and bending vibrations of O-H bonds in surface water molecules. Thus the synthesized iron oxide shows the absorption bands which are in good agreement with the reported absorption bands of Hematite (Fe_2O_3) type of iron oxide. Therefore, the FT-IR analysis provides the evidence that Hematite (Fe_2O_3) type of iron oxide was electrochemically generated in this research.

Table 3.3: FT-IR absorption bands of Silicon(IV) oxide, iron oxide, Fe_2O_3 - SiO_2 nanocomposite

Absorption band of silicon (IV) oxide (cm^{-1})	Absorption band of iron (III) oxide (cm^{-1})	Absorption band of Fe_2O_3 - SiO_2 nanocomposite (1:1) (cm^{-1})
466	457	462
797	795	795
964	955	955
1084	1018	1080
1643	1630	1636
2349	2360	2360
3450	3420	3420

Close, examination of **Table 3.3** shows that major absorption bands at 462, 795, 955, 1080, 1636, 2360 and 3420 cm^{-1} shown by $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1) were in good agreement with those shown by its constituents silicon (IV) oxide and iron (III) oxide. These FT-IR results indicate the presence of both silicon (IV) oxide and iron (III) oxide in $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1).

In case of the prepared nanocomposite, formation of new bands and absence of several bands of their respective constituents clearly indicate that interaction between constituents silicon (IV) oxide and iron (III) oxide has occurred during formation of the nanocomposite. Therefore, the FT-IR analysis suggests that $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite have been formed.

Table 3.4: FT-IR absorption bands of $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1) and Cr (VI) treated $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1)

Absorption band of $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1) (cm^{-1})	Absorption band of Cr (VI) treated $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1) (cm^{-1})
462	459
795	800
955	964
1080	1090
1636	1630
2360	2361
3420	3385

Examination of **Table 3.4** reveals that new bands appear at 679, 1450, 1550 and 2361 cm^{-1} in Cr(VI) treated $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1). Formation of these new bands is probably due to the presence of adsorbed Cr (VI) in the nanocomposite. The bands that appeared at 462, 795, 955, 1636 and 3420 cm^{-1} in untreated $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1) have been shifted to 459, 800, 964, 1630 and 3385 respectively after treating the

same nanocomposite with Cr(VI). The shifting of bands may be due to substrate-sorbent interaction. The vibrational changes along with shifting of vibrational bands clearly suggest chemical interaction of Cr(VI) with $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1). These results support that Cr(VI) interacts with and $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1) upon adsorption.

3.1.2 X-Ray Diffraction Analysis

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. The XRD pattern of silicon oxide, iron oxide and iron oxide-silicon oxide nanocomposite (1:1) is listed in Figure 3.5, 3.6 and 3.7. The scattering pattern as a function of Bragg angle, 2θ at $\lambda=0.154\text{nm}$ for the studied samples powder are present in those figures.

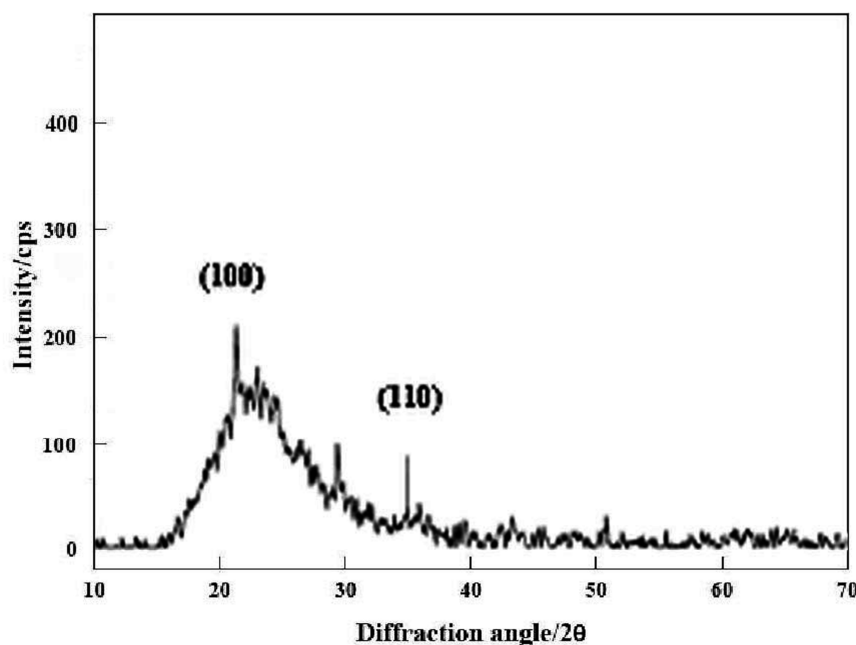


Figure 3.5: XRD pattern of SiO_2

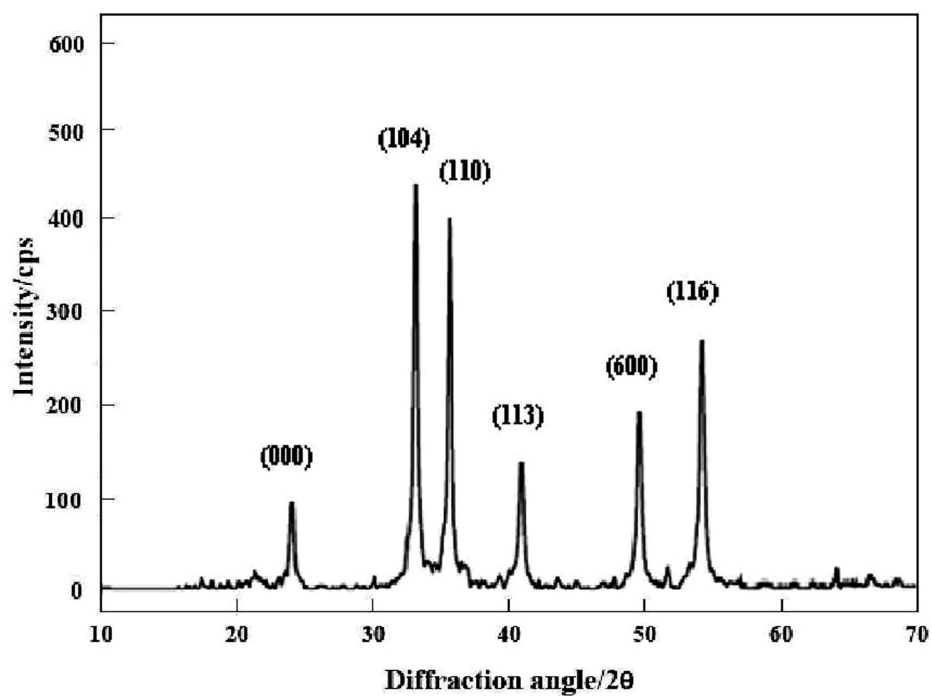


Figure 3.6: XRD pattern of iron oxide

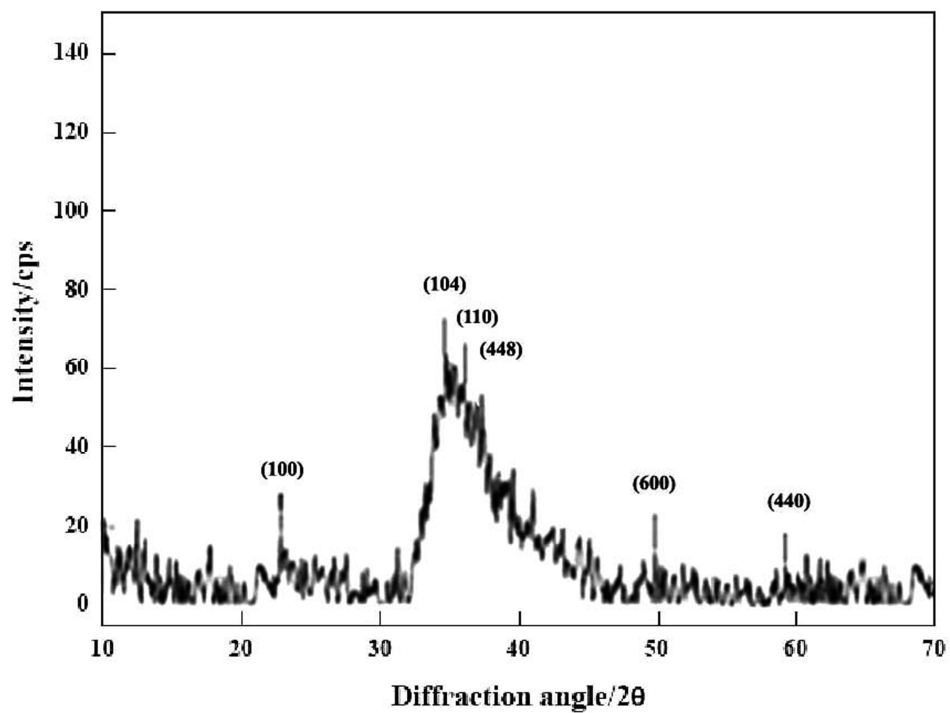


Figure 3.7: XRD pattern of $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1)

Figure 3.5 the XRD pattern of Silica Oxide displays the characteristic peaks 100 (20.4°) and 110 (35.8°) which are similar to the JCPDS card 110252.

Figure 3.6 shows the XRD results of the reference sample. The content of our results matches with JCPDS (Joint Committee on Powder Diffraction Standard) card 730603 on Annes A indentifying the sample to be α -Fe₂O₃.

The XRD pattern of Iron oxide – Silica nanocomposite is illustrated in Figure 3.7 The distinguishing lattice plane peaks are present in 100 (23.7°), 104(34.8°), 110(35.8°), 448 (36.8°), 600(49.5°) and 440 (59.4°). The peaks 100 and 110 are counterpart of JCPDS card 110252; 600, 440 and 448 are match with JCPDS card 361216; 104 is match with JCPDS card 730603; The Miller Indice (h, k, l) lattice planes of Iron and Silica single oxide are present in (Fe-Si) oxide nanocomposite with partial deviation of 2 θ angle of the plane. The XRD pattern shows the evidence which is perfectly synthesized our desired (Fe-Si) oxide nanocomposite.

Crystallite size of Iron Oxide, Silicon oxide and Fe₂O₃-SiO₂ nanocomposite

The finite crystallite sizes is found of as a broadening of the peaks in an X-ray diffraction as is explained by the Scherrer Equation . The Scherrer Equation is

$$D_p = \frac{0.94\lambda}{\beta_{1/2} \cos \theta}$$

Where, θ = Bragg angle,

$\lambda=0.154\text{nm}$ = wave length of X-ray

$\beta_{1/2}$ =Full Width Half- maxima (FWHM),

D_p = crystallite size of particle

For using Scherrer Equation the crystallite size of these materials are obtained. The particle size of, iron oxide-silicon oxide nanocomposite, iron oxide and silicon oxide is 18, 24 and 37 nanometer, respectively.

3.1.3 Thermo gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

The experimental procedures were described in **Section 2.3.3**. The thermograms of silicon (IV) oxide, iron (III) oxide and $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1) are presented in **Figures 3.8 to 3.10** respectively.

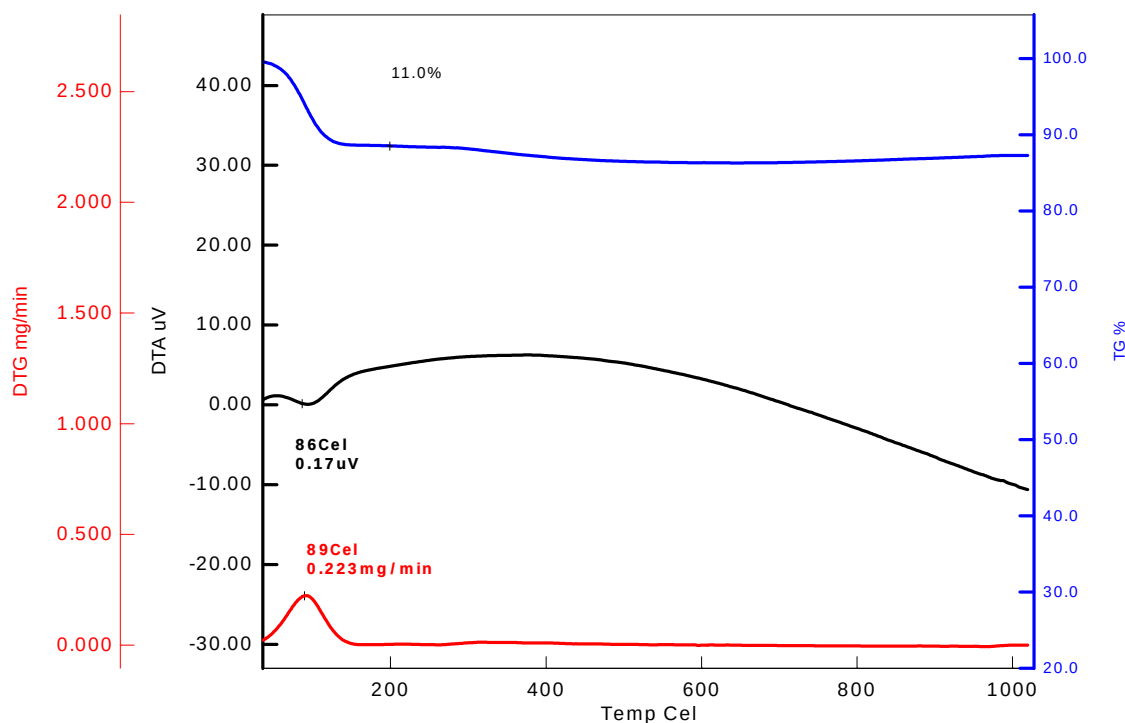


Figure : 3.8 TGA /DTA pattern of silicon (IV) oxide

Thermograph of silica (IV) oxide (**Figure 3.8**) shows gradual weight loss from 40⁰ to 160⁰C (11.0%), almost a steady state from 160⁰C onward. Weight loss may be due to removal of free water (absorbed from atmosphere) and presence of any structural water.

Differential Thermal Analysis (DTA) (**Figure 3.8**) shows an endothermic effect between 86-150⁰ C temperature ranges. The endothermic effect may be due to removal of structural water. The result is in good agreement with the result reported by Qingyin Wu³³.

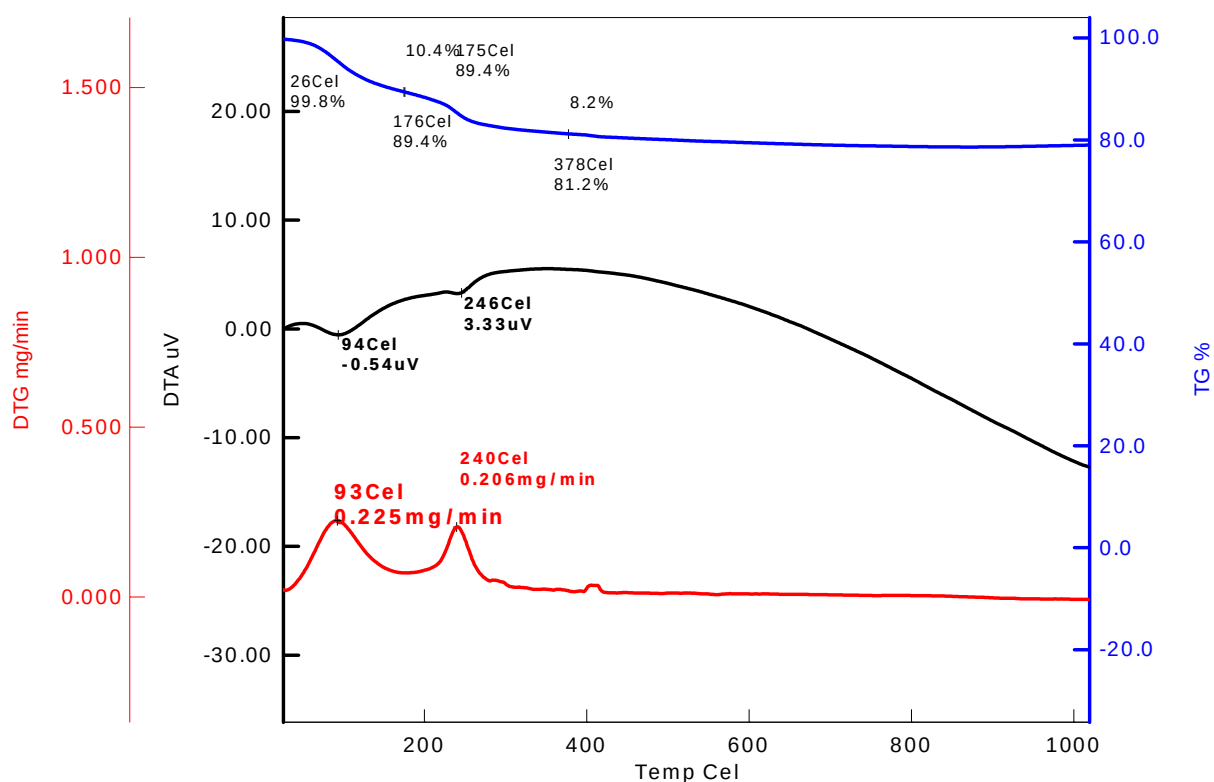


Figure: 3.9 TGA /DTA pattern of iron (III) oxide

Thermograph of iron (III) oxide (**Figure 3.9**) shows gradual weight loss from 26⁰ to 176⁰C (10.4%) and 176⁰ to 378⁰C (8.2 %), almost a steady state from 378⁰C onward. Weight loss may be due to removal of free water absorbed from atmosphere and

presence of any structural water. Gradual weight loss from 250⁰ to 400⁰C (8.2%) was due to dehydroxylation for structural OH.

Differential Thermal Analysis (DTA) (**Figure 3.9**) shows two endothermic peak at 94⁰ C and 246⁰ C temperature. The endothermic effect at 94⁰ C may be due to removal of physically bound water and the endothermic effect at 246⁰ C is due to removal of structurally bound water. Exotherm between 250⁰ to 300⁰C is due to recrystallization process involving transformation of smaller crystals into larger one. The DTA/TG result shown above for iron oxide is in good agreement with the data reported by Balek et al³⁴.

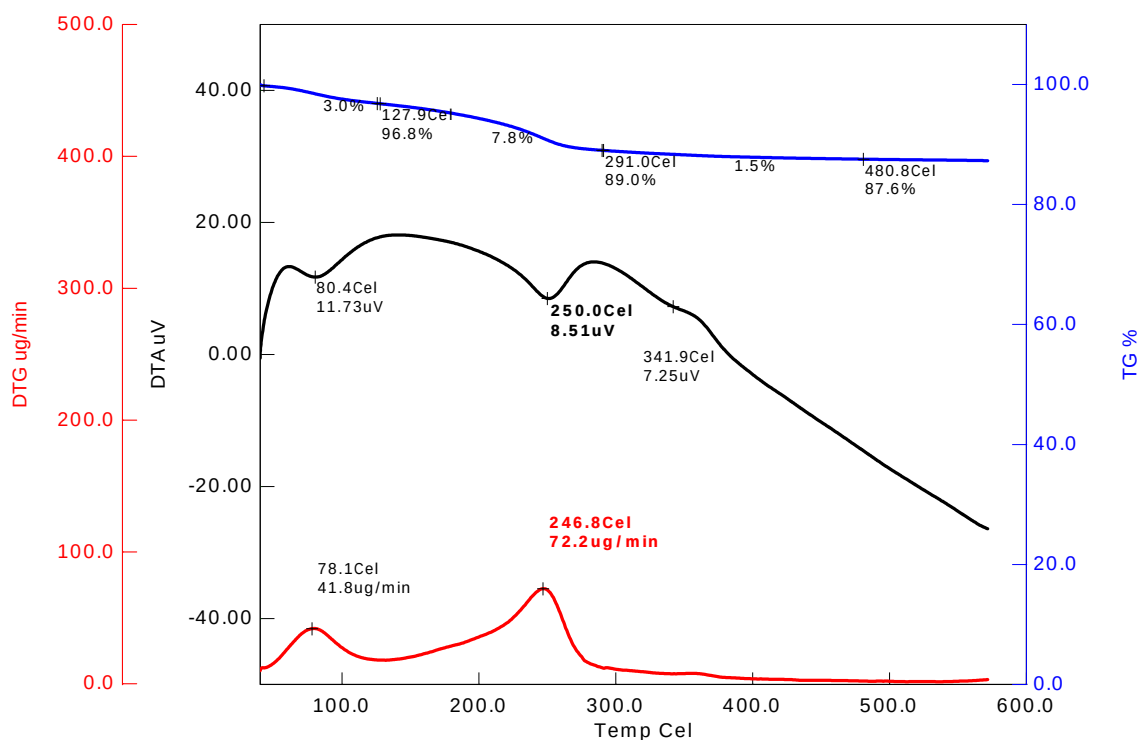


Figure : 3.10 TGA /DTA pattern of iron oxide-silica nanocomposite (1:1)

Thermograph of $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1) (**Figure 3.10**) shows gradual weight loss from 26°C to 290°C (11.0%), almost a steady state from 290°C onward. Weight loss may be due to removal of free water absorbed from atmosphere and presence of any structural water.

Differential Thermal Analysis (DTA) (**Figure 3.10**) shows two endothermic peak at 80.4°C and 250°C and three exothermic peak at 160°C , 300°C and 360°C . The endothermic effect at 80.4°C and 250°C may be due to removal of structural water. Endothermic peak at 341.9°C corresponds to decomposition of goethite phase. Exothermic peak at 300°C can be considered to be due to the growth of goethite ($\alpha\text{-FeOOH}$), an intermediate step of hematite. Other exothermic peaks are due to recrystallization process involving transformation of smaller crystals into larger one. The DTA/TGA result shown above are in good agreement with the result shown by Ennas et al³⁵ and Palomares^{36(a)}.

3.1.4 Energy Dispersive X-ray Spectroscopy (EDS) and Scanning Electron Microscopic (SEM) Analysis

The chemical composition of the samples were determined by energy dispersive X-ray spectroscopy (EDS). The topographical and morphological examination of silicon (IV) oxide, iron oxide and the nanocomposite were carried out by SEM examination. SEM images of the prepared samples are presented in the **Figures 3.11, 3.13 and 3.15** respectively. EDS of the prepared samples are presented in the **Figures 3.12, 3.14 and 3.16** respectively.

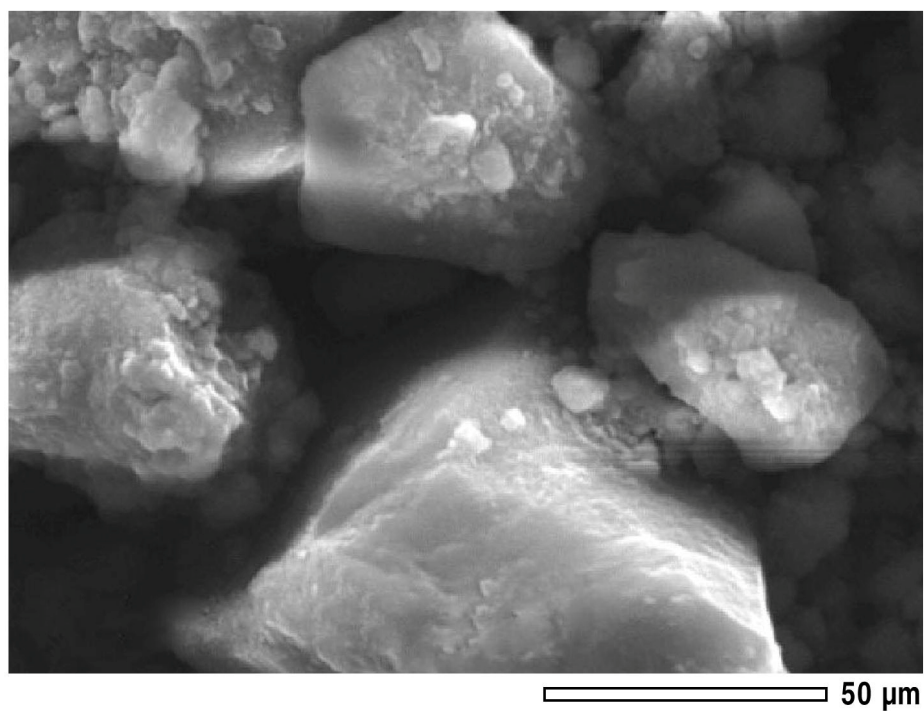


Figure 3.11 SEM image of prepared silicon (IV) oxide

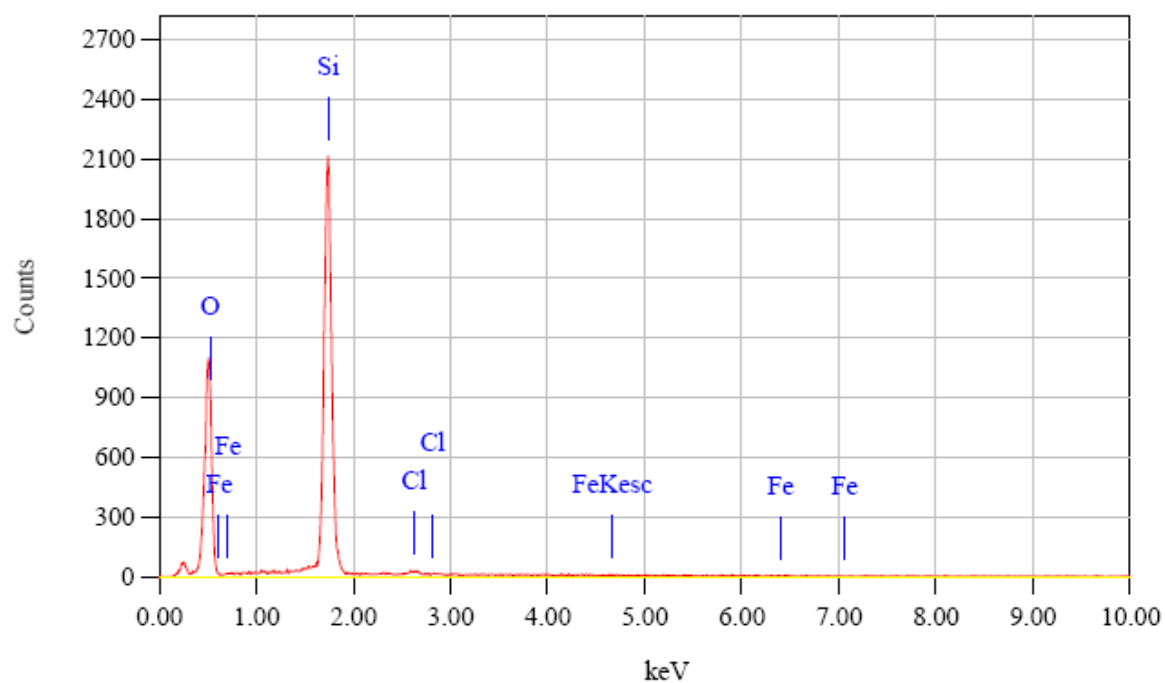


Figure 3.12: EDS of prepared silicon (IV) oxide

ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.2927

Element	(keV)	Mass%	Error%	Atom%
O K	0.525	57.86	0.37	70.74
Si K	1.739	41.60	0.23	28.97
Cl K	2.621	0.45	0.27	0.25
Fe K	6.398	0.09	0.81	0.03
Total		100.00		100.00

The SEM and EDS results of Silicon(IV) oxide are shown in the **Figure 3.11 and 3.12**. . This is expected as the XRD measurement a mean of the actual crystallite size. Albeit, the particles were found to be crystallite according to the X-ray diffraction studies but from the SEM images a thin amorphous layer surrounding each particle was observed^{36(b)}. EDS result suggests the presence of Si and oxygen elements, confirming the formation of SiO₂ particles. Theoretically Si-O ratio is 0.875 and experimentally the value is 0.72, which is very close to the expected value. EDS result indicate the presence of trace amount of Cl as impurities.

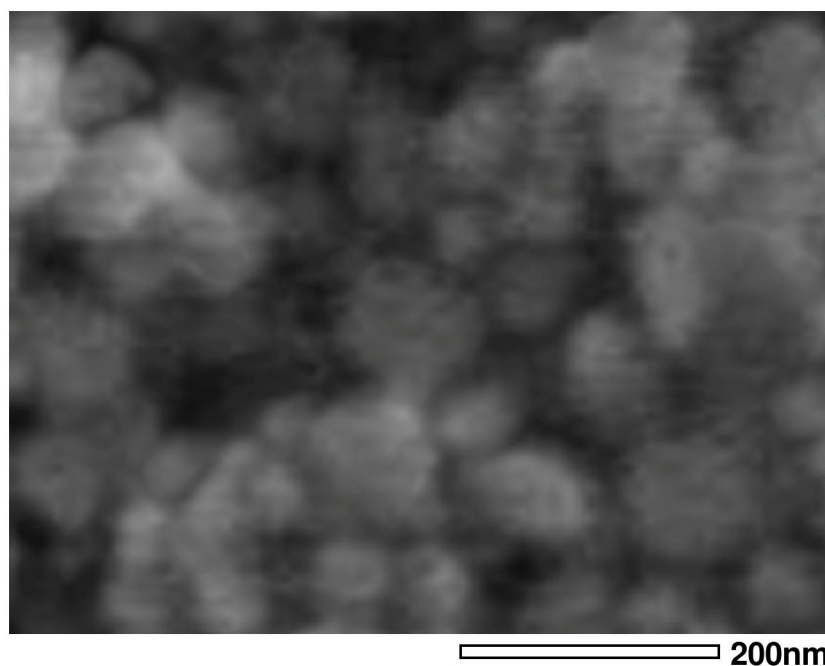


Figure 3.13: SEM image of prepared iron (III) oxide

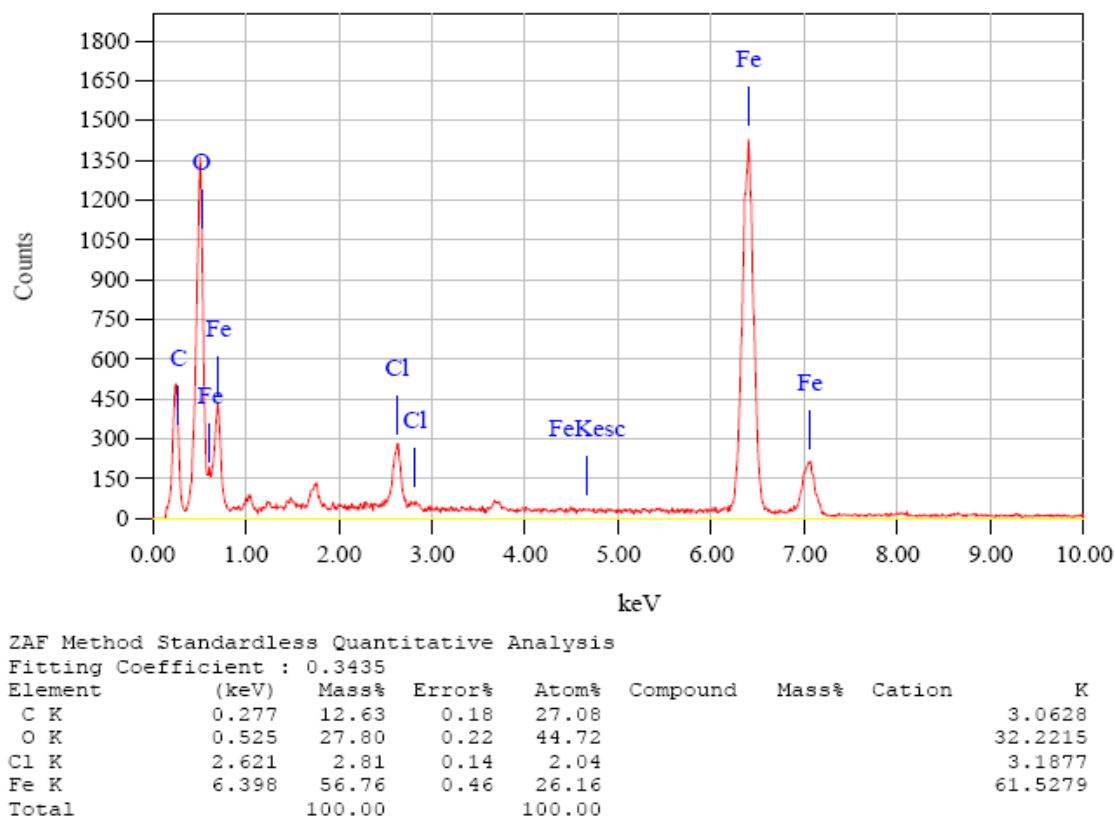


Figure 3.14: EDS of prepared iron (III) oxide

Figure 3.13 and 3.14 represents the SEM and EDS images of iron(III) oxide. The nano Iron oxide was observed in SEM analysis. The average particle size of synthesized particle was 65 nm. However the elemental analysis suggests the presence of Fe and O atomic percentage indicates the formation of the iron oxide. Theoretically Fe-O ratio is 2.33 and experimentally the value is 2.04 , which is very close to the expected value. EDS result indicate the presence of small amount of Cl as impurities.

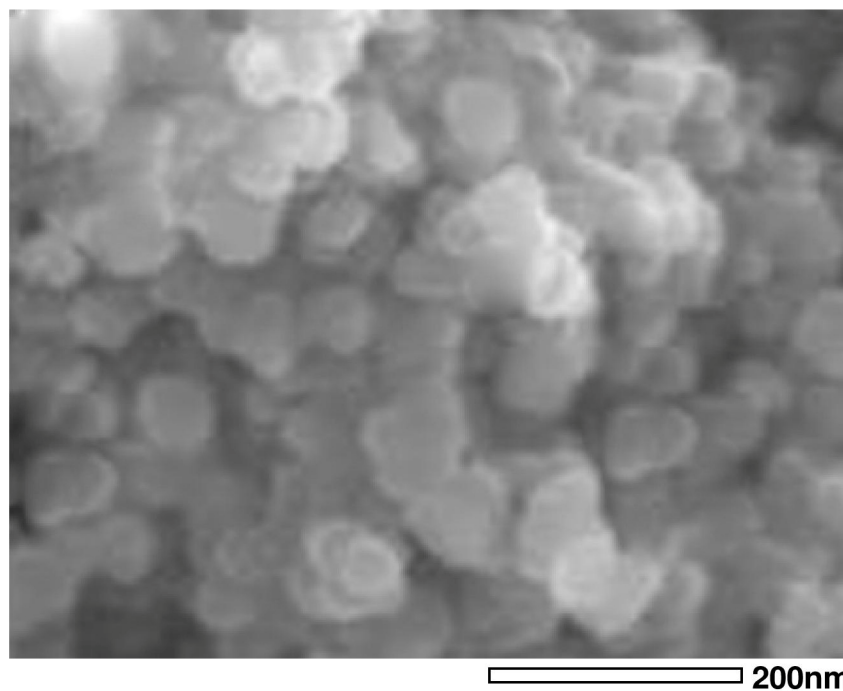
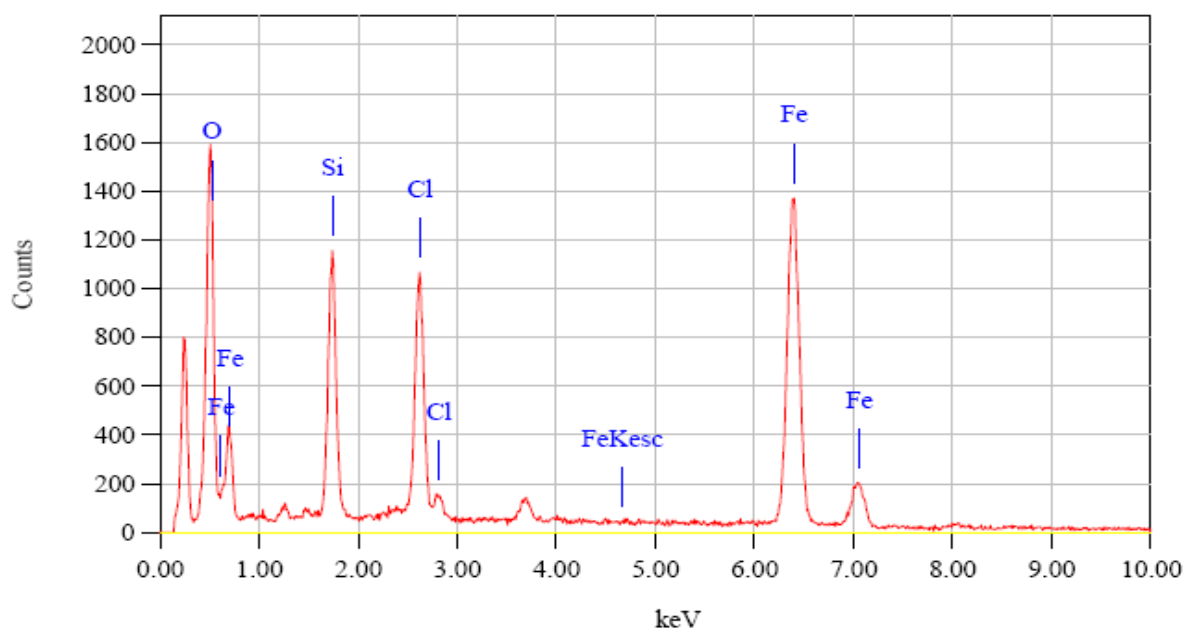


Figure 3.15: SEM image of prepared $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1)



ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.3552

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
O K	0.525	30.07	0.29	54.95				32.6701
Si K	1.739	10.47	0.25	10.90				7.3565
Cl K	2.621	10.07	0.20	8.30				10.2908
Fe K	6.398	49.39	0.63	25.85				49.6827
Total		100.00		100.00				

Figure 3.16: EDS of prepared $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1)

The SEM and EDS results of the prepared nanocomposite, shown in the **Figures 3.15 and 3.16** . The nano Iron oxide – silica nanocomposite was observed in SEM analysis. The average particle size of synthesized particle was 50 nm. The EDS result indicates the formation of the nanocomposite of composition (1:1). Theoretically Fe-Si to O ratio is 1.75 and experimentally it is found as 1.99, which is close to the expected value, confirming the formation of $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1). The EDS result also indicate the presence of small amount of Cl as impurities.

The results of the prepared nanocomposite compositions, shown above , are in good agreement with the result reported by Meera Basa³⁷.

3.2.0 Interactions of Cr(VI) in aqueous solution with the $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite

The interactions of Cr(VI) with the $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite were studied by investigating the

- (i) effects of different (a) dosages of nanocomposite as a sorbent , (b) initial concentrations and shaking time , (c) pH of Cr(VI) solution and (d) shaking time on adsorption of Cr(VI) on the nanocomposite .
- (ii) adsorption isotherm and sorption kinetics of Cr(VI) on the nanocomposite as adsorbents.

Experimental results and discussion are presented in following Sections:

3.2.1 Investigation of the adsorption efficiency of Cr(VI) in aqueous solution for Fe₂O₃, SiO₂ and Fe₂O₃ - SiO₂ nanocomposite (1:1)

Details of the experimental procedures have been described in **Section 2.4.6.1**. The experimental data are presented in **Table 3.5**.

Table 3.5 : The adsorption efficiency of Cr(VI) in aqueous solution for Fe₂O₃, SiO₂ and Fe₂O₃ - SiO₂ nanocomposite (1:1)

Experimental conditions: Volume of Cr(VI) solution = 20.0 cm³, pH of Cr(VI) solution = 4.8 ± 0.2, Temperature = (30.0 ± 0.2) °C, Shaking speed = 250 rpm, Shaking Time = 20 minutes

Assumed Conc. (mgL ⁻¹) /Initial absorbance	Actual Conc. (mgL ⁻¹)	Adsorbent	Absorbance	Conc. at time t (Ct)	Amount adsorbed, x (mg)	Percentage of Cr (VI) adsorbed
10.00 / 1.062 (× 10)	11.93	Fe ₂ O ₃	0.296 (×10)	3.33	0.172	72.10
		SiO ₂	0.799 (×10)	8.98	0.059	24.73
		Fe ₂ O ₃ - SiO ₂ nanocomposite	0.065 (×10)	0.73	0.224	93.88

The experimental data shown above, indicate that maximum amount of Cr(VI) removal is achieved by using Fe₂O₃-SiO₂ nanocomposite (1:1) and thus in this study the removal efficiency of Cr(VI) is studied by using the Fe₂O₃-SiO₂ nanocomposite (1:1).

3.2.2 Investigation of the effect of variation of adsorbent dosage on adsorption of Cr(VI) in aqueous solution for Fe₂O₃-SiO₂ nanocomposite (1:1)

Details of the experimental procedures have been described in **section 2.4.6.2**. The experimental data and corresponding plots are presented in **Table 3.6** and **Figure 3.17** respectively.

Table 3.6: The effect of variation of adsorbent dosage on adsorption of Cr(VI) in aqueous solution for Fe₂O₃-SiO₂ nanocomposite (1:1)

Experimental conditions: Volume of Cr(VI) solution = 25.0 cm³, pH of Cr(VI) solution = 4.8 ± 0.2, Temperature = (30.0 ± 0.2) °C, Shaking speed = 250 rpm, Shaking Time = 20 minutes

Assumed Conc. (mg/L)	Actual Conc. (mg/L)	Dosage (g)	Conc.(Ct) at time t	Amount adsorbed, x (mg)	Amount adsorbed, x/m (mg/g)	Percentage of Cr (VI) removed
50.00	48.88	0.051	23.37	0.638	12.510	52.21
		0.102	9.06	0.996	9.765	81.51
		0.151	2.90	1.15	7.616	94.11
		0.201	2.27	1.17	5.821	95.90
		0.252	1.24	1.19	4.722	97.54
		0.302	1.97	1.17	3.874	95.90

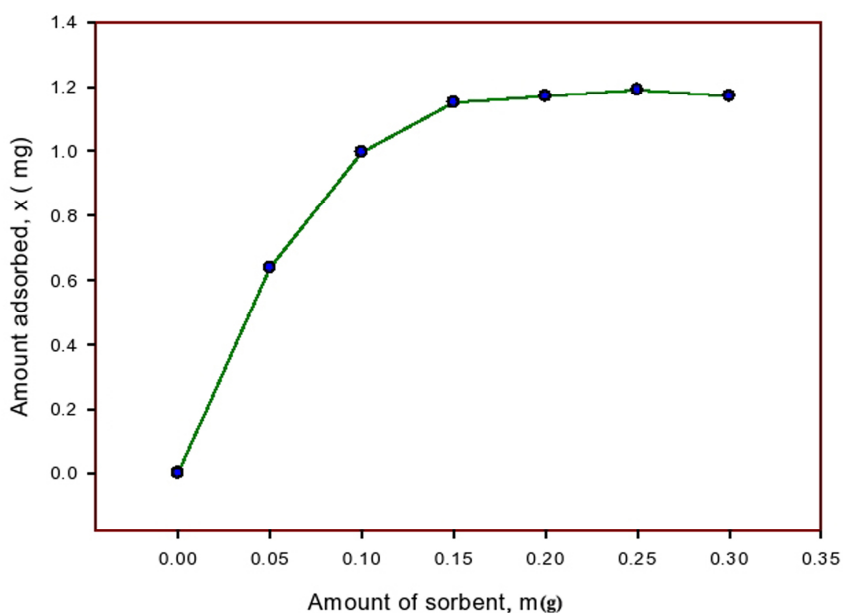


Figure 3.17: Effect of adsorbent [Fe₂O₃-SiO₂ nanocomposite (1:1)] dosage on Cr(VI) adsorption

The **Figure 3.17** shows that adsorption increases from 0.05g to 0.15g and stays almost constant up to 0.30 g of the sorbent dosage. This analysis provides a good guideline in choosing 0.20 g of as a perfect dosage which was sufficient to investigate sorption effect of Cr(VI) on the nanocomposite for a definite amount of Cr(VI) solution.

3.2.3. Determination of the effects of initial concentrations of Cr(VI) solution and shaking time on adsorption of Cr (VI) on Fe₂O₃-SiO₂ nanocomposite

In order to investigate the effect of different initial concentrations, viz, 40 and 50 mgL⁻¹ of Cr(VI) solution at constant pH 4.8 and shaking time on Cr(VI) adsorption on the Fe₂O₃-SiO₂ nanocomposite, amount of Cr(VI) adsorbed per gram of the nanocomposite (x/m) were determined. Details of the experimental procedures for these measurements have been described in **Sections 2.4.6.3**. The adsorption data for Fe₂O₃-SiO₂ nanocomposite (1:1) are presented in **Table 3.7** and the corresponding plots of x/m against shaking time, t are shown in the **Figure 3.18**.

Table 3.7: Determination of the effects of initial concentrations of Cr(VI) solution and shaking time on adsorption of Cr (VI) on Fe₂O₃-SiO₂ nanocomposite (1:1)

Experimental conditions: Volume of Cr(VI) solution = 25.0 cm³, pH of Cr(VI) solution = 4.8 ± 0.2, Temperature = (30.0 ± 0.2) °C, Shaking speed = 250 rpm, Mass of adsorbent taken ≈ / = 0.20 gm

Assumed Conc. (mg/L)	Actual Conc. (mg/L)	Shaking time (minutes)	Conc. (Ct) at time t	Amount adsorbed, x (mg)	Mass of adsorbent, m (g)	Amount adsorbed, x/m (mg/g)	Percentage of Cr(VI) removed
40.00	41.51	0	0.000	0.000	0.000	0.000	0.00
		10	3.548	0.949	0.202	4.70	91.43
		20	2.711	0.972	0.201	4.83	93.46
		40	1.709	0.995	0.203	4.90	95.86
		60	1.577	0.999	0.201	4.97	96.24
		90	1.543	0.999	0.202	4.95	96.24
		120	1.388	1.003	0.203	4.94	96.63
50.00	48.88	0	0.000	0.000	0.000	0.000	0.00
		10	4.101	1.12	0.202	5.54	91.80
		20	3.152	1.14	0.201	5.68	93.80
		40	2.012	1.17	0.203	5.76	95.90
		60	1.871	1.18	0.201	5.87	96.72
		90	2.288	1.17	0.202	5.79	95.90
		120	2.148	1.17	0.201	5.82	95.90

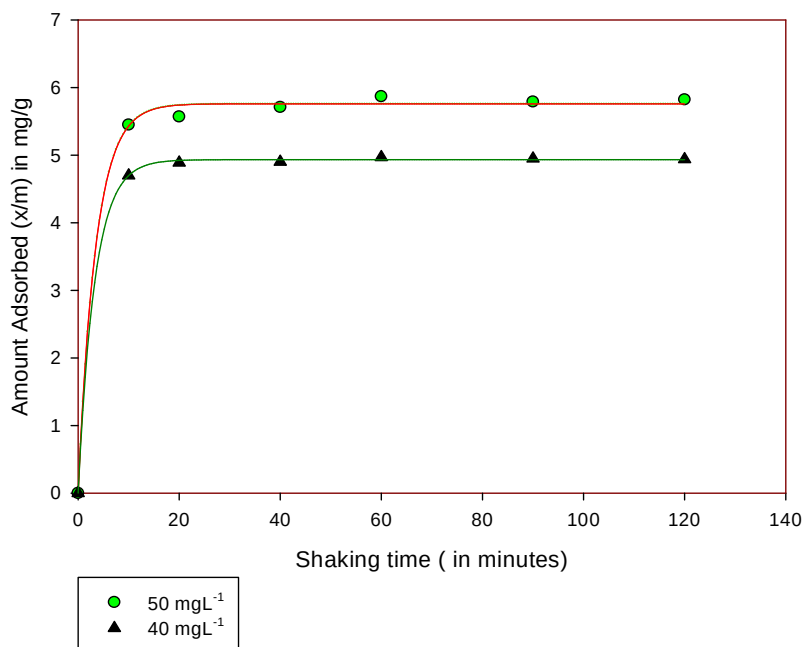


Figure 3.18: Effects of initial concentrations of Cr(VI) solution and shaking time on adsorption of Cr(VI) on Fe₂O₃-SiO₂ nanocomposite (1:1)

The progresses of Cr(VI) adsorption at different initial concentrations 40 and 50 mgL⁻¹ of Cr(VI) solution on iron oxide-silica nanocomposite with shaking time are shown graphically in **Figure 3.18**. The result show that the rate of adsorption in all the cases are significantly rapid initially within first 15 minutes (about 78-94%) at all concentrations of Cr (VI) solution which gradually decrease until equilibrium was attained. However, equilibrium was practically attained in about 20 minutes.

The experimental data indicate that the amount (mgg⁻¹) of Cr(VI) adsorbed by the Fe₂O₃-SiO₂ nanocomposite at equilibrium increased with increase in initial concentration of Cr(VI) in aqueous solution. However, the percentage removal efficiency for Cr(VI) from aqueous system by the Fe₂O₃-SiO₂ nanocomposite appears to increase with increase in the initial concentration of Cr(VI) in aqueous solution.

3.2.4. Determination of the effects of variation in pH of Cr(VI) solution and shaking time on adsorption of Cr (VI) on Fe₂O₃-SiO₂ nanocomposite (1:1)

Investigation for these studies was conducted according to the procedure described in **Section 2.4.6.4**.

Preliminary experiments showed that the nanocomposite remain stable over a pH range of 2-9. Presence of iron in the supernatant liquid could not be detected by chemical tests.

Adsorption of Cr(VI) on Fe₂O₃-SiO₂ nanocomposite (1:1) at ambient temperature was investigated at different pH, viz. 3.0, 4.8 and 8.0. The kinetics of adsorption was measured by measuring the amount of Cr(VI) adsorbed as function of shaking time. The data are presented in **Table 3.10**. The corresponding plots of the amount of Cr(VI) adsorbed per gram of adsorbent (x/m) against shaking time, t are shown in **Figure 3.19**. The rate of adsorption of Cr(VI) seems to be very little influenced by pH ; the time required to reach equilibrium is about 20 minutes over the whole range of pH investigated.

However, the amount of Cr(VI) adsorbed on the nanocomposite was profoundly influenced by pH. **Figure 3.20** shows the variation of the amount of Cr(VI) adsorbed per gram of the adsorbents with pH. At pH 3.0 maximum amount of Cr(VI) was adsorbed (about 98%) , at pH 4.8 the amount of Cr(VI) adsorbed was 96.5% and about 77% at pH 8.0 . So it can be said that the Cr(VI) removal efficiency decreases with increases in pH.

Table 3.8: Determination of the effects of variation in pH of Cr(VI) solution and shaking time on adsorption of Cr (VI) on Fe₂O₃-SiO₂ nanocomposite (1:1)

Experimental conditions: Volume of Cr(VI) solution = 25.0 cm³, Temperature = (30.0 ± 0.2) °C, Shaking speed = 250 rpm, Mass of adsorbent taken ≈ / = 0.20 gm (for pH 3.0 and 4.8) and 0.25 gm for pH 8.0

pH	Assumed Conc. (mg/L)	Actual Conc. (mg/L)	Shaking time (minute s)	Conc. (Ct) at time t	Amount adsorbed, x (mg)	Mass of adsorbent, m (g)	Amount adsorbed, x/m (mg/g)	Percentage Cr (VI) removed
3.0	50.00	48.88	0	0.000	0.000	0.000	0.000	0.00
			10	1.956	1.173	0.201	5.84	95.99
			20	1.468	1.185	0.201	5.90	96.97
			40	1.147	1.193	0.202	5.91	97.63
			60	1.001	1.197	0.201	5.96	97.95
			90	0.840	1.201	0.200	6.00	98.28
4.8	50.00	48.88	0	0.000	0.000	0.000	0.000	0.00
			10	4.101	1.12	0.202	5.54	91.80
			20	3.152	1.14	0.201	5.68	93.80
			40	2.012	1.17	0.203	5.76	95.90
			60	1.871	1.18	0.201	5.87	96.72
			90	2.288	1.17	0.203	5.79	95.90
8.0	50.00	48.88	0	0.000	0.000	0.000	0.000	0.00
			10	3.243	1.14	0.251	4.54	74.45
			20	2.522	1.16	0.251	4.62	75.53
			40	2.221	1.17	0.250	4.68	76.27
			60	1.866	1.18	0.252	4.68	77.25
			90	1.673	1.18	0.250	4.72	77.25

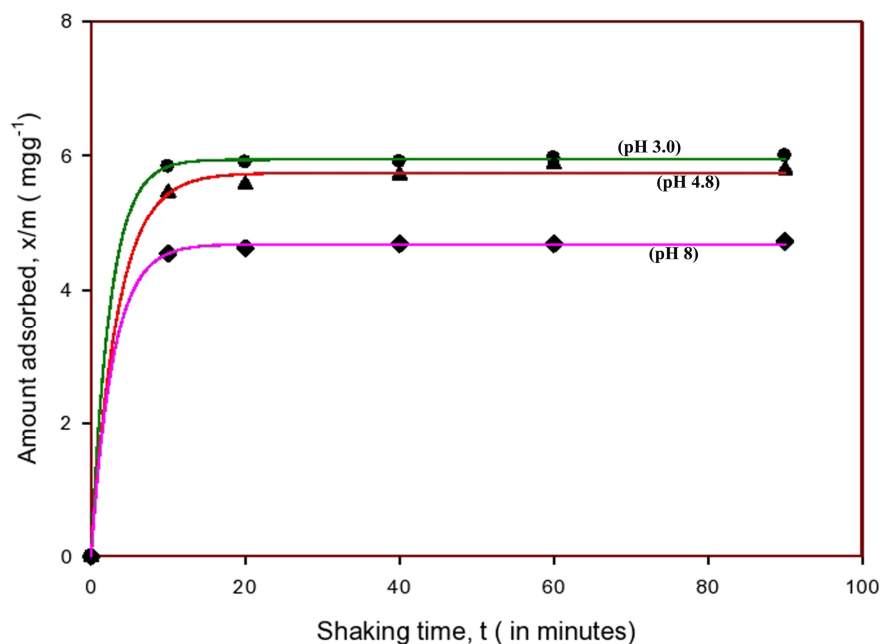


Figure 3.19: Effects of effects of variation in pH of Cr(VI) solution and shaking time on adsorption of Cr (VI) on Fe₂O₃-SiO₂ nanocomposite (1:1)

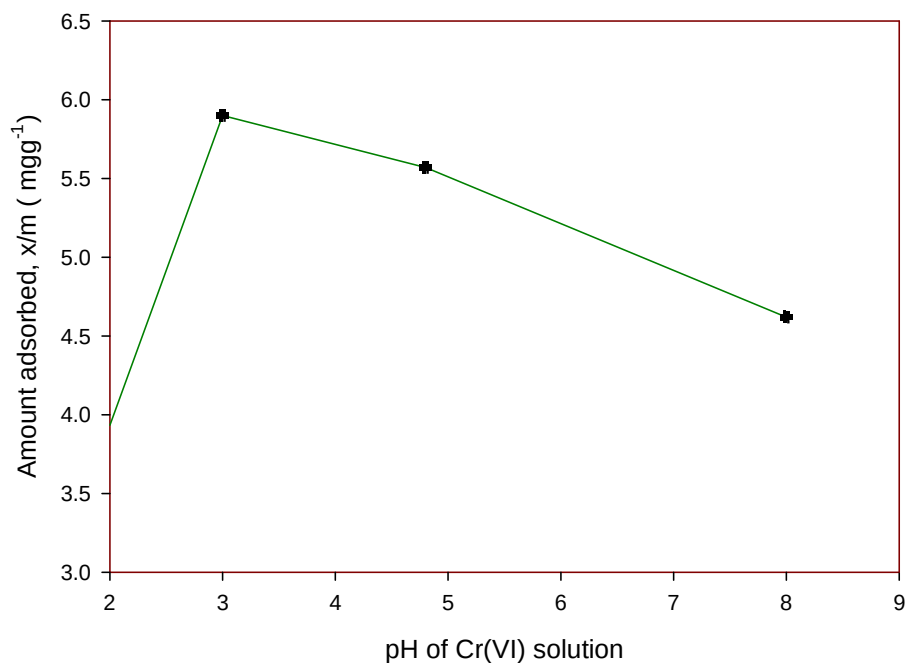


Figure 3.20: Variation of Cr(VI) solution adsorption with shaking time on Fe₂O₃-SiO₂ nanocomposite (1:1) at pH 3.0, 4.8 and 8.0 of Cr(VI) solution

Surfaces of $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1) were likely to be covered with hydroxyl groups in aqueous medium that vary in forms at different pH. At lower pH Cr(VI) can easily adsorbed to the adsorbent surface. On the other hand at higher pH, the concentration of OH^- anions increases in the aqueous medium, which competes with Cr(VI) species in solution and for this reason a decrease in percentage removal of Cr(VI) from the adsorption medium. Besides this, chances of hydrogen bonding by the hydroxyl protons with the oxygen present on the silica surface cannot be ignored.

3.3.0 Adsorption isotherm

Isotherm for adsorption of Cr(VI) from aqueous solution on the $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1) has been investigated to study interaction of Cr(VI) with the nanocomposite.

3.3.1. Adsorption isotherm of Cr(VI) on $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1)

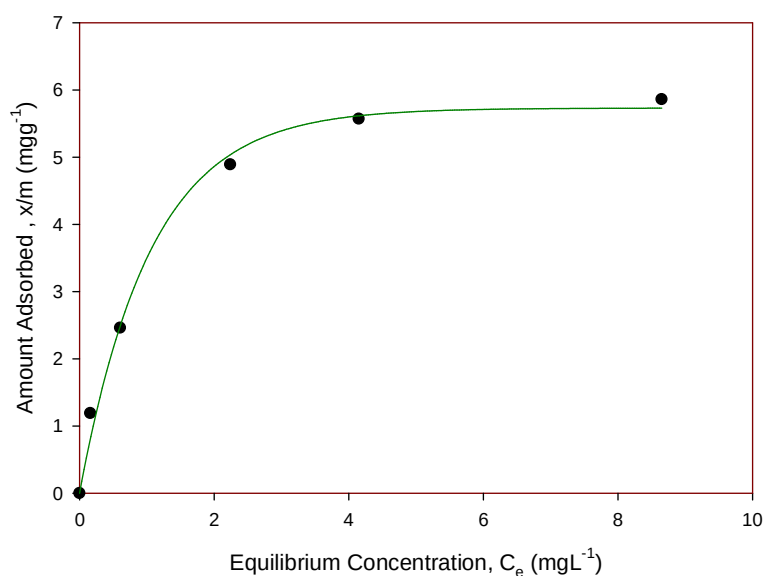
Experimental procedure has been described in **Section 2.4.6.5**.

The experimental data and corresponding plots for adsorption isotherm of Cr(VI) are shown in **Table 3.9** and **Figure 3.21** respectively.

Table 3.9: Adsorption isotherm of Cr(VI) on Fe₂O₃-SiO₂ nanocomposite (1:1)

Experimental conditions: Volume of Cr(VI) solution = 25.0 cm³, Temperature = (30.0 ± 0.2) °C, Shaking speed = 250 rpm, Mass of adsorbent taken ≈ / = 0.20 gm, pH = 4.8

Assumed Conc. (mg/L)	Actual Conc. C ₀ (mg/L)	Equilibrium Conc. C _e (mg/L)	Amount adsorbed, x (mg)	Mass of adsorbent, m (g)	Amount adsorbed, x/m (mg/g)	Percentage adsorbed
0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	10.06	0.16	0.2475	0.208	1.19	98.41
20	20.49	0.605	0.4973	0.202	2.46	97.05
40	41.51	2.24	0.982	0.201	4.89	94.61
50	48.88	4.15	1.118	0.201	5.57	91.80
60	58.05	8.65	1.235	0.210	5.85	85.11

**Figure 3.21: Adsorption isotherm of Cr (VI) on Fe₂O₃-SiO₂ nanocomposite (1:1)**

The experimental result of adsorption isotherm for adsorption of Cr(VI) on Fe₂O₃-SiO₂ nanocomposite (1:1) shows that 5.57 mg (91.80%) of Cr(VI) was removed from its aqueous solution per gram of Fe₂O₃-SiO₂ nanocomposite (1:1) when 48.88 mgL⁻¹ of Cr(VI) solution at pH 4.8 at 30.0 °C was put in contact with Fe₂O₃-SiO₂ nanocomposite (1:1) for 20 minutes.

3.3.1.1 Nature of the experimental adsorption isotherm for adsorption of Cr(VI) on Fe₂O₃-SiO₂ nanocomposite (1:1)

The experimental isotherm appeared to be a Langmuir isotherm. Therefore, a through test was performed by fitting the experimental data to the Langmuir equation. According to the Langmuir equation

$$\frac{C_e}{Q} = \frac{1}{K_a Q_m} + \frac{C_e}{Q_m}$$

A plot of $C_e / (x/m)$ against C_e should be a straight line, where $x/m=Q$ is the amount adsorbed per gram of adsorbent at an equilibrium concentration of C_e and Q_m is corresponding amount for the formation of a monolayer. The calculated data for the Langmuir plot are shown in **Table 3.10** and the Langmuir plot is shown in the **Figure 3.22**.

Table 3.10: Langmuir adsorption isotherm of Cr(VI) on Fe₂O₃-SiO₂ nanocomposite (1:1)

Experimental conditions: Volume of Cr(VI) solution = 25.0 cm³, Temperature = (30.0 ± 0.2) °C, Shaking speed = 250 rpm, Mass of adsorbent taken ≈ / = 0.20 gm, pH = 4.8

Assumed Conc. (mg/L)	Actual Conc. C ₀ (mg/L)	Equilibrium Conc. C _e (mg/L)	Amount adsorbed, x (mg)	Q (x/m) mg/g	C _e / Q mg/L
0.00	0.00	0.00	0.00	0.00	0.00
10	10.06	0.16	0.2475	1.19	0.13
20	20.49	0.605	0.4973	2.46	0.25
40	41.51	2.24	0.982	4.89	0.46
50	48.88	4.15	1.118	5.56	0.75
60	58.05	8.65	1.235	5.85	1.48

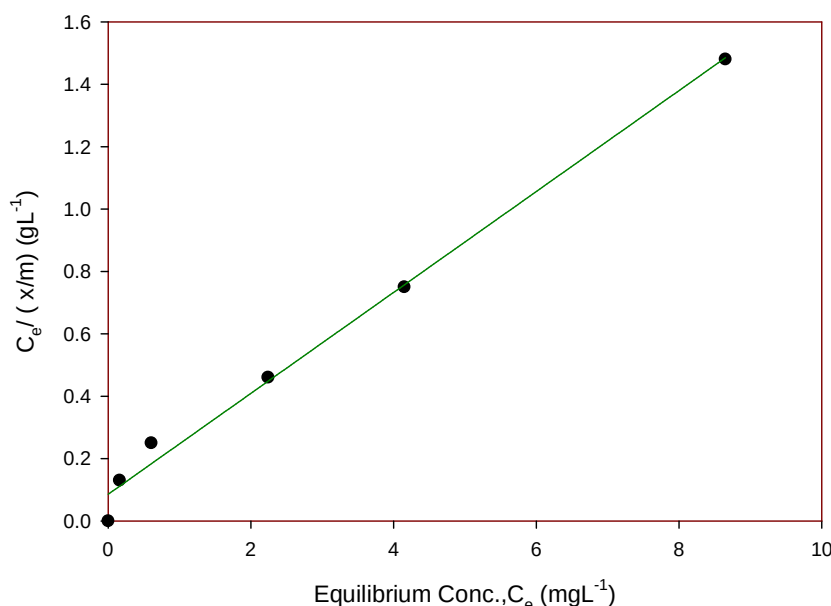


Figure 3.22: Langmuir plot for the adsorption of Cr (VI) on Fe₂O₃-SiO₂ nanocomposite (1:1)

The figure shows a linear plot of $C_e / (x/m)$ against C_e . The fitting of the experimental data to a straight line is excellent, indicating the validity of the Langmuir model of adsorption. The values of the Langmuir constants, Q_m and K_a were determined from the plot and found to be 6.17 mgg⁻¹ and 1.80 Lmg⁻¹ respectively. The essential characteristics of Langmuir isotherm is expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L which is defined by the relation:

$$R_L = [1 / (1 + K_a C_0)]$$

Where K_a is the Langmuir constant and C_0 is the initial concentration of Cr(VI).

The equilibrium parameter, R_L can easily be calculated using the values C_0 and K_a as found earlier. Data for calculating the values of R_L are shown in **Table 3.12**.

Table 3.11: Determination of equilibrium parameters from Langmuir adsorption isotherm of Cr(VI) on Fe₂O₃-SiO₂ nanocomposite (1:1)

Initial Concentration C _o mg/L	K _a L/mg	1+ K _a C _o	R _L
10.06	1.80	19.108	0.052
20.49		37.882	0.026
41.51		75.718	0.013
48.88		88.984	0.011
58.05		105.49	0.009

It is found from the **Table 3.10** that $0 < R_L < 1$. This indicates favorable adsorption of Cr(VI) on Fe₂O₃-SiO₂ nanocomposite (1:1) at all concentrations and the pH of Cr(VI) studied.

3.4.0 Sorption dynamics

Experimental procedure has been described in **Section 2.4.6.6**.

The rate constant for the sorption of Cr(VI) on Fe₂O₃-SiO₂ nanocomposite (1:1) has been determined from the first order rate expression given by Lagergren³⁸.

$$\ln(Q_e - Q) = \ln Q_e - k_{ad} t$$

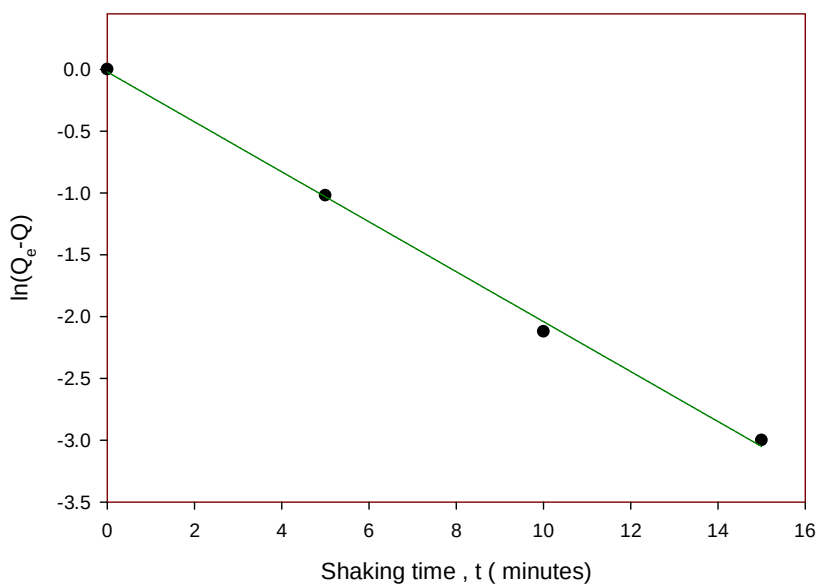
Where k_{ad} is the rate constant for adsorption, Q (mg/g) is the amount of Cr(VI) adsorbed per gram of adsorbent at time t and Q_e (mg/g) is the amount of Cr(VI) adsorbed per gram of adsorbent at equilibrium time.

The data and plot of $\ln(Q_e - Q)$ vs shaking time are presented in the **Table 3.11** and **Figure 3.23** respectively.

Table 3.12: Data for sorption kinetics

Experimental conditions: Volume of Cr(VI) solution = 25.0 cm³, Temperature = (30.0 ± 0.2) °C, Shaking speed = 250 rpm, Mass of adsorbent taken ≈ / = 0.20 gm, pH = 4.8

Assumed Conc. (mg/L)	Actual Conc. (mg/L)	Shaking time (minutes)	Conc.(Ct) at time t	Amount adsorbed, x (mg)	Q (x/m) (mg/g)	Q _e -Q (mg/L)	ln (Q _e -Q)	t ^{1/2} (min ^{1/2})
50.00	48.88	0	0.000	0.000	0.000	0.00	0.00	0.00
		5	6.850	1.05	5.21	0.36	-1.02	2.24
		10	4.795	1.10	5.45	0.12	-2.12	3.16
		15	4.550	1.11	5.52	0.05	-3.00	3.87
		20	4.154	1.12	5.57	-	-	-
		40	2.595	1.16	5.71	-	-	-
		60	1.871	1.18	5.87	-	-	-
		90	2.288	1.17	5.79	-	-	-
		120	2.148	1.17	5.82	-	-	-

**Figure 3.23:** Lagergren plot for the adsorption of Cr (VI) on Fe₂O₃-SiO₂ nanocomposite (1:1)

Linear plot of $\ln(Q_e - Q)$ vs shaking time indicates the applicability of Lagergren equation and the first order nature of the adsorption process. The value of the rate constant k_{ad} for adsorption was computed from the slope of the straight line in **Figure 3.23** and was found to be 0.2 min⁻¹ at 30.0 °C.

The rate constant of intra-particle transport, k_d , was calculated using the equation of Weber and Morris³⁹.

$$Q = k_d t^{1/2}$$

Where Q is the amount of Cr(VI) adsorbed (mg/g) per gram of the adsorbent at time t . A plot of Q vs $t^{1/2}$ is shown in **Figure 3.24**.

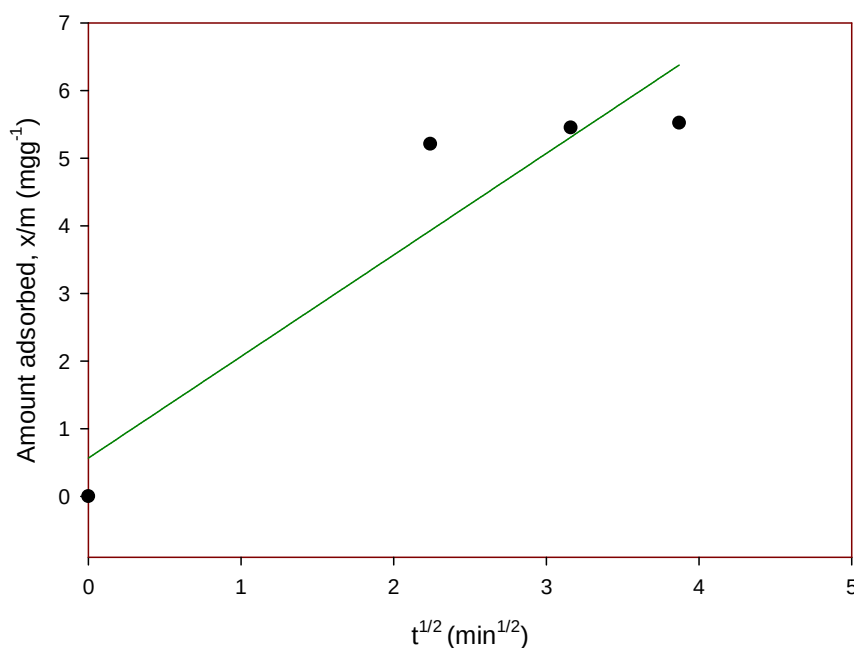


Figure 3.24: Validation of Morris-Weber equation for sorption of Cr (VI) on $\text{Fe}_2\text{O}_3\text{-SiO}_2$ nanocomposite (1:1)

It is clear that the linear plot of Q vs $t^{1/2}$ does not pass through the origin. It thus indicates that the pore diffusion is not the only rate-controlling step in the removal of Cr(VI) in aqueous system, especially for the first minutes of shaking time⁴⁰. The rate constant k_d of intra-particle transport was computed from the slope of the **Figure 3.24** and was found to be $1.51 \text{ mg g}^{-1} \text{ min}^{-1/2}$ at 30.0°C .

Chapter 4

CONCLUSION

4.0 Conclusion

Iron oxide-SiO₂ nanocomposite was successfully prepared by Sol-Gel method. This nanocomposite was used to remove Cr(VI) from aqueous solution. XRD and FT-IR results confirm that Hematite (Fe₂O₃) type of iron (III) oxide and Tridymite (SiO₂) type of silicon (IV) oxide were prepared in this research.

Iron oxide-SiO₂ nanocomposite prepared by Sol-Gel method has been characterized by FT-IR, XRD, TGA/DTA, SEM and EDS techniques. Analytical results obtained by the above techniques lead us to conclude that iron oxide- SiO₂ nanocomposite were formed due to interaction between silicon (IV) oxide and iron (III) oxide.

Removing efficiency of Cr(VI) by the iron oxide- SiO₂ nanocomposite were determined by studying adsorption of Cr(VI) in aqueous solution on the nanocomposite under different experimental conditions , such as sorbent dosages, initial concentration and pH of Cr(VI) solution and shaking time. Adsorption was found to be dependent on pH and initial concentration of Cr(VI) solution. Results of adsorption studies suggest that iron oxide removes 72.1% , silicon (IV) oxide removes 24.73% and iron oxide – silicon (IV) oxide composite removes 93.88% Cr(IV) from aqueous solution. Therefore, it can be said that iron oxide – silicon (IV) oxide nanocomposite plays effective role in adsorption of Cr(VI) from aqueous solution. Studies of the sorption kinetics show that equilibrium adsorption was attained in 20 minutes depending on other experimental conditions. The

kinetic data justified Lagergren first-order kinetic equation. Adsorption isotherm study showed that the results fulfilled the Langmuir Model of adsorption isotherm.

However, effects of the following parameters on Cr(VI) adsorption on SiO₂-iron oxide nanocomposite are recommended for further studies:

- (i) Cr(VI) adsorption on iron oxide- SiO₂ nanocomposite may be studied at different temperatures in order to observe effect of temperature on Cr(VI) adsorption on the composites. This will enable to calculate the enthalpy of adsorption.
- (ii) Surface charge and zpc should be determined to better understand the surface properties of the adsorbent.
- (iii) Determination of surface area of the composites materials may be studied.
- (iv) Adsorption of other heavy metals present in waste water on the prepared composites may be studied.

Chapter 5

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