

CHAPTER-I

INTRODUCTION

1.1. Environmental pollution

Pollution means the undesirable substances that cause adverse effects in the atmosphere. Toxic pollution affects more than 200 million people worldwide. In some of the world's worst polluted places, babies are born with birth defects, children have lost 30 to 40 IQ points, and life expectancy may be as low as 45 years because of cancers and other diseases [1].

1.1.1. Types of pollution

- Land pollution
- Air pollution
- Noise pollution
- Light pollution
- Water pollution

1.1.2 Land pollution

Land can become polluted by household garbage and by industrial waste. In 2014, Americans produced about 258 million tons of solid waste, according to the U.S. Environmental Protection Agency. A little over half of the waste 136 million tons was gathered in landfills. Only about 34% was recycled or composted.

1.1.3 Air pollution

The air we breathe has a very exact chemical composition. The 99% of it is made up of nitrogen, oxygen, water vapor and inert gases. Air pollution occurs when things that aren't normally there are added to the air. A common type of air pollution happens when people release particles into the air from burning fuels. This pollution looks like soot, containing millions of tiny particles, floating in the air.

1.1.4 Noise pollution

Noise pollution happens when the sound coming from planes, industry or other sources reaches harmful levels. The direct health problems caused by noise, including stress-related

illnesses, high blood pressure, speech interference, hearing loss. WHO Noise Environmental Burden on Disease working group found that noise pollution may contribute to hundreds of thousands of deaths per year by increasing the rates of coronary heart disease [2].

1.1.5 Light pollution

Light pollution, also known as photo pollution, is the presence of anthropogenic and artificial light in the night environment. It is exacerbated by excessive, misdirected or obtrusive uses of light, but even carefully used light fundamentally alters natural conditions. As a major side-effect of urbanization, it is blamed for compromising health, disrupting ecosystems and spoiling aesthetic environments [3].

1.1.6 Water pollution

Water pollution is the contamination of water bodies by human activities when contaminants are introduced into the natural environment. By releasing inadequately treated waste water into natural water bodies can lead to degradation of aquatic ecosystems and is the leading worldwide cause of death and disease due to water-borne disease [4].

Water pollution is a major environmental issue in India. Most rivers, lakes and surface water in India are polluted. The pressure of increasing population, growth of industries, urbanization, deforestation, lack of environmental awareness, lack of implementation of environmental rules and regulations and environment improvement plans, untreated effluent discharge from industries and municipalities, use of non-biodegradable pesticides, fungicides, herbicides, insecticides, use of chemical fertilizers instead of organic manures, etc are causing water pollution. The pollutants from industrial discharge and sewage besides finding their way to surface water reservoirs and rivers are also percolating into ground to pollute ground water sources. The polluted water may have undesirable colour, odour, taste, turbidity, organic matter contents, harmful chemical contents, toxic and heavy metals, pesticides, oily matters, industrial waste products, radioactivity, high Total Dissolved Solids (TDS), acids, alkalis, domestic sewage content, virus, bacteria, protozoa, rotifers, worms, etc. The organic content may be biodegradable or non-biodegradable. Pollution of surface waters (rivers, lakes, ponds) , ground waters, sea water is all harmful for human and animal health [5].

In recent years, water pollution has become a serious problem across the country, mostly due to the presence of untreated effluents, chemicals and pesticides in it. Improperly treated or untreated effluents have been continuing to pollute not only surface water sources but also the ground waters.

1.1.6.1 Causes of water pollution by industries

Most Indian rivers and other sources of fresh water are polluted by industrial wastes or effluents. All these industrial wastes are toxic to life forms that consume this water. Many industrial facilities use freshwater to carry away waste from the plant and into rivers, lakes and oceans. About 11.4 mld (million litres per day) wastewater have been generated by textile, bleaching and dyeing industries out of 501 mld of total wastewater generated [6]. The figure 1.1 shows the water bodies polluted by effluents.



Fig.1.1: Water bodies polluted by effluents

The sources of industrial wastewater are from various entities. In the manufacturing of electronic devices the effluents includes cadmium, chromium, cobalt, cyanide, iron, lead, manganese, mercury, oil & grease, silver and zinc. The pollutants discharged by organic chemical manufactures are benzene chloroform, naphthalene, phenols, toluene and vinyl chloride. Metal pollutant discharges may include chromium, copper, lead, nickel and zinc. The pollutants from fossil fuel power plants includes waste water streams of flue gas desulfurization, fly ash, bottom ash and flue gas mercury control .The contamination of waste streams of iron and steel industries includes gasification products such as benzene, naphthalene, anthracene, cyanide,

ammonia, phenols, cresols together with a range of complex organic compounds known as polycyclic aromatic hydrocarbons (PAH).

1.2. Textile effluents:

Textile industries generate wastewater from a wide variety of processes, including wool cleaning and finishing, yarn manufacturing and fabric finishing (such as bleaching, dyeing, resin treatment, waterproofing and flame proofing). Pollutants generated by textile industries include BOD (Bio-Chemical Oxygen Demand), oil and grease, sulfide, phenols and chromium. Insecticide residues in fleeces are a particular problem in treating waters generated in wool processing. Animal fats may be present in the wastewater, which if not contaminated, can be recovered for the production of tallow or further rendering. The highly polluting production technologies are use of azo dyes in fabrics, tanning of leather, use of cadmium in ornaments and silver-ware, electroplating with cyanide baths, production of dye-intermediates and other refractory and toxic chemicals, etc. [7]. Figure 1.2 shows the discharge of wastewater from textile effluents.



Fig 1.2. Wastewater from textile industries

Textile dyeing plants generate wastewater that contain synthetic and natural dyestuff, gum thickener (guar) and various wetting agents, pH buffers and dye retardants or accelerators [8]. Textile effluent is heavily contaminated with pollutants such as dyes, dissolved solids, suspended solids and toxic metals. The main factor to be consider in textile effluent is total dissolved solids (TDS). Because of the use of common salt and glauber salt, the level of TDS increases in textile waste water. The direct discharge of textile effluents may increase the level of TDS in ground water and surface water. The presence of TDS (high or low concentration) in

water may affect the osmotic balance, causing swelling or dehydration in aquatic organisms and a change in taste. The quality of irrigation of water depends on the salt content. When the salt content increases, it contaminates the water and makes it unsuitable for domestic, industrial and agricultural use [9].

The table-1.1 shows the composition of textile dye effluents with its permissible limits

Parameters	Permissible limits
Ph	6.5-8.5
Biochemical Oxygen Demand(mg/l)	100-300
Chemical Oxygen Demand(mg/l)	150-250
Total Suspended Solids(mg/l)	100-600
Total dissolved Solids(mg/l)	500-2000
Chloride(mg/l)	250-1000
Total nitrogen(mg/l)	70-100

Table-1.1: Composition of textile dye effluents with permissible limit

1.2.1 Toxicity and pollution of textiles:

Water pollution due to dyeing industry is the matter of great concern since large quantity of effluent is discharged into the water bodies. Central pollution control board has listed the dyeing industry as one of the heavily polluting industries. The dye effluent is highly toxic in nature as it contains high suspended solids, COD, dye and chemicals along with high concentration of heavy metals like Cu, Cd, Zn, Ni and Pb. The dye effluents contaminates the surface and ground water thereby, making it unfit for irrigation and drinking. Dye effluents contain certain chemicals that could be toxic, carcinogenic or mutagenic to living organisms. Some other harmful effects of water pollution are teratogenic, retards photosynthetic activity and inhibits the growth of aquatic biota [10].

Waste water from textile dyeing is a huge pollutant around the world. Some dyes don't even degrade in water. Others that do degrade produce harmful substances as they decompose. Additives used during the dyeing process include harmful substances such as alkalis and acid. Wastewater from textile dyeing also affects plant life in the water because many dyes have substances that decrease photosynthesis. It is necessary for us to remove the

colour, COD, BOD, pH, TDS etc. The type of dye used in the process has its impact on the parameters of toxicity of water [11].

1.3 Dye

A dye is a coloured substance that have affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness and intensifies the dye on the fiber. Dyes are colored, because they absorb only some wavelengths of visible light. Dyes are usually soluble in water [12]. Dyes and pigments have an extensive range of applications such as textiles, paper, paints, coatings, plastics, construction, cosmetics, food, glass, automotive, and printing inks [13]. The figure 1.3 shows the chemical structure of a reactive dye.

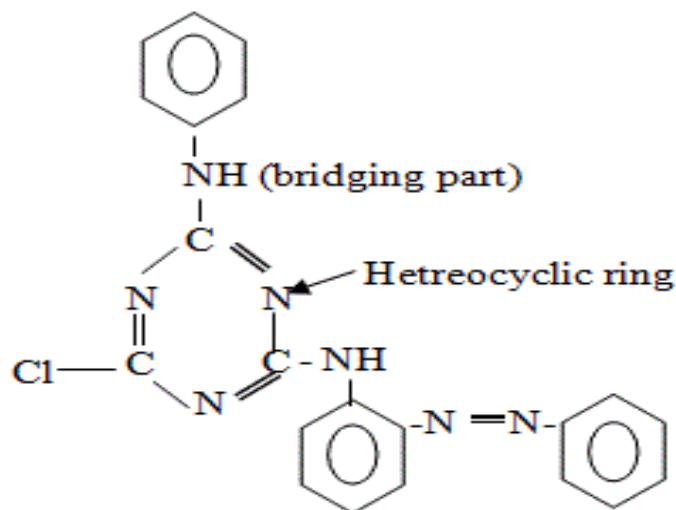


Fig.1.3. Chemical structure of a reactive dye

The colour of a dye is dependent on the ability of the substance to absorb light within the visible region of the electromagnetic spectrum (400-700nm). A coloured dye had two components, a chromophore and an auxochrome [12]. A covalently unsaturated group responsible for absorption in the UV or visible region is known as a chromophore. For example, C=C, C≡C, C=O, C≡N, N=N, NO₂ etc. An auxochrome is a functional group of atoms (hydroxyl, amino, aldehyde) with one or more lone pairs of electrons when attached to a chromophore, alters both the wavelength and intensity of absorption. An auxochrome attached to a chromophore which modifies the ability of the chromophore to absorb light [13].

1.4. Classification of dyes:

Based on the chromophore present in the molecule the dyes are classified as azo dyes ($\text{N}=\text{N}$), quinone dyes ($\text{C}=\text{O}$), indigo dyes, phthalocyanine dyes, sulfur dyes, nitro and nitroso dyes. The classification of dye based on the method of application of dyes to the fiber are

- Reactive dyes
- Disperse dyes
- Acidic dyes
- Basic dyes
- Direct dyes
- Vat dyes
- Mordant dyes

1.4.1. Reactive dyes utilize a chromophore attached to a substituent that is capable of directly reacting with the fiber substrate. The covalent bonds that attach reactive dye to natural fibers make them among the most permanent of dyes. The dye contains molecules with one or more reactive groups forming covalent bond with a compatible fiber group. The reactive group is normally attached to the chromophore via a bridging group such as $-\text{NH}-$, $-\text{CO}-$, and SO_2- . The solubility of dye is due to attaching at least one sulphonic acid group to the molecule. The popularity of dye is due to high wet-fastness, brilliance and range of hues. It is mostly used in coloration of cellulosic fibers.

1.4.2. Disperse dyes contains azo, anthraquinone, nitro groups and they are substantially water-insoluble dyes having substantivity for one or more hydrophobic fibers such as nylon, cellulose, cellulose acetate, and acrylic fibers with usually applied from fine aqueous dispersion. Dyeing is usually followed by a reduction-clear to prevent staining from the unfixed dye. During the dyeing process, the dye molecules in solution are attached to the fibers and then dispersed dye molecules transfers to solution despite to their low solubility.

1.4.3. Acid dyes are water-soluble anionic dyes that are applied to fibers like silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths. It is attached to the fibre to form salt between anionic and cationic groups in the dyes and fiber respectively. The most acid dyes are sulfonic acid salts and they contain azo, anthraquinone, triphenylmethane, nitro and nitroso chromophoric groups. Most synthetic food colors are acid dyes. Their colors are generally bright and fastness to light and washing range from poor to excellent, depending on the chemical structure of the dyestuff. Examples of acid dye are Alizarine Pure Blue B, Acid red 88, etc.

1.4.4. Basic dyes are water-soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper, polyacrylonitrile, modified nylons, and modified polyesters. It is used for silk, wool, and tannin-mordanted cotton for its brightness of shade. Generally, these dyes are not applied along with acid or direct dyes because precipitation may occur. On most fibers, basic dyes have low colorfastness. Examples of basic dyes are crystal violet, safranin, basic fuchsin and methylene blue.

1.4.5. Direct dyes are water-soluble dyes, comprises the largest group of dyes easily applied to cellulose fibers. It do not require the use of a mordant and have a high molecular mass that promotes dye aggregation and substantivity to the fiber. Water solubility is conferred by sulphonation. The high substantivity of direct dyes leads to higher exhaustion values, and good color reproducibility besides it has higher adsorption ratios on the activated sludge of wastewater treatment plants. High substantivity may therefore result in a double environmental benefit.

1.4.6. Vat dyes are essentially insoluble in water and incapable of dyeing fibers directly. These dyes are held to cellulose molecules by van der Waals forces and hydrogen bonding. Once the reduced dye has diffused into the fiber, it is oxidized and becomes water insoluble again. Vat dyes are colorfast to laundering and have good fastness to light. Vat dyes are very resistant to washing and sunlight. They are used on cotton, linen, rayon, and cellulose acetate. Examples of vat dyes are synthetic alizarin and alizarin yellow [13].

1.4.7. Mordant dyes require a mordant, which improves the fastness of the dye against water, light and perspiration. The choice of mordant is very important as different mordants can change the final color significantly. Most natural dyes are mordant dyes. The most important mordant dyes are the synthetic mordant dyes, or chrome dyes [14].

1.5. Treatment of dye in waste water:

Industrial wastewaters may be treated in four stages includes pretreatment, primary treatment, secondary treatment, and tertiary treatment. The initial preparatory phase for later phases is pretreatment comprising equalization and neutralization. In primary treatment pollutants are least handled, the suspended solids are subjected to physical or chemical removal techniques followed by secondary treatment which aims at biological removal. Finally, tertiary treatment is conducted to give up all pollutants out of water to reduce its potential toxicity for ecosystem [15].

The primary treatments of removal of dyes from waste water includes

- Screening
- Sedimentation
- Equalization
- Neutralization
- Mechanical flocculation & Chemical coagulation

The secondary treatments include

- Aerated lagoons
- Trickling filtration
- Activated sludge processes
- Oxidation ditch and pond
- Anaerobic digestion

The tertiary treatment includes

- Oxidation techniques
- Electrolytic precipitation and foam fractionisation
- Membrane technologies
- Electrochemical processes

- Ion exchange method
- Photo catalytic degradation
- Thermal evaporation
- Adsorption [16]

1.6. METHODS FOR TREATMENT OF DYES:

The conventional techniques used for the treatment of waste water includes

- Biological methods
- Chemical methods
- Physical methods

1.6.1 Biological Methods:

Biological treatments rely on bacteria, nematodes, or other small organisms to break down organic wastes using normal cellular processes. Wastewater typically contains a buffet of organic matter, such as garbage, wastes, and partially digested foods. It may also contain pathogenic organisms, heavy metals, and toxins. The biodegradation of dyes is more difficult than other organic pollutants because the dyes are usually stable organic molecules. Other factors affecting the biodegradation are high water solubility and high molecular weight of dyes, which makes permeation through cell membranes difficult. Biological treatment of dyes can be broadly classified into two groups:

- **Aerobic treatment:** The free oxygen molecules dissolved in wastewater are used by microorganisms to degrade organic constituents.
- **Anaerobic treatment:** the anaerobic sludge digestion process is carried out by microbes under anaerobic conditions (i.e., oxygen is not used in the degradation process reactions). This makes it different from aerobic digestion wherein oxygen is used.

Any of these methods are not sufficient to decolorize the dye wastewater alone, thus they could be combined with chemical pretreatment [17].

1.6.2. CHEMICAL METHODS:

1.6.2.1. Oxidation:

Oxidation method is one of the traditional methods that have been applied for decolorization process. It is based on the mechanism involving generation of hydroxyl radicals (as oxidizing agents), that when attack upon chromo-genic groups, leads to produce organic peroxide radicals and ultimately transform them into CO_2 , H_2O and inorganic salts. Ozone on decomposition generates oxygen and free radicals and the later combines with colouring agents of effluent resulting in the destruction of colours.

1.6.2.2. Ozonation:

Ozone is the most powerful oxidant than other oxidizing agents like Cl_2 , H_2O_2 . It is found to be quite capable in oxidizing chlorinated hydrocarbons, phenols and some other hydrocarbons. The reaction mechanism involves reaction occurring at pH value of 5-6, where ozone is present as in form of O_3 and undergoes reaction with double bond of dye molecules selectively. Ozonization has been found successful in removing dyes from textile effluents. It has the advantage application of ozone in its gaseous state and there is no sludge generation which makes it an effective tool of decolourisation but, its high cost and short half-life are the barriers associated with ozonization process [18].

1.6.2.3. Photo catalysis:

In photo catalytic degradation the light and catalysts are concurrently used to support or speed up a chemical reaction “catalysis driven acceleration of a light-induced reaction”. Homogeneous photo catalytic processes mostly are used with metal complexes as catalysts. Heterogeneous photo catalysis can be used for the degradation of various organic pollutants in wastewater. It has the advantage of inherent destructive nature, no waste disposal problem and can be carried out under ambient conditions and using atmospheric oxygen as the oxidant [19].

1.6.3. PHYSICAL METHODS:

1.6.3.1. Coagulation:

Chemical coagulants are capable of dissociating polyelectrolytes when in solution. The polyelectrolytes will neutralize the negatively charged dye molecules to form particle-polymer-particle complexes [20]. These contaminants will be precipitated in the form of chemical sludge when the treated water is further added with flocculants. It is an emerging

trend in wastewater treatment industry using natural coagulants such as *Moringa oleifera*, *Strychnos potatorum* (Nirmali), *Cactus opuntia* etc. Natural coagulants possess a few crucial advantages compared to chemical coagulants, such as environmentally friendly (sustainable and biodegradable), toxic-free and safer for application [21].

1.6.3.2. Filtration

Water flows through a filter designed to remove particles in the water. The filters are made of layers of sand and gravel, and in some cases, crushed anthracite. Filtration collects the suspended impurities in water and enhances the effectiveness of disinfection. The filters are routinely cleaned by backwashing [22].

1.6.3.3. Adsorption:

Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. It is the phenomenon of attracting and retaining the molecules of a substance on the surface of a solid or liquid resulting into higher concentration of the molecules on the surface. Adsorption is a surface phenomenon, while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of it [23]. Figure 1.3 shows the adsorption of atoms on the surface.

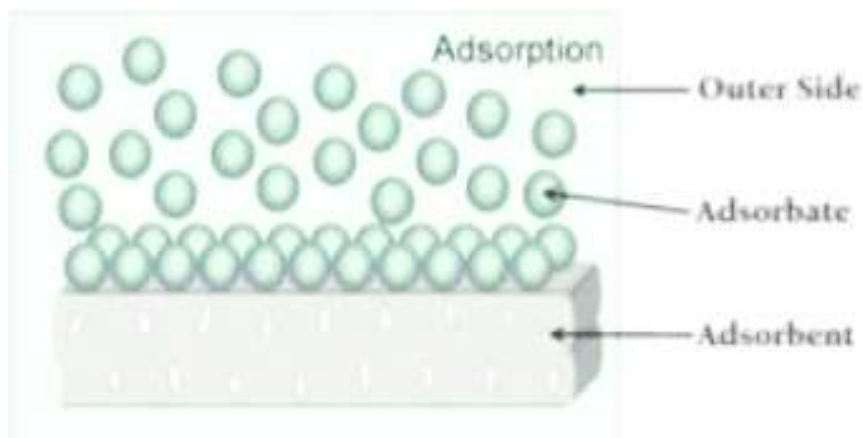


Fig.1.4: Adsorption of atoms on the surface

The principle of adsorption and the ability of certain solid materials to remove dissolved substances from water have long been known. For about 100 years, adsorption technology has been used to broader extent for water treatment. Its practical applications in

industry and environmental protection are of paramount importance. The adsorption of substrates is the first stage in many catalytic processes. The methods for separation of mixtures on a laboratory and on an industrial scale are increasingly based on utilizing the change in concentration of components at the interface. Moreover, such vital problems as purification of water, sewages, air and soil are involved here too. On the other hand, many areas in which technological innovation has covered adsorption phenomena have been expanded more through art and craft than through science. A basic understanding of the scientific principles is far behind; in part because the study of interfaces requires extremely careful experimentation if meaningful and reproducible results are to be obtained. Moreover, during the last 15 years new classes of solid adsorbents have been developed, such as activated carbon fibers and carbon molecular sieves, fullerenes and hetero fullerenes, micro porous glasses and nano porous both carbonaceous and inorganic materials. Nanostructured solids are very popular in science and technology and have gained extreme interest due to their sorption, catalytic, magnetic, optical and thermal properties [24].

1.6.3.3.1 Types of Adsorption:

There are two types of adsorption namely physical adsorption or physisorption and chemical adsorption or chemisorption.

- **Physical Adsorption or physisorption:** It involves adsorption of gases on solid surface via weak Vander Waal's forces. They being weak in nature result in reversible adsorption.
- **Chemical Adsorption or Chemisorption:** When the gas molecules or atoms are held to the solid surface via chemical bonds, this type of adsorption is chemical adsorption or chemisorption [23]. The strength of the bonding is higher in chemisorption so it is difficult to remove chemisorbed species from the solid surface [30].

The table 1.2 shows the differences of physisorption and chemisorption

Physisorption	Chemisorption
Low heat of adsorption (<2 or 3 times the	High heat of adsorption (>2 or 3 times the

latent heat of evaporation)	latent heat of evaporation)
Low activation energy.	High activation energy.
Relatively low temperature, always under the critical temperature of the adsorbate.	High temperatures.
Non-specific interaction	Type of interaction: strong; covalent bond between adsorbate and surface
Adsorption takes place in monolayer or multilayer	Adsorption takes place only in a monolayer
Rapid, non-activated, reversible	Reversible only at high temperature
No dissociation of adsorbed species	Increase in electron density in the adsorbent-adsorbate interface

Table-1.2: Differences of physisorption and chemisorption

1.7. ADSORPTION KINETICS:

Adsorption Isotherm Modelling

Adsorption isotherms are used to describe the adsorption capacity of an adsorbent. The experimental data obtained from the adsorption experiments by conventional batch technique were fitted to isotherm models. There are two widely used adsorption isotherm models that were proposed by Langmuir and Freundlich.

1.7.1. Langmuir Isotherm Model

Langmuir model basically assumes that

- Adsorption takes place at specific sites.
- Adsorption energy of all sites is identical and independent of the surface coverage.
- Once a dye molecule is bound to an active site, no further adsorption can occur at that site.

- Adsorption is restricted to monolayer.

The equation of Langmuir isotherm can be represented as:

$$q_e = \frac{q_m k_a C_e}{1 + k_a C_e}$$

where q_e is the equilibrium amount of dye adsorbed per g of adsorbent (mg/g), q_m is the maximum amount of dye which can be adsorbed per g of adsorbent (mg/g), C_e is the equilibrium concentration of free dye molecules in the solution (mg/L), K_a is a constant related to the energy of adsorption (L/mg) which shows the affinity between dye and adsorbent.

The values of K_a and q_m can be extracted using the linearized form of Langmuir Isotherm

$$\frac{1}{q_e} = \frac{1}{k_a q_m C_e} + \frac{1}{q_m}$$

The linearized form of Langmuir isotherm is represented by a plot of $1/q_e$ vs. $1/C_e$, where q_m and K_a can be determined from the interception and slope, respectively.

1.7.2. Freundlich isotherm model

Freundlich isotherm model is usually used to describe heterogeneous systems and involves the formation of multilayer adsorption. It can be represented as

$$q_e = k C_e^{\frac{1}{n}}$$

where q_e is the amount of dye adsorbed per g of adsorbent (mg/g) in equilibrium, k is related to the adsorption capacity, $1/n$ is heterogeneity factor which ranges from 0 to 1 and C_e is the equilibrium concentration of free dye molecules in the solution (mg/L).

The linearized form of Freundlich isotherm is

$$\log q_e = \log k + \frac{1}{n} \log C_e$$

The intercept of a linear plot of $\ln(q_e)$ vs $\ln(C_e)$ plot is represented by $\ln(k)$ and the slope yields $1/n$ [25].

1.8. ADSORBENTS:

Dyes that are difficult to biological breakdown can be removed by using the adsorbents. A good adsorbent should generally possess a porous structure (resulting in high surface area) and the time taken for adsorption equilibrium to be established should be as small as possible so that it can be used to remove dye wastes in lesser time. Some of the adsorbents, which are generally used for dye wastewater treatment, are

Alumina, a synthetic porous crystalline gel, which is available in the form of granules of different sizes having surface area ranging from 200 to 300 m² g⁻¹

Silica Gel, prepared by the coagulation of colloidal silicic acid results in the formation of porous and noncrystalline granules of different sizes. It shows a higher surface area than alumina ranging from 250 to 900 m² g⁻¹. Though it has high adsorption capacities it is an expensive adsorbent.

Zeolites are micro porous adsorbents found naturally and are prepared synthetically too. They are also considered as selective adsorbents and show ion exchange property as well as molecular adsorption.

Activated carbon is the oldest adsorbent prepared from coal, coconut shells, lignite, wood etc., by physical and chemical activation methods. The product formed by either of the methods has a very porous structure with a large surface area ranging from 500 to 2000 m² g⁻¹. The adsorption on activated carbon is not usually selective as it occurs through van der Waals forces. The activated carbons after their use become exhausted and are no longer capable of further adsorbing the dyes. Once AC has been exhausted, it has to be regenerated for further use in purifying water and a number of methods like thermal, chemical, oxidation, electrochemical are used for this purpose, the most common being thermal and it is cost expensive. So there is a need for an attempt to low cost alternative adsorbents either by naturally or synthetically prepared materials [30].

1.8.1. PVA

Polyvinyl alcohol, also known as *PVOH*, *PVA*, or *PVAL*, is a synthetic polymer that is soluble in water. It is effective in film forming, emulsifying, and has an adhesive quality. It is ductile but strong, flexible, and functions as a high oxygen and aroma barrier [27]. It is a biocompatible, biodegradable, and non-toxic water-soluble polymer prepared by the hydrolysis of polyvinyl acetate. PVA has desirable physical properties, such as high elasticity, high degree

of swelling in aqueous solutions, good emulsification and adhesion behavior, and excellent film-forming properties [26]. The figure 1.5 shows the structure of pva

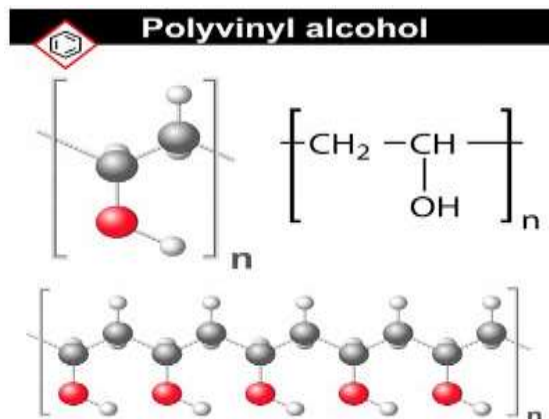


Fig.1.5: Structure of PVA

PVA is a semi-crystalline hydrophilic polymer with good chemical and thermal stability. It is a highly biocompatible and non-toxic polymer and it can be processed easily and has high water permeability. PVA can form physical gels in various types of solvents which lead to the use of PVA in a wide range of applications in medical, cosmetic, food, pharmaceutical and packaging industries. Its flexibility and toughness are good, so that it is used to improve the physical properties through mixing with other materials that have poor physical properties. PVA with functional groups is useful in practical investigations of functional polymers because of its easy preparation as a bulk material, films, and fibers [28, 29].

1.8.2. ALGINATE:

Alginate is an abundant polysaccharide, which can be supplied in plenty from marine algae. It has a molecular formula of $(\text{C}_6\text{H}_8\text{O}_6)_n$. It has density of 1.6 g/cm^3 and molar mass of 10,000 – 600,000. Alginates are refined from brown seaweeds. A wide variety of brown seaweeds of the class Phaeophyceae are harvested throughout the world to be converted into the raw material commonly known as sodium alginate. Sodium alginate has a wide use across a wide variety of industries including food, textile printing, and pharmaceutical [31].

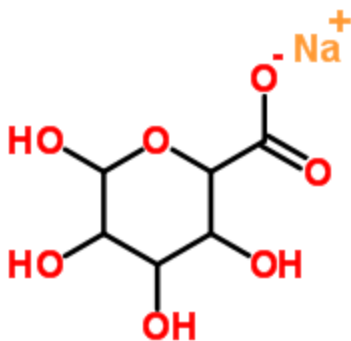


Fig.1.6: Structure of sodium alginate

The alginate is a copolymer composed of -d-mannuronate (M) and -l-glucuronate (G) residues in various M/G ratios; these residues are arranged in a block-wise fashion, constructed not only of homopolymer blocks (MM or GG) but also alternating blocks (MG). This carbohydrate polymer has been re-evaluated recently as an attractive natural resource, possessing a potential to be further developed for medical, pharmaceutical, and bio- and other industrial applications [30].

1.8.3. HYDROXYAPATITE:

Hydroxyapatite, also called hydroxyl apatite (HA), is a naturally occurring mineral form of calcium apatite with the formula $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, but it is usually written $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ to denote that the crystal unit cell comprises two entities. Hydroxyapatite is the hydroxyl end member of the complex apatite group. The OH^- ion can be replaced by fluoride, chloride or carbonate, producing fluorapatite or chlorapatite. It crystallizes in the hexagonal crystal system. Pure hydroxyapatite powder is white in colour [31].

Calcium phosphates are known to be good adsorbents for the last six decades. Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, (HA)], a calcium phosphate phase with Ca / P ratio of 1.67 [32]. A first approach to porous and ceramic adsorbent materials was attempted in 1969 by Davis et al. who described the dye adsorption on the surfaces of untreated and pretreated ceramic raw materials [33]. The adsorption of dye on alumina, bone, ceramic colors, and flint could be related to the specific surface areas. Porous materials such as flint exhibit a hysteresis effect, which was manifestly a difference in the rates of adsorption and of desorption. Adsorption affinity of HA has made it useful for separation and purification process has been studied by Alessia Corami *et al.* Nanocrystalline HA has been identified as a cost effective

sorbent for defluoridation of drinking water. HA has received special attention because of its physicochemical properties of this material, which is similar to bone mineral, as well as its biocompatibility, osteoconduction, and bioresorption properties.

It is widely investigated in biomaterials research for its bioactive characteristics. It is an inorganic bio ceramic material, which shows efficient adsorption towards various pollutants. It is an important inorganic material in biology and chemistry due to their availability structure, ionic exchange property, adsorption affinity, and their characteristic to establish bonds with organic molecules of different sizes.

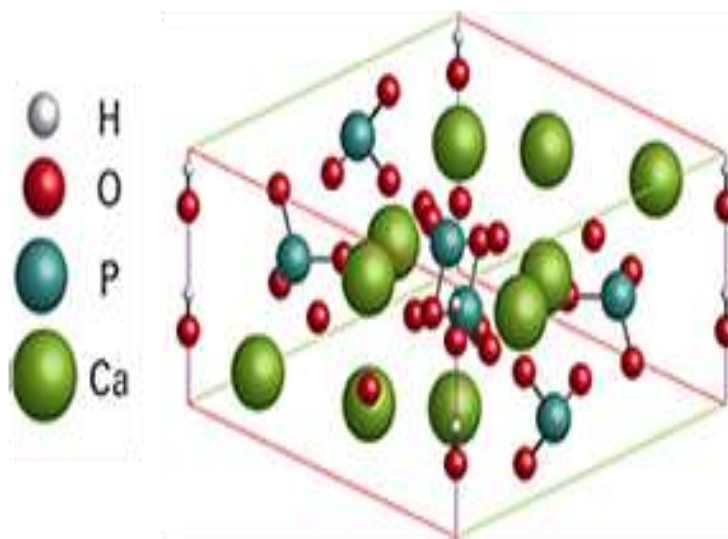


Fig.1.7. Molecular structure of Hydroxyapatite

Fig.1.7 shows the molecular structure of Hydroxyapatite. Nanostructured materials offer much improved performances than their conventional materials due to their large surface to volume ratio and unusual chemical/electronic synergistic effects. It was found that nanocrystalline HA powders have better bioactivity than conventional HA. The nanocrystalline HA can be synthesized by a variety of methods such as precipitation, sol-gel, micro-emulsion, mechanochemical and hydrothermal. Depending upon the method, materials with various morphology, stoichiometry and level of crystallinity can be obtained. Nano sized hydroxyapatite have been considered as an ideal low cost adsorbent due to their least solubility and high sorption capacity for dyes and metal ions [34-36] .

1.9. ELECTROSPINNING:

Electrospinning is a versatile and viable technique for generating ultrathin fibers that allows for the facile production of continuous fibers with diameters ranging from tens of nanometers to several micrometers. Electrospinning received its attention for the fabrication of composite and ceramic nanofibers. The method is for producing long and continuous fibers of synthetic or natural polymers.

1.9.1. Principle

Electrospinning involves an electrohydrodynamic process. In this process a liquid droplet is electrified to generate a jet, followed by stretching and elongation to generate fibers. The figure 1.8 shows the basic setup for electrospinning.

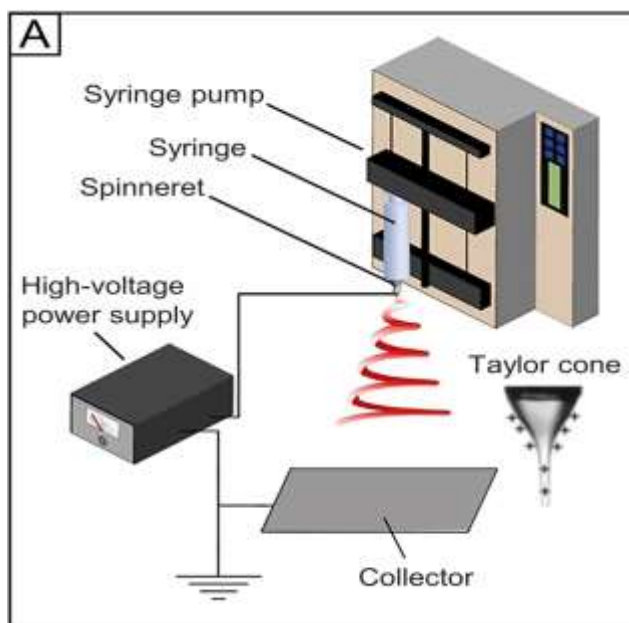


Fig.1.8: Basic setup for electrospinning

The major components of electrospinning include a high-voltage power supply, a syringe pump, a spinneret (usually, a hypodermic needle with blunt tip), and a conductive collector. On applying direct current (DC) or alternating current (AC) the liquid is extruded from the spinneret to produce a pendant droplet as a result of surface tension. On electrification, the electrostatic repulsion among the surface charges that feature the same sign deforms the droplet into a Taylor cone, from which a charged jet is ejected. The jet initially extends in a straight line and then undergoes vigorous whipping motions because of bending instabilities. As the jet is stretched

into finer diameters, it solidifies quickly, leading to the deposition of solid fibers. The figure 1.9 shows the deposition of nanofibres.



Fig.1.9: Deposition of nanofibres

The conventional electrospinning setup comprises a capillary nozzle connected to a high-voltage DC power supply, a grounded collector, and a solution reservoir to supply solution. This type of electrospinning setup works based on the capillary effect: the solution is transported to the tip of a thin nozzle and jet initiation happens at the nozzle tip. In the past two decades, many advancements have been made to control nanofiber collection, and various fiber-generating designs including needleless, near-field, melt electrospinning, yarn electrospinning, and multicomponent electrospinning designs, have been developed.

1.9.2. Mechanism:

The electrospinning process can be divided into four consecutive steps:

- (i) Charging of the liquid droplet and formation of Taylor cone or cone-shaped jet.
- (ii) Extension of the charged jet along a straight line.

- (iii) Thinning of the jet in the presence of an electric field and growth of electrical bending instability (also known as whipping instability).
- (iv) Solidification and collection of the jet as solid fibers on a grounded collector.

Spinning fluid is fed to the capillary tube (usually a syringe needle) from a fluid reservoir. When a high voltage is applied to the needle (typically around 10 kV–20 kV), a high electric field between the needle and collector (grounded or oppositely charged), applies electrostatic force on the fluid droplet. The repulsion between charges on the free surface of fluid droplet works against surface tension and fluid viscosity to deform the droplet into a cone shape (Taylor cone) with increasing applied voltage (higher electric field intensity). When the applied voltage exceeds a critical value, the electrostatic force can overcome fluid surface tension, and jet initiation proceeds from the vertex of the Taylor cone. The internal and external charge forces cause the whipping of the liquid jet in the direction of the collector where the whipping motion of the jet allows the polymer chains within the solution to stretch. The generated fluid jets fly to the grounded collector under the action of electrostatic force. During the flying process, solvent evaporation from the fluid jet results in dry nanofibers depositing on the collector [38].

1.9.3. Effects of electrospinning parameters:

In electrospinning process the fiber morphology, fibrous structure, and fiber production rate are governed by a number of parameters, e.g. applied voltage, flow rate, nozzle diameter, collecting distance, solution properties (e.g. polymer molecular weight, concentration, electrical conductivity, surface tension, solvent properties), and ambient conditions (temperature, humidity) (figure). Although, many of these electrospinning parameters are interdependent and there are interactions between them, we can derive a general trend of influences of some parameters on the electrospinning process [39]. The figure 1.10 shows the important parameters and conditions during electrospinning.

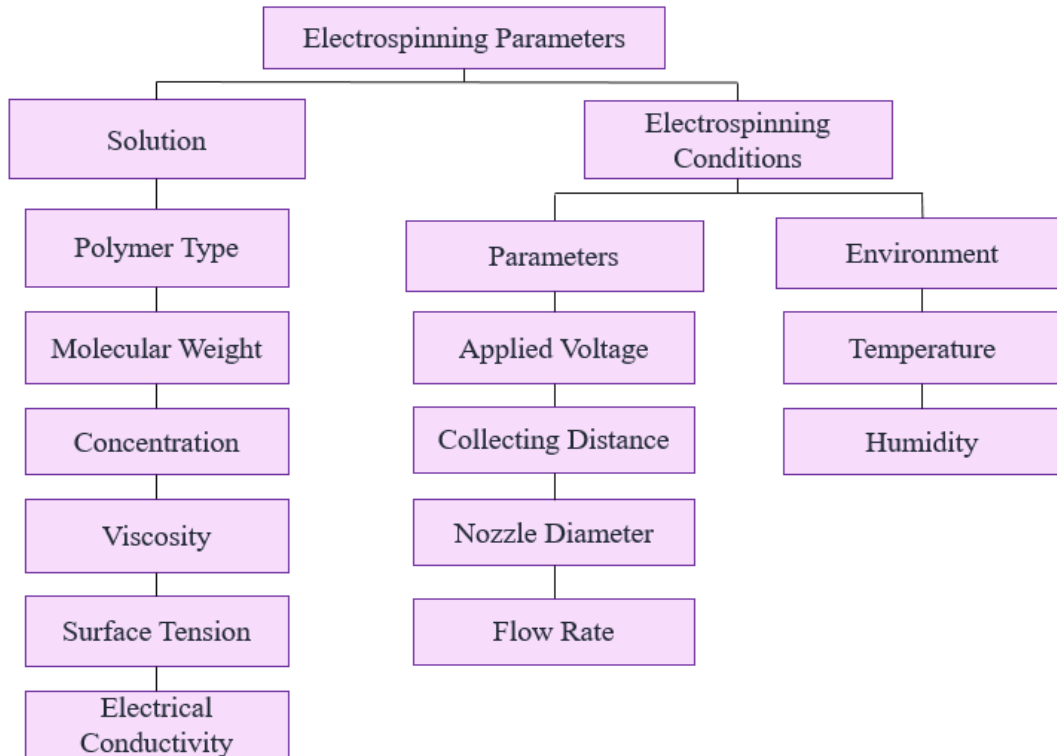


Fig.1.10: Important parameters and conditions during electrospinning

1.9.3.1. Applied voltage:

With increasing applied voltage (5 to 50kv), the electrostatic force increases, leads to jet initiation, and the electrospinning process starts. The fiber diameter decreases with increasing voltage. It can decrease the fiber diameter and increase the fiber production rate because high voltage can increase the jet number on the free solution surface of a spinneret and increases the jet flying speed. The figure 1.11 shows the effect of formation of jet when on applying voltage.

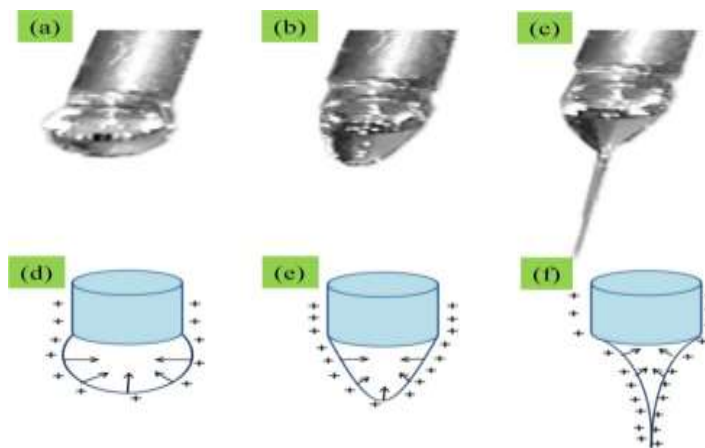


Fig. 1.11: Formation of jet on applying voltage

1.9.3.2. Collecting distance:

An optimum distance for electrospinning should be long enough for fiber stretching and solvent evaporation. The solvent in the solution jet needs to have sufficient time to evaporate and turn the jets into dry nanofibers. When the collecting distance is very short, interconnected nanofibers are often collected.

1.9.3.3. Flow rate:

The flow rate of solution in nozzle electrospinning has a direct effect on fiber production rate. A large flow rate results in a high production rate and a small flow rate results in a low production rate. A large flow rate will produce coarser nanofibers because more solution is drawn out at the same time. When the flow rate of solution exceeds a critical value, the congestion of excess solution at the nozzle tip can affect the jet formation process, leading to the formation of an unstable jet, beaded fibers, and other defects, such as branching, splitting, and flattened fibers.

1.9.3.4. Solution properties:

The molecular weight of the polymer has a substantial effect on electrospinning performances. The increasing molecular weight enables the polymer solution to be electrospun into uniform fibers at relatively low concentrations because a high molecular weight induces a large degree of chain entanglement. It was found that polyvinyl alcohol (PVA) solutions produced fibers with morphologies ranging from beaded fiber, uniform fiber, to coarse non-uniform fibers with increasing concentration. The critical voltage for electrospinning may go up when increasing the solution concentration. The minimum solution concentration to produce smooth nanofibers is dependent on the polymer type, polymer molecular weight, and solvent used [39].

1.9.4. Applications:

Polymer nanofibers exhibit several properties that make them favorable for many applications. Nanofibers have a very large surface area to volume ratio, flexibility in surface functionalities, and mechanical properties superior to larger fibers. Some potential applications for nanofibers include: tissue engineering scaffolds, filtration devices, sensors, materials development, and electronic applications.

Electrospinning offers a simple and versatile method for producing non-woven mats with large surface to volume ratio and high porosity for niche applications related to environment and

sustainability. Nonwoven mats of electrospun nanofibres have been extensively explored as filters for the treatment of water as it has ability to separate and degrade the pollutants simultaneously in waste water. Electrospun nanofibers also offer an alternative approach to the removal of toxic ions (e.g., heavy metal ions and phosphate) and organic pollutants (e.g., dyes, pesticides and plasticizers) from waste water via physisorption, chemisorption, electrostatic attraction, or a combination of these mechanisms.

Electrospinning has been utilized to generate nanofibres from various types of materials. The most commonly used materials are organic polymers in the form of either solution or melt. Small molecules can also be directly electrospun into nanofibres if they self-assemble and generate sufficient chain entanglement. Ceramics alone are usually considered to be non-electrospinnable, although, in principle, a ceramic melt can be electrospun as fibers at an extremely high temperature. When combined with sol-gel chemistry, a variety of composite materials have been directly electrospun into nanofibres [37]. By introducing nanoscale components with different dimensions and morphologies (nanoparticles, nanorods, nanotubes and nanosheets) into polymer solutions, the as-obtained mixtures have also been used for electrospinning. In the present study the ceramic nanocrystalline particles of hydroxyapatite(HA) with a carrier polymeric solution of PVA is used to produce composite nanofibres of HA/PVA and HA/PVA/SA.

OBJECTIVE OF THE WORK

The objectives of the present work is

- To synthesis eggshell derived hydroxyapatite(HA) by wet chemical precipitation method and to study its characterization
- To fabricate the electrospun nanofibres of ceramic-polymer composites of HA by the method of electro spinning.
- To investigate the adsorption of reactive blue dye from aqueous solution using electrospun nanofibres of Hydroxyapatite-Polymer composite.

CHAPTER-II

EXPERIMENTAL PROCEDURE

2.1. MATERIALS

The reagents used for synthesis were calcium oxide [CaO], nitric acid [HNO₃], di-ammonium hydrogen phosphate [(NH₄)₂HPO₄], Ammonia solution [NH₃] and polyvinyl alcohol and sodium alginate. Double distilled water was used as a solvent. The textile dye reactive blue 21 was purchased from the textile company. The properties of the dye are listed in table 2.1.

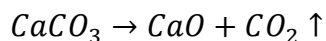
Table 2.1. Properties of reactive blue dye (RB 21)

S.No	Properties	Dye
1	Colour index name	Reactive blue (RB)
2	Molecular formula	C ₄₀ H ₂₆ CuN ₁₀ O ₁₆ S ₆
3	Molecular weight	1159.62 g
4	Chromophore group	Pthalocyanine group
5	CAS Registry number	12236-86-1/73049-92-0

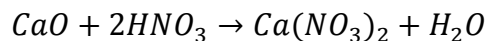
2.2. SYNTHESIS

2.2.1. Synthesis of HA by wet precipitation method

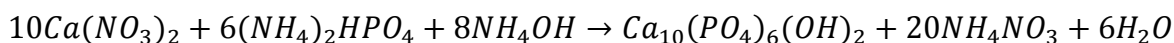
Flowchart describing the synthesis of HA using wet precipitation is given in figure 2.1. Eggshells were cleaned manually in tap water and boiled in double distilled water for 10 minutes. The uncrushed and washed eggshells were taken in a silica crucible and were calcined in a muffle furnace at 900°C for 1 hour. At this temperature eggshells were transformed into calcium oxide by evolving carbon dioxide.



0.1 mol of this CaO was dissolved in 0.2 mol of HNO₃ (70%) by warming to form calcium nitrate solution and the reaction is given below:



0.06 mol of (NH₄)₂HPO₄ was dropped slowly into the above solution with vigorous stirring at room temperature and NH₄OH was used to maintain the pH above 10.



Calcium solution was stirred vigorously at room temperature and (NH₄)₂HPO₄ solution was added in drops into it. The reaction mixture was stirred for 1 hr and the suspension was aged for 24 hrs. The resultant precipitate was separated from the suspension by centrifuging then washed with water. HA slurry is obtained and it is dried at 110⁰ C for 5 hrs to get white powder of HA.

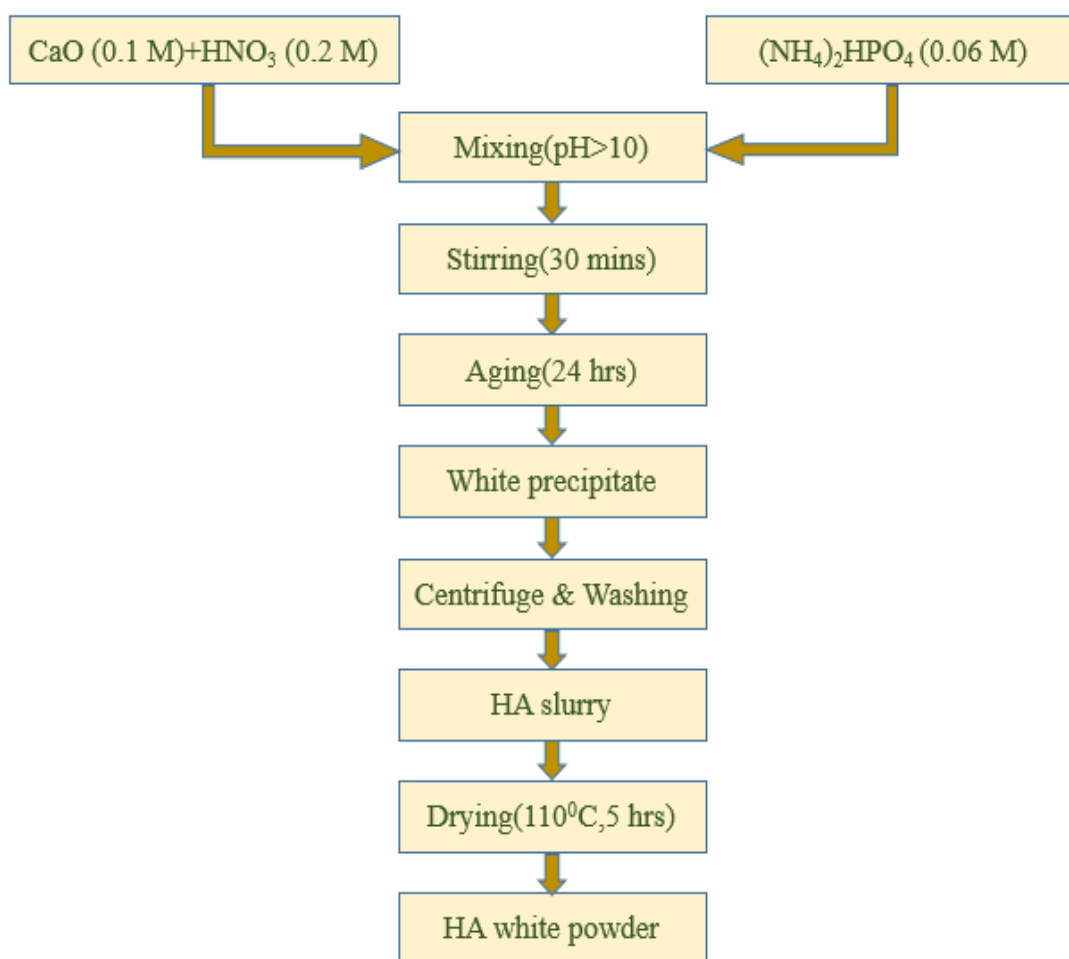


Fig 2.1. Flowchart for the synthesis of HA

2.2.2 Fabrication of PVA/HA composite nanofiber

2.2.2.1. Preparation of PVA/HA blend solution

The PVA solution was prepared by mixing PVA in hot water of 10% (w/v) in double distilled water at 60 °C for 4 h using a magnetic stirrer at 600 rpm. Thus polymeric solution of PVA is obtained. Then 1% (w/v) of HA slurry is added in 30 ml of PVA solution and ultrasonicated for 10 mins and it is stirred for 1h to get homogeneous solution. Thus the blending solution of PVA/HA composite is obtained.

2.2.2.2. Electrospinning of PVA/HA blend nanofibers

During electrospinning, high voltage power was applied to the PVA/HA solution in a syringe via an alligator clip attached to the syringe needle. The applied voltage was adjusted at +16 kV to -2kV. The solution was delivered to the blunt needle tip via a syringe pump to control the solution flow rate. Fibers were collected on electrically grounded aluminum foil placed at a 15 cm vertical distance to the needle tip. Thus PVA/HA electrospun nanofibres were obtained. The flowchart shows the fabrication of PVA/HA fiber membrane. The ambient temperature was 30⁰ C and the electrospinning was carried out at a flow rate of 3ul/m.

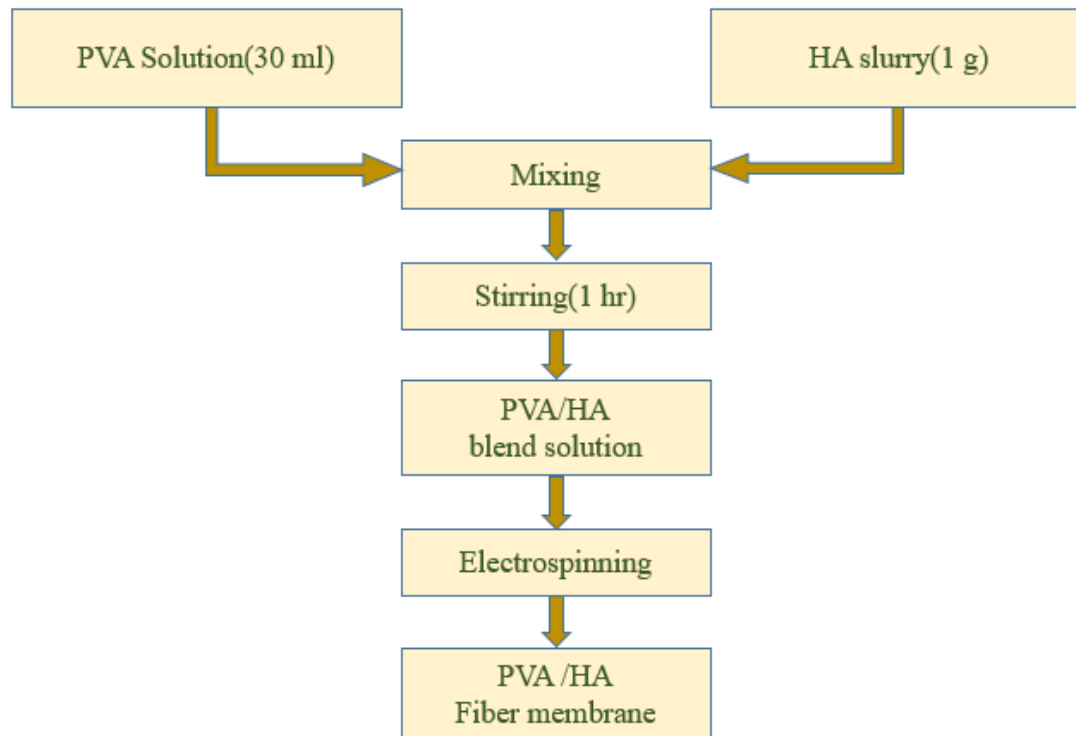


Fig 2.2: Flowchart for fabrication of PVA/HA nanofibres

2.2.3 Fabrication of PVA/AL/HA composite nanofiber

2.2.3.1. Preparation of PVA/AL/HA blend solution

The PVA solution was prepared by mixing PVA in hot water of 10% (w/v) in double distilled water at 60 °C for 4 hrs using a magnetic stirrer at 600 rpm. Thus polymeric solution of PVA is obtained. The alginate solution was prepared by mixing sodium alginate of 2% (w/v) in double distilled water at room temperature for 1 hr. Then 1% (w/v) of HA slurry is added with 20 ml of PVA solution and 10 ml of alginate solution and ultrasonicated for 10 mins and it is stirred for 1h to get homogeneous solution. Thus the blending solution of PVA/AL/HA composite is obtained.

2.2.3.2. Electrospinning of PVA/AL/HA blend nanofibers

During electrospinning, high voltage power was applied to the PVA/AL/HA solution in a syringe via an alligator clip attached to the syringe needle. The applied voltage was adjusted at +16 kV to -2kV. The solution was delivered to the blunt needle tip via a syringe pump to control

the solution flow rate. Fibers were collected on electrically grounded aluminum foil placed at a 15 cm vertical distance to the needle tip. Thus PVA/AL/HA electrospun nanofibres were obtained. The flowchart shows the fabrication of PVA/AL/HA fiber membrane. The ambient temperature was 30⁰ C and the electrospinning was carried out at a flow rate of 3ul/m.

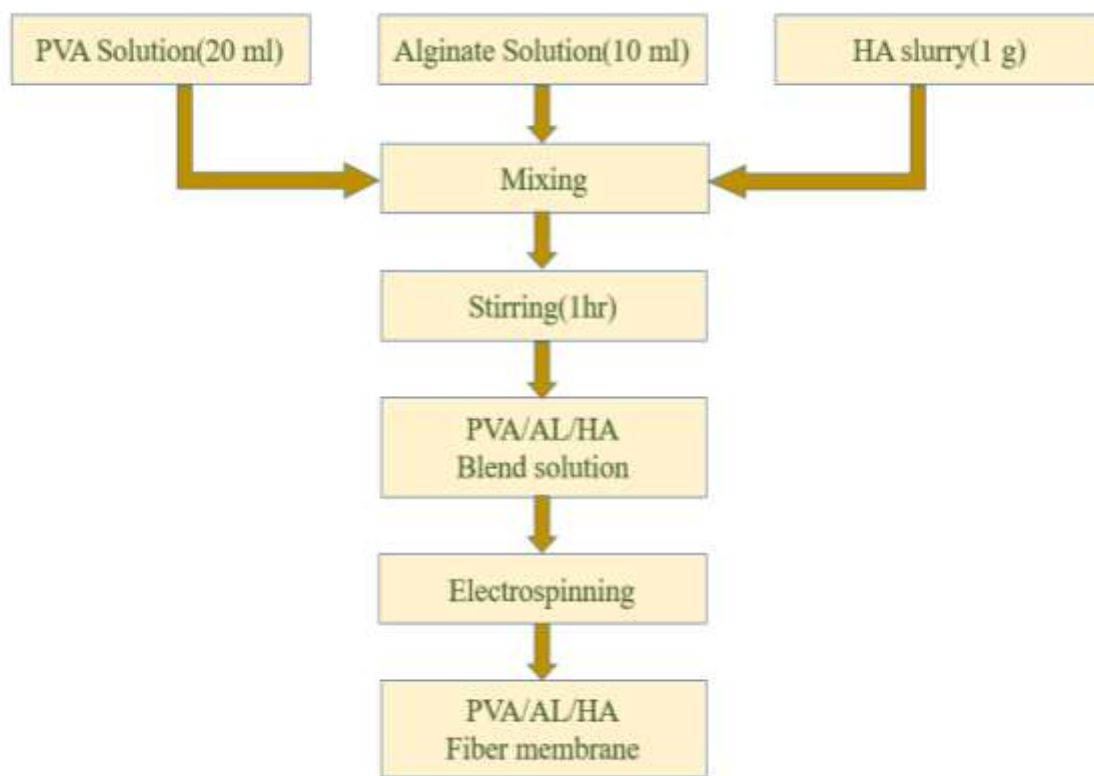


Fig 2.3: Flowchart for the fabrication of PVA/AL/HA nanofibres

2.3 BATCH STUDIES

50mg/L of textile dye (Reactive Blue) was prepared from the stock solution by suitable dilution. Batch adsorption studies were carried out by adsorbent with 30ml of dye solution with predetermined adsorbents dosage of 0.03 g and at pH 7 in room temperature. Experiments were conducted for various time intervals to trace the adsorption equilibrium. The dye concentration was estimated by monitoring the absorbance before and after the addition of adsorbent at λ_{max}

wavelength using UV spectrophotometer. The amount of dye adsorbed on the adsorbent q_e (mg/g) was calculated using the mass balance equation:

$$q_e = \frac{(c_0 - c_e)V}{W}$$

where,

C_0 is the initial concentration (mg/L)

C_e is the equilibrium concentration (mg/L)

V is the volume of solution (L)

W is the weight of the adsorbent (g).

The dye removal efficiency of the adsorbent was calculated by the equation:

$$\% \text{ of dye removal} = \frac{(c_0 - c_e)}{c_0} \times 100$$

The table 2.2 shows the experimental parameters for batch technique

Table 2.2. Batch techniques – Experimental parameters

Adsorption experiment	Batch technique
Adsorbents	HA, PVA/HA, PVA/AL/HA
Adsorbate	Reactive blue dye (RB)
Adsorbent dosage (mg)	30
Adsorbate dosage (mg/L)	50
Adsorbate volume (ml)	10
Ph	7
Temperature (°C)	33 °C

2.4 CHARACTERISATION TECHNIQUES

- Powder X-ray diffraction (P-XRD)
- Fourier Transform Infrared Spectroscopy (FT-IR)
- Ultraviolet - Visible spectroscopy (UV-Vis)
- Scanning Electron Microscopy (SEM)

2.4.1. Powder X-Ray diffraction

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions [40]. It is one of the most important characterization tools used in solid state chemistry and material science. It can determine the size and shape of the unit cell for any compound using X-ray diffraction. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the distribution of atoms within the lattice. Consequently, the X-ray diffraction pattern is the fingerprint of periodic atomic arrangements in a given material [41].

2.4.1.1. Principle:

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample (Figure 1). The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's law:

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

where n is an integer, λ is the wavelength of the X-rays, d is the interplanar spacing generating the diffraction, and θ is the diffraction angle. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed, and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d -spacings allows identification of the compound because each compound has a set of unique d -spacings. Typically, this is achieved by comparison of d -spacings with standard reference patterns [41].

The figure shows the geometrical illustrations of crystal planes and Bragg's law.

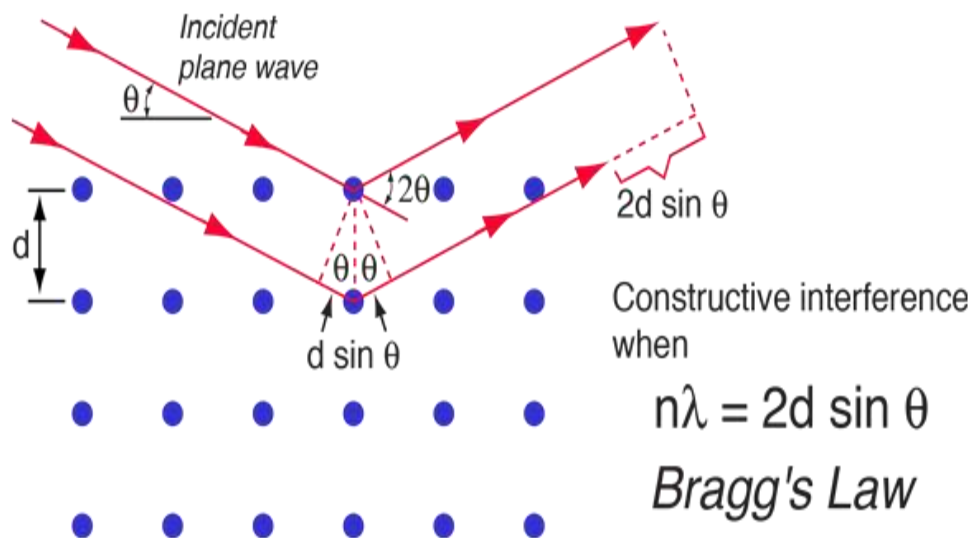


Fig.2.4. Geometrical illustrations of crystal planes and Bragg's law

2.4.1.2. Instrumentation of Powder X-Ray diffraction- Working:

X-ray diffractometers consist of three basic elements,

- X-ray tube,
- sample holder,
- X-ray detector.

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K_α and K_β . K_α consists, in part, of $K_{\alpha 1}$ and $K_{\alpha 2}$. $K_{\alpha 1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha 2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr).

Monochromatic X-rays needed for diffraction. $K_{\alpha 1}$ and $K_{\alpha 2}$ are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuK_α radiation = 1.5418\AA . These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample

satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor [41].

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ . The instrument used to maintain the angle and rotate the sample is termed a goniometer. For typical powder patterns, data is collected at 2θ from $\sim 5^\circ$ to 70° , angles that are preset in the X-ray scan. The figure shows the Bruker's X-Ray diffraction D8-Discover instrument.



Fig.2.5. Bruker's X-Ray diffraction D8-Discover instrument

2.4.1.3. Applications

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to

studies in geology, environmental science, material science, engineering and biology. Other applications include

- 1) Identification of fine grained minerals such as clays and mixed layer clays that are difficult to determine optically.
- 2) Characterization of crystalline materials and determine crystal structures.
- 3) Determination of unit cell dimensions and measurement of sample purity.
- 4) Determine of modal amounts of minerals (quantitative analysis)
- 5) Determining the thickness, roughness and density of the film using glancing incidence X-ray reflectivity measurements
- 6) To make the textural measurements, such as the orientation of grains, in a polycrystalline sample.

2.4.1.4 Advantages

- 1) Powerful and rapid (< 20 min) technique for identification of an unknown mineral
- 2) It provides an unambiguous mineral determination
- 3) Minimal sample preparation is required
- 4) Widely available in XRD units
- 5) Data interpretation is relatively straight forward.

2.4.1.5 Limitations

- 1) Homogeneous and single phase material is best for identification of an unknown
- 2) To access standard reference file of inorganic compounds.
- 3) Requires tenths of a gram of material which must be ground into a powder.
- 4) For mixed materials, detection limit is ~ 2% of sample [40].

2.4.2 FOURIER TRANSFORMATION INFRARED SPECTROSCOPY (FT-IR)

Infrared absorption spectroscopy is the study of interaction of infrared radiation with matter as a function of photon frequency. Fourier transform infrared spectroscopy is a technique

used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FT-IR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time.

2.4.2.1 Principle

Fourier Transform Infrared Spectroscopy (FT-IR) provides specific information about the vibration and rotation of the chemical bonding and molecular structures, making it useful for analyzing organic materials and certain inorganic materials. An infrared 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 exact same infrared spectrum. Therefore, infrared 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.

2.4.2.2 Instrumentation

There are three basic spectrometer components in an FT source, an interferometer, and Interferometer divides radiant beams, generates an optical path difference between the beams, interference signals measured as a function of optical path difference by a detector. The interferometer produces interference signals, which contain infrared spectral information generated after passing through a sample, commonly used interferometer is a Michelson interferometer. It consists of three components: a moving mirror, a fixed mirror, and a beam splitter. The two mirrors are perpendicular to each other. The beam splitter is a semi-reflecting device and is often made by depositing a thin film of germanium onto a flat KBr substrate. Radiation from the broadband IR source is collimated and directed into the interferometer, and impinges on the beam splitter.

2.4.2.3 Sample preparation

IR spectra can be measured using liquid, solid, or gaseous samples that are placed in the beam of infrared light. A drop of a liquid can be placed as a thin film between two salt plates made of NaCl or KBr, which are transparent to infrared light at most important frequencies. A solid can be ground with KBr and pressed into a disk that is placed in the light beam.

Alternatively, a solid sample can be ground into a pasty mull with paraffin oil. As with a liquid, the mull is placed between two salt plates. Solids can also be dissolved in common solvents such as CH_2Cl_2 , CCl_4 , or CS_2 that do not have absorptions in the areas of interest. Gases are placed in a longer cell with polished salt windows. These gas cells often contain mirrors that reflect the beam through the cell several times for stronger absorption. Fig.2.6 shows the Michelson interferometer [42].

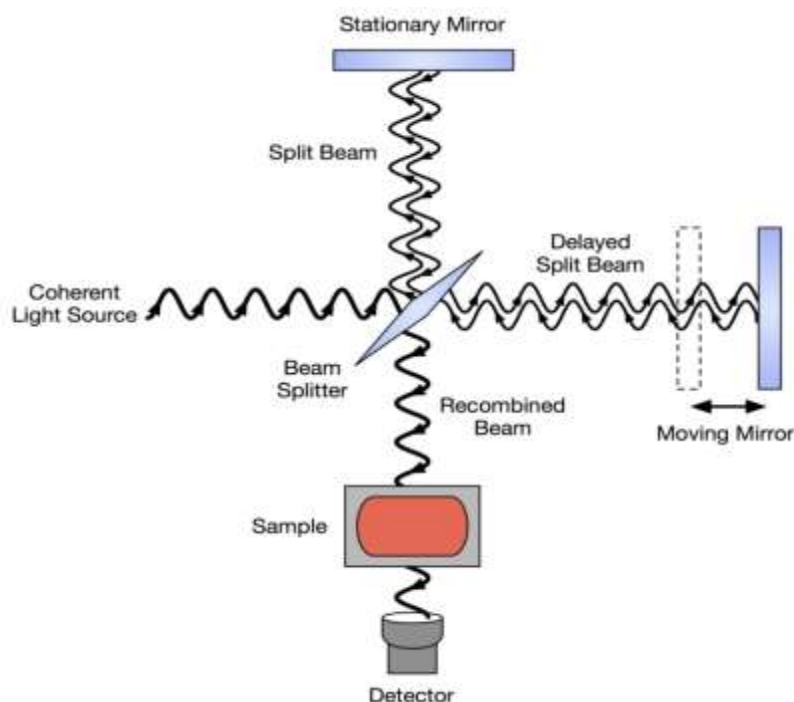


Fig.2.6. Michelson interferometer

2.4.2.4 Working of an FT-IR spectrometer

The normal instrumental process is as follows

➤ Source

Infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample (and, ultimately, to the detector).

➤ Interferometer

The beam enters the interferometer where the 'spectral encoding' takes place. The resulting interferogram signal then exits the interferometer.

➤ Sample

The beam enters the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed.

➤ **Detector**

The beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

➤ **Computer**

The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation [43].

2.4.2.5 Advantages

The FT-IR spectrometer has several major advantages over the dispersive instrument.

- Its sensitivity is better because it measures all frequencies simultaneously rather than scanning through the individual frequencies.
- Less energy is needed from the source and less time (typically 1 to 2 seconds) is needed for a scan.
- Several scans can be completed in a few seconds and averaged to improve the signal. Resolution and accuracy are also improved because a laser beam is used alongside the IR beam to control the speed of the moving mirror and to time the collection of data points.

2.4.2.6 Limitations

Few limitations of FTIR spectrometer are listed below:

- Minimal elemental information is given for most samples.
- Background solvent or solid matrix must be relatively transparent in the spectral region of interest.
- Molecule must be active in the IR region; i.e. when exposed to IR radiation, a minimum of one vibrational motion must alter the net dipole moment of the molecule in order for absorption to be observed [42].

2.3.3 SCANNING ELECTRON MICROSCOPY (SEM)

SEM is basically a type of electron microscope. It is used for various purposes.

- ✓ Topographic studies
- ✓ Microstructure analysis
- ✓ Elemental analysis if equipped with appropriate detector
- ✓ Chemical composition
- ✓ Elemental mapping.

2.3.3.1 Fundamental principles of SEM

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence (CL)), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination).

X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly. The figure2.7 shows the SEM instrument.

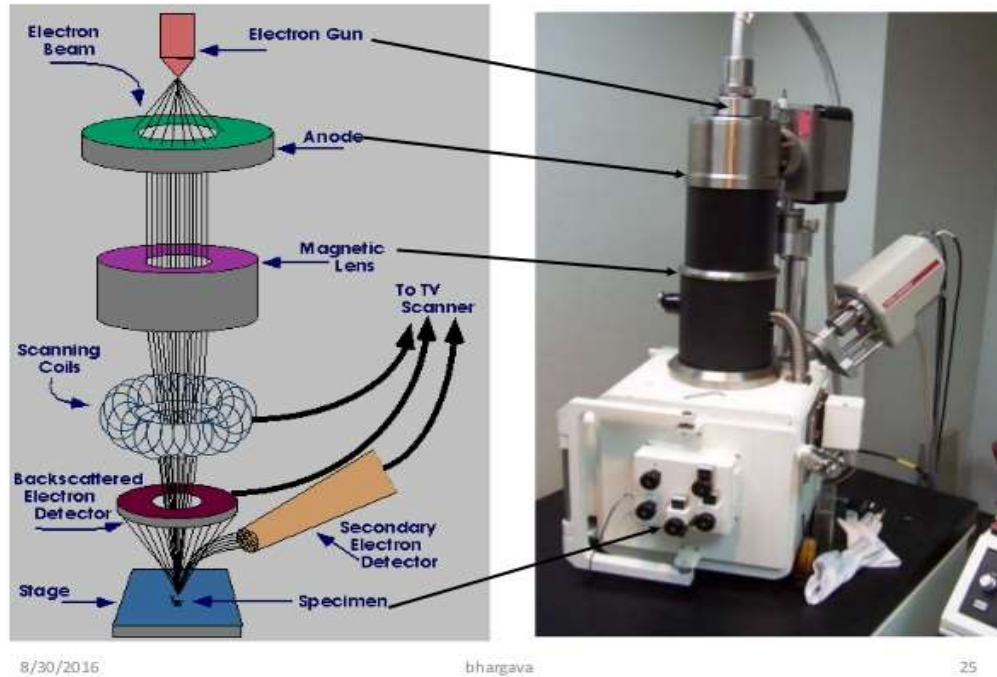


Fig.2.7. SEM instrument

2.3.3.2 SEM Instrument

A scanning electron microscope is a complicated instrument. It takes a high amount of precision to manipulate a beam of electrons to create these incredibly detailed magnified images.

Electron Gun

The first part of the SEM is the electron gun, an electron gun fires electrons at the sample when magnifying. The electrons can be created a few different ways, but the most common method heats up a tungsten wire to produce the electrons.

Condenser Lens

This is used to narrow the electron beam given off by the electron gun. This lens isn't made of glass like you might expect. Instead it is a lens made of coils of wire that create an electromagnetic field which compresses the electrons as they travel through it.

Aperture

To control the diameter of the electron beam being passed through them. The aperture consists of a metal rod with different size holes cut into it. The diameter of the electron beam is controlled by changing which hole it travels through. The aperture also blocks off any extra electrons that didn't get fully condensed into the beam from hitting the sample.

Objective Lens and Sample Chamber

After the apertures is another electromagnetic lens called the objective lens. This is the final lens that focuses the electron beam down onto the sample. Once passing through the objective lens, the electron beam passes into the sample chamber. This chamber holds the sample under a vacuum to eliminate interference of unwanted particles. The target itself needs to be conductive to prevent charging, and allow for better image quality. If the target isn't made of a naturally conductive material it can be coated in one, such as gold.

Detector

It is used to create magnified images, and collect other data. They detect various signals given off by the sample as it is struck by electrons from the beam scanning over it. These signals include secondary electrons, backscattered electrons, and x-rays among others.

2.3.3.3 Applications of SEM

- SEM is a widely used to identify phases based on qualitative chemical analysis and/or crystalline structure.
- Backscattered electron images (BSE) can be used for rapid discrimination of phases in multiphase samples.

2.3.3.4 Advantages

- It includes its wide array of applications, the detailed three dimensional and topographical imaging and the versatile information garnered from different detectors.
- It is also easy to operate with the proper training and advance in computer technology and associated software make operation user friendly.
- Samples must be prepared before placed in the vacuum chamber, most SEM samples require minimal preparation actions.

2.3.3.5 Limitations

- SEMs are expensive, large and must be housed in an area free of any possible electric, magnetic or vibration interference.
- Maintenance involves keeping a steady voltage, current to electromagnetic coils and circulation of cool water.
- Special training is required to operate an SEM as well as prepare samples.[44]

2.3.4 ULTRAVIOLET VISIBLE ANALYSIS

Ultraviolet and visible (UV-Vis) absorption spectroscopy is refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet – visible spectral region. It is the measurement of the attenuation (weakening of strength) of a beam of light after it passes through a sample or after reflection from a sample surface.

2.3.4.1 Principle of Ultraviolet – Visible absorption

The energy of the radiation in the visible range is generally 36 to 72 kcal/mole while that in the ultraviolet range goes as high 143 kcal/mole. This energy irradiated on the molecules can result in changes in the electronic nature of the molecule i.e. changes between ground state and excited states of electrons within the system. As a result, UV-Visible spectroscopy is also known as electronic spectroscopy.

The electrons when imparted with energy in the form of light radiation get excited from the highest molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) and the resulting species as the excited state or anti bonding state.

2.3.4.2 Types of instrument

The types of spectroscopic instrument are

- ✓ Single beam instrument
- ✓ Double beam instrument
- ✓ Multichannel instrument

2.3.4.2.1 Single beam instrument

In a single beam instrument, the light passes through the sample cell. I_0 must be measured by removing the sample. This was the earliest design and is still in common use in both teaching and industrial labs.

2.3.4.2.2 Double beam instrument

The light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. The reference beam intensity is taken as 100% transmission and the measurement displayed is the ratio of the two beams intensity. Some double beam instruments have two detectors, and the sample and reference beam are measured at the same time.

2.3.4.2.3 Multichannel instrument

In the multichannel instrument radiation from the lamp is focused upon the sample or solvent container and then passes into a monochromator with fixed grating. The resulting charging currents, which are proportional to the radiant power, are amplified, digitalized, and stored in computer memory. The entire cycle is completed in a few milliseconds.

2.3.4.3 Instrumentation of UV or Visible Spectroscopy

Instruments for measuring the absorption of U.V. or visible radiation are made up of the following components:

- Sources (UV and visible)
- Filter or monochromator
- Sample containers or sample cells
- Detector

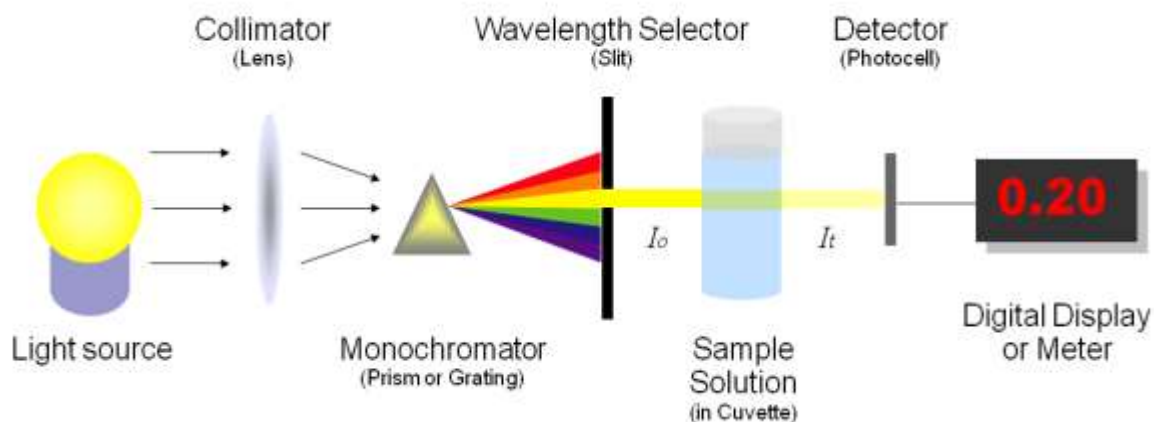


Fig.2.8. UV Visible spectrophotometer

2.3.4.3.1 Radiation source

The electrical excitation of deuterium or hydrogen at low pressure produces a continuous UV spectrum. Both Deuterium and Hydrogen lamps emit radiation in the range 160-375 nm. Quartz windows must be used in these lamps and quartz cuvettes must be used, because glass absorbs radiation of wavelengths less than 350 nm. Various UV radiation sources are as follows:

- Deuterium lamp
- Hydrogen lamp
- Tungsten lamp
- Xenon lamp
- Mercury lamp

2.3.4.3.2 Filters or Monochromators

All the monochromators contain the following components parts

- An entrance slit
- A collimating lens
- A dispersing device (a prism or a grating)
- A focusing lens
- An exit slit

Polychromatic radiation (radiation of more than one wavelength) enters the monochromator through the entrance slit. The beam is collimated, and then strikes the dispersing element at an angle. The beam is split into its component wavelengths by the grating or prism. By moving the dispersing element or the exit slit, radiation of only a particular wavelength leaves the monochromator through the exit slit.

2.3.4.3.3 Sample containers or sample cells

A variety of sample cells available for UV region. The sample cell is based on

- The path length, shape, size
- The transmission characteristics at the desired wavelength

- The relative expense

The cell holding the sample should be transparent to the wavelength region to be recorded. Quartz or fused silica cuvettes are required for spectroscopy in the UV region. Silicate glasses can be used for the manufacture of cuvettes for use between 350 and 2000nm. The thickness of the cell is generally 1 cm. Cells may be rectangular in shape or cylindrical with flat ends.

2.3.4.3.4 Detectors

In order to detect radiation, three types of photosensitive devices are

- Photovoltaic cells or barrier layer cell
- Phototubes or photo emissive tubes
- Photomultiplier tubes

Photovoltaic cell is known as barrier layer or photonic cell. It consists of a metallic base plate like iron or aluminum which acts as one electrode. On its surface, a thin layer of a semiconductor metal like selenium is deposited. Then the surface of selenium is covered by a very thin layer of silver or gold which acts as a second collector tube.

When the radiation is incident upon the surface of selenium electrons are generated at the selenium- silver surface and the electrons are collected by the silver. This accumulation at the silver surface creates an electric voltage difference between the silver surface and the basis of the cell.

Phototubes are also known as photo emissive cells. A phototube consists of an evacuated glass bulb. There is light sensitive cathode inside it. The inner surface of cathode is coated with light sensitive layer such as potassium oxide and silver oxide.

When radiation is incident upon a cathode, photoelectrons are emitted. These are collected by an anode. Then these are returned via external circuit. And by this process current is amplified and recorded.

Photomultiplier tube is a commonly used detector in UV spectroscopy. It consists of a photo emissive cathode (a cathode which emits electrons when struck by photons of

radiation), several dynodes (which emit several electrons for each electron striking them) and an anode. A photon of radiation entering the tube strikes the cathode, causing the emission of several electrons. These electrons are accelerated towards the first dynode (which is 90V more positive than the cathode). The electrons strike the first dynode, causing the emission of several electrons for each incident electron. These electrons are then accelerated toward the second dynode to produce more electrons which are accelerated towards dynode three and so on. Eventually, the electrons are collected at the anode. By this time, each original photon has produced 10^6 - 10^7 electrons. The resulting current is amplified and measured.

Photomultipliers are very sensitive to UV and visible radiation. They have fast response times. Intense light damages photomultipliers. They are limited to measuring low power radiation.

2.3.4.4 Advantages

- Simple and inexpensive instrumentation (portable)
- Most organic molecule absorb UV-Vis light.
- Quantitative (Beer's law)

2.3.4.5 Disadvantages

- Mixtures of molecules can be a problem due to overlap (hence, routinely requires significant sample preparation)
- Spectra are not highly specific for particular molecules.[45]

CHAPTER III

RESULTS AND DISCUSSION

3.1. XRD ANALYSIS

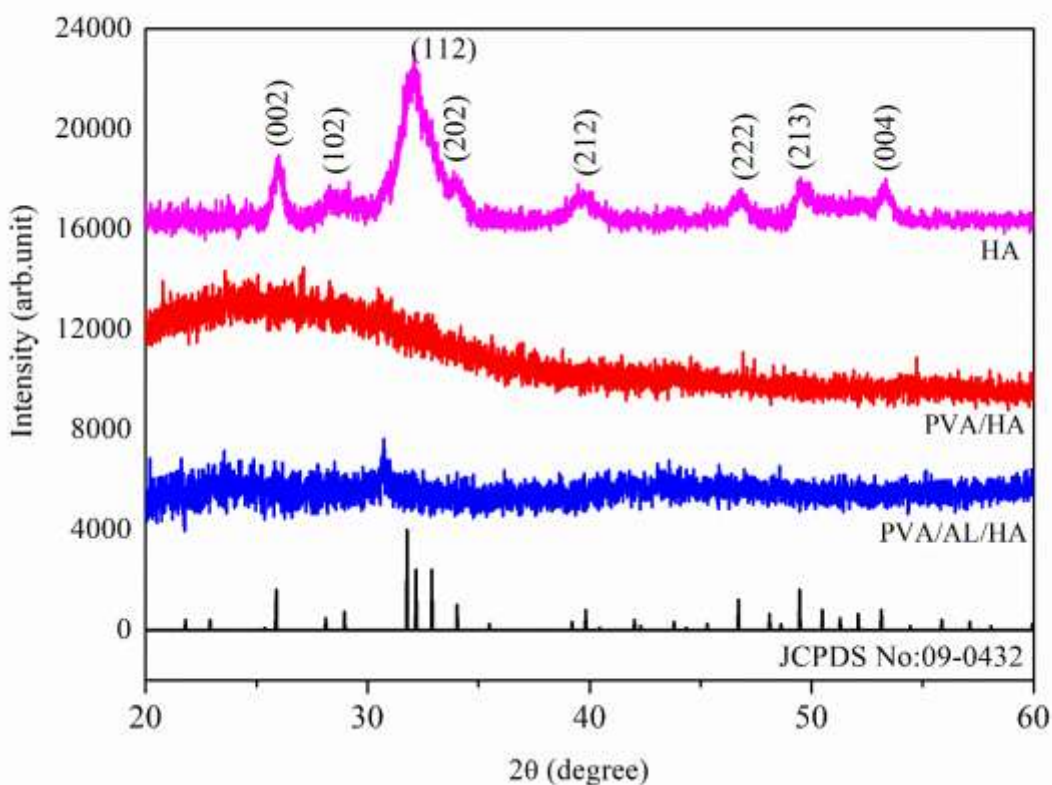


Fig.3.1: XRD pattern for a) HA, b) PVA/HA, c) PVA/AL/HA

X-ray diffraction (XRD) pattern of as prepared nano HA powder and electrospun nanofiber mats was determined by a X-ray Diffractometer with scanning range 20°–60° to assess different crystalline phases and structures. XRD pattern of as synthesized adsorbents was given in fig 3.1.

The observed pattern for pristine HA matches with the JCPDS file no.09-0432 which indicates the formation of hexagonal phase. The hydroxyapatite characteristic peaks were

observed at 21.89° , 25.99° , 28.3° , 32.1° , 33.9° , 39.5° , 39.8° , 43.9° , 46.8° , 49.49° , 53.33° , 55.89° and 57.23° corresponds to the plane (200), (002), (102), (112), (202), (212), (310), (113), (222), (213), (004), (322) and (313) respectively. By using Debye-Scherrer formula the average crystallite size was calculated as 13.8147 nm. The lattice parameters values are calculated as $a=9.4049 \text{ \AA}$ and $c=6.8538 \text{ \AA}$ respectively. The crystallite size was calculated considering the (002) plane. The crystalline parameters can be calculated by using the formulae

- The interplanar spacing (d spacing) of the crystal lattice is calculated by using Bragg's law

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

Where,

λ is the wavelength of the X-ray (1.5406 \AA)

d is the interplanar spacing between the lattices

θ is the diffraction angle (degree)

- The lattice parameter for the hexagonal phase is calculated by using the formula

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + k^2 + l^2}{a^2} \right) + \frac{l^2}{c^2}$$

Where,

d is the interplanar spacing

h, k, l are the miller indices

a, c are the lattice constants

- The unit cell volume (V) for the hexagonal crystal system was determined by

$$V = \frac{\sqrt{3}}{2} \times a^2 \times c$$

- The degree of crystallinity of the samples was calculated using the relation,

$$X_c = \left(\frac{0.24}{\beta_{hkl}} \right)^3$$

Where, β is the full width at half maximum (FWHM) for the diffraction peak under consideration (in degree).

- The average crystallite size of the sample was calculated by using the Debye-Scherrer formula

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where, D = Crystallite size (nm)

λ is the Wavelength of X-ray

θ is the diffraction angle (degree)

K is the broadening constant (0.9)

β is the full width at half maximum (FWHM) for the diffraction peak under consideration (in radian).

The table-3.1 shows the crystalline parameters of HA calculated by using the above relations

Table -3.1. Crystalline parameters of HA

Sample	Lattice parameters(Å)		Crystallite size D_{hkl} (nm)	Degree of crystallinity (X_c)	Unit cell volume $V(\text{\AA}^3)$
	a=b	C			
JCPDS	9.418	6.884			
HA	9.4049	6.8538	13.8147	0.8328	525

The XRD pattern of PVA/HA composite nanofiber indicates the semi crystalline nature of the polymer matrix. Being PVA as semi-crystalline in nature it can be observed that it does not possess any such reasonable peaks which indicates its semi-crystalline nature. Since the crystallinity of PVA can be altered by additives thus increases the broadening of peak with a bump at the 2θ region of 20 to 30 degree. The XRD pattern of PVA/AL/HA nanofiber composite indicates the amorphous nature of polymer matrix with crystalline phase of HA.

3.2 FTIR ANALYSIS

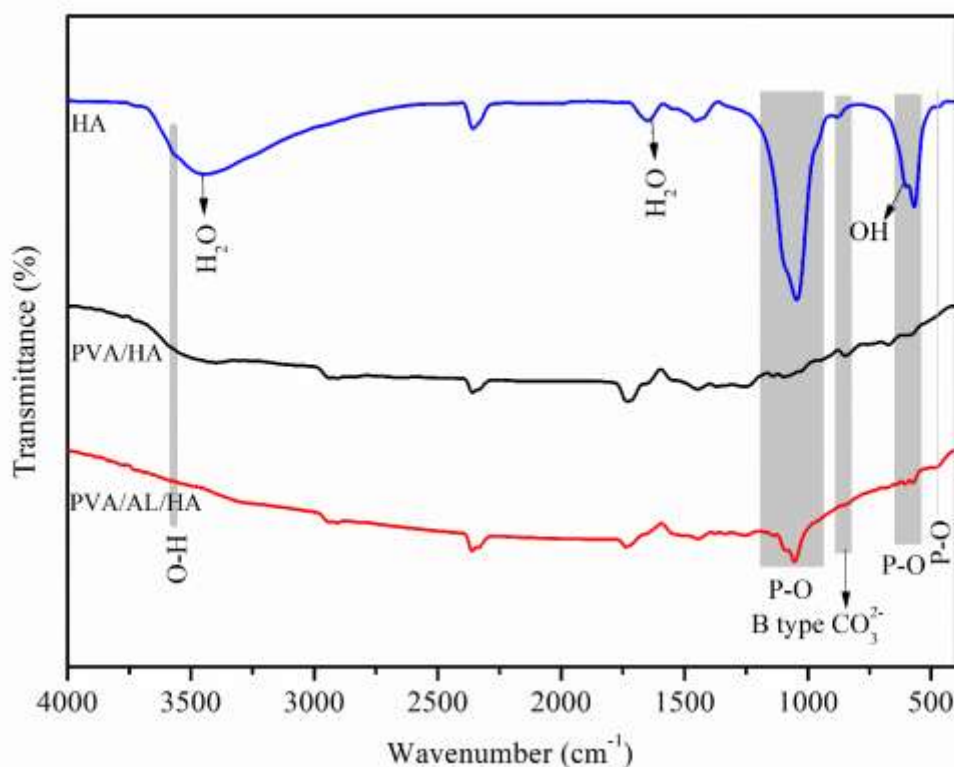


Fig.3.2: FTIR spectra for a) HA, b) PVA/HA, c) PVA/AL/HA

FT-IR was performed to determine the various functional groups and to investigate the possible interaction between polymer and ceramics phase of the composite. The FTIR spectra of synthesized samples were shown in the figure 3.2. The FTIR spectra of HA shows the characteristics PO_4^{3-} vibrations of HA appeared at 459, 568, 1037 cm^{-1} . The peaks at 3552 and 601 cm^{-1} is characteristic OH^- vibration of HA. The peak present at 873 cm^{-1} in the HA spectrum is attributed to the CO_3^{2-} ions, which is due to the adsorbed carbonate from the atmosphere. The strong band at 1456 cm^{-1} and broad band between 3000 and 3600 cm^{-1} observed may be attributed to the adsorbed water for HA. The characteristic peaks of

composite fiber also observed and the other phosphate peaks were observed at 565, 1056 cm^{-1} . The peaks observed at 2326 cm^{-1} may be due to calcium/sodium. The absorption peak of PVA is present at 2362 cm^{-1} . The PVA/AL composite peak is observed at 1080 cm^{-1} .

3.3 SEM ANALYSIS:

The surface morphology of as synthesized HA is shown in the figure 3.3. It shows the formation of agglomerated nanostructured HA with grain size of around 5-50 μm . SEM morphology of fabricated nanofibres of PVA/HA and PVA/AL/HA composites by electrospinning method at different magnifications are shown in the figure 3.4 and 3.5 respectively. Electrospinning generated nanofibres with relatively uniform diameter. A beads-free continuous and nonwoven structure with interconnected porous morphology is obtained. The incorporated HA nanoparticles in the nanofiber matrix is shown in the images. The HA nanoparticles undergone agglomeration indicated by white clumps.

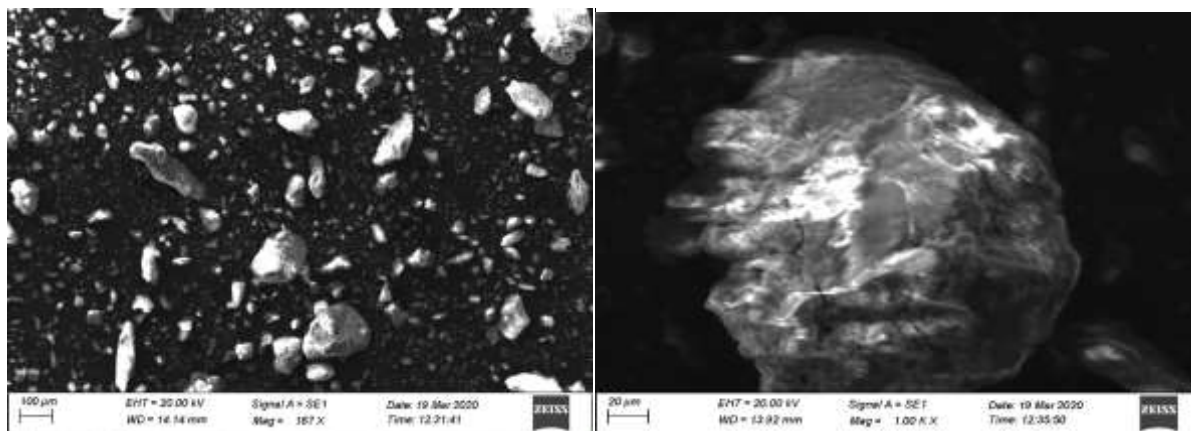


Figure-3.3 SEM micrographs of as synthesized HA

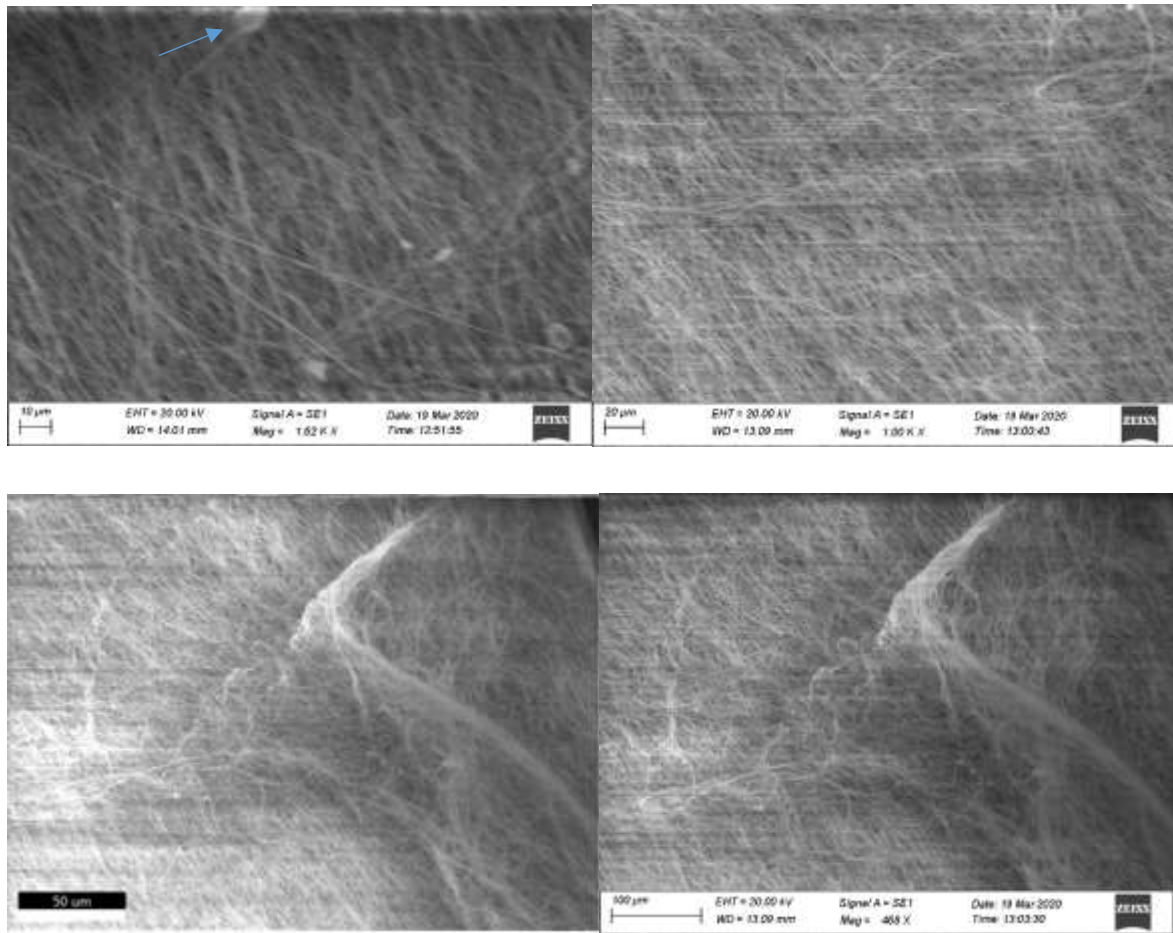


Figure-3.4 SEM micrographs of PVA/HA composite nanofiber

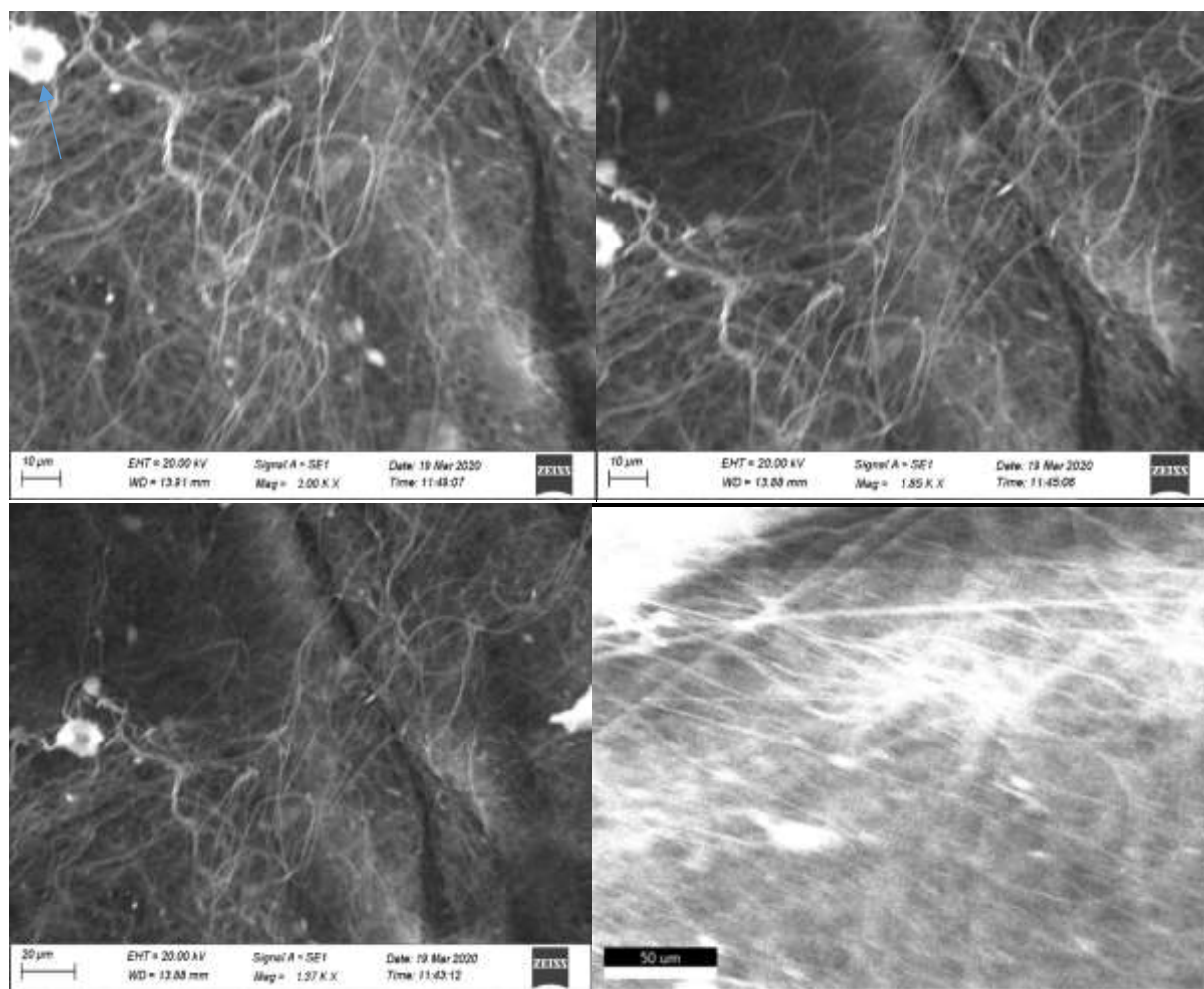


Figure- 3.5 SEM images of PVA/AL/HA composite nanofiber

3.4 EDAX and elemental mapping

Energy Dispersive X-ray Analysis (EDAX or EDX) is used to identify the elemental composition of materials. EDAX spectrum results acquired from the as synthesized HA, PVA/HA and PVA/AL/HA composite nanofibers is shown in the figure 3.6, 3.8 and 3.10 respectively. The elemental mapping of the homogeneous distribution of elements of as synthesized HA is shown in figure 3.7. The energy dispersive analysis further confirmed the presence of Calcium [Ca], Phosphorus [P] and Oxygen [O] elements indicating the HA chemical composition and carbon [C] elements indicating the chemical composition the polymers. Thus the incorporation of HA nanoparticles can be confirmed from elemental

analysis results acquired from the embedded particles into the polymer nanofibres matrix is shown in the figure 3.9 and 3.11.

HA

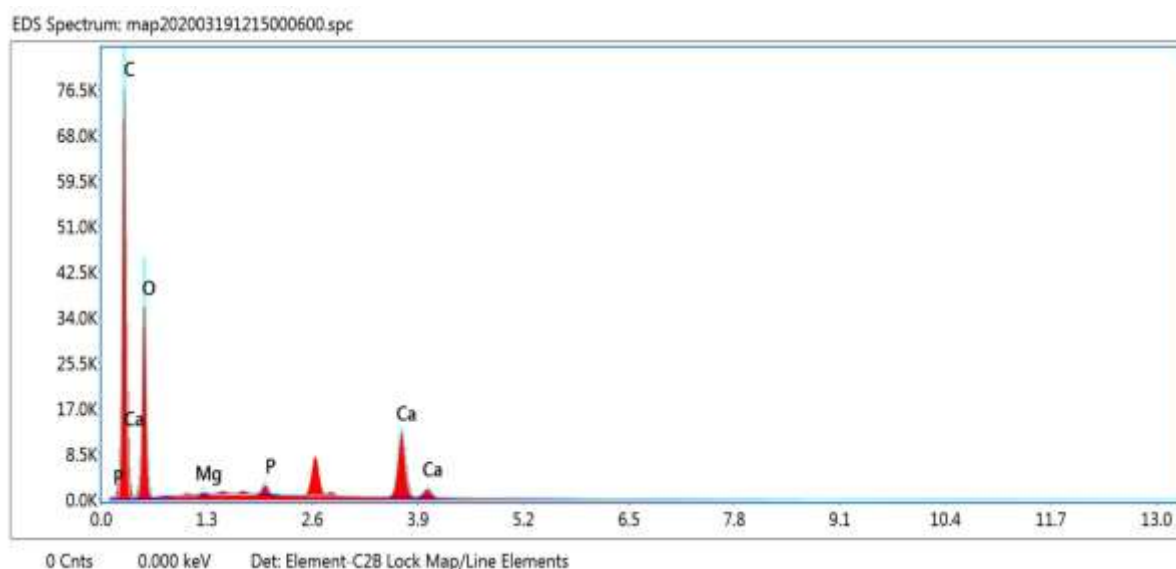
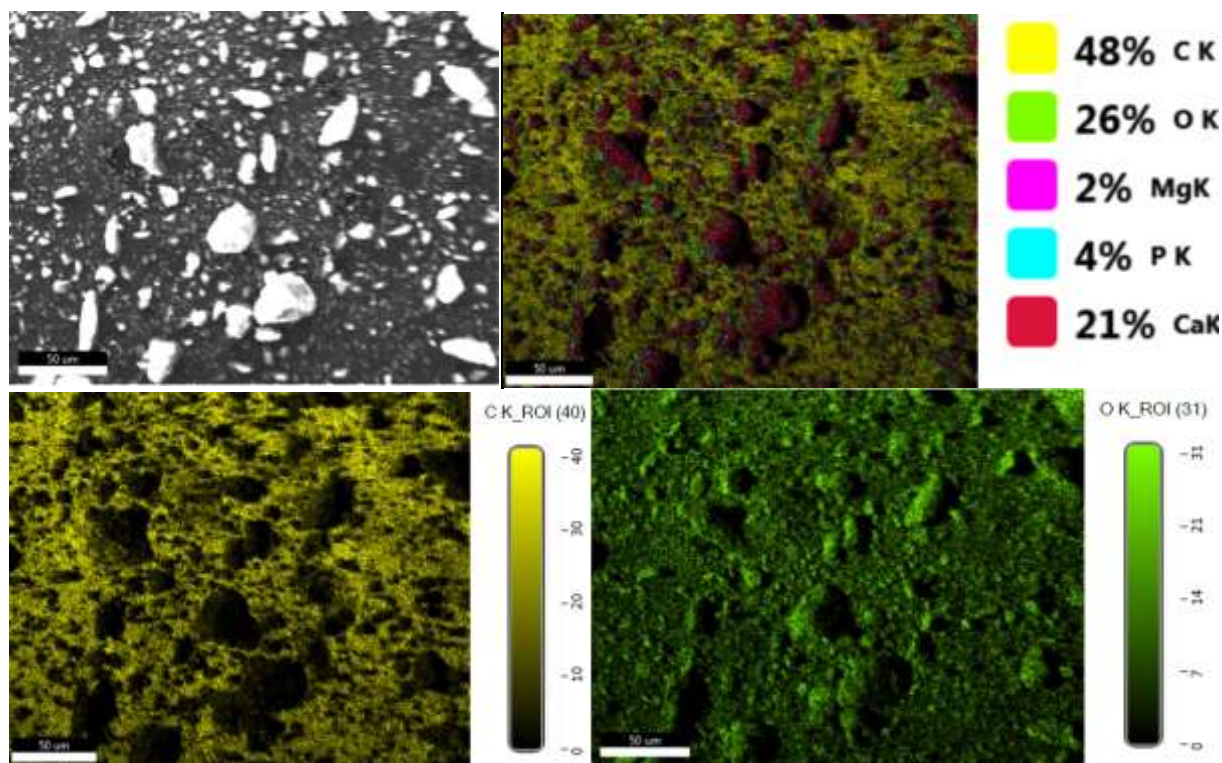


Figure-3.6 EDAX spectrum of as synthesized HA



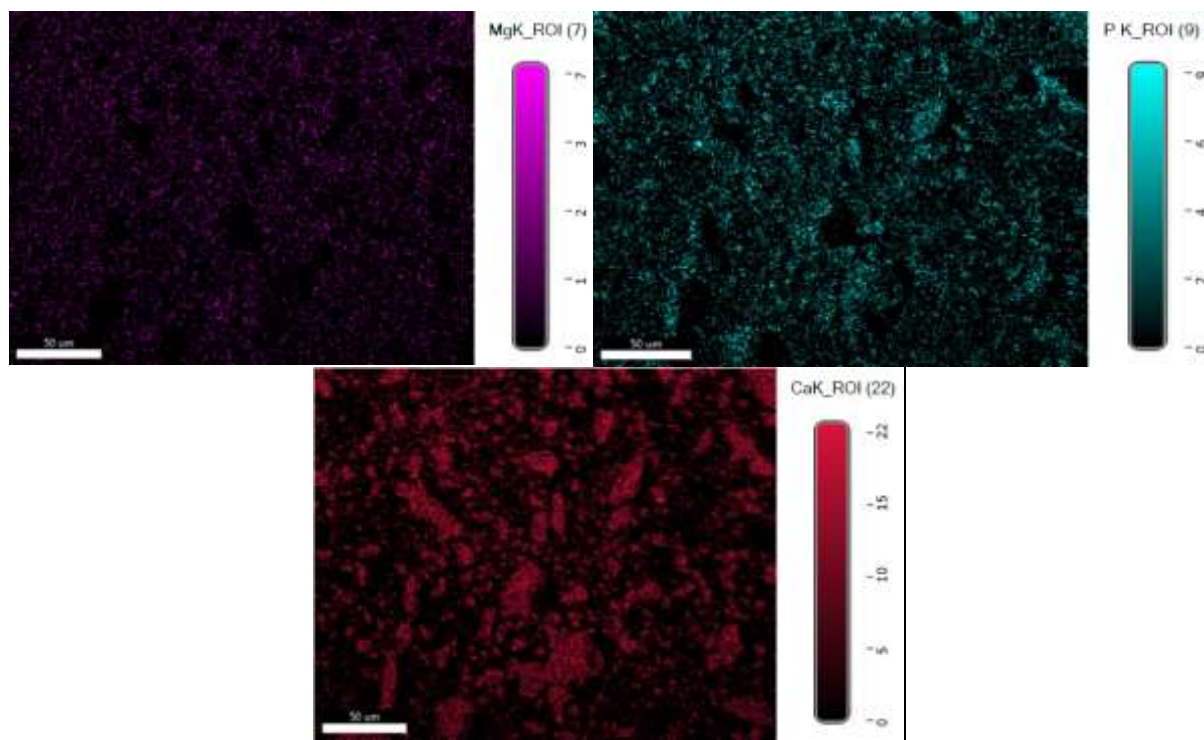


Figure-3.7 Elemental mapping of as synthesized HA

PVA/HA composite nanofiber

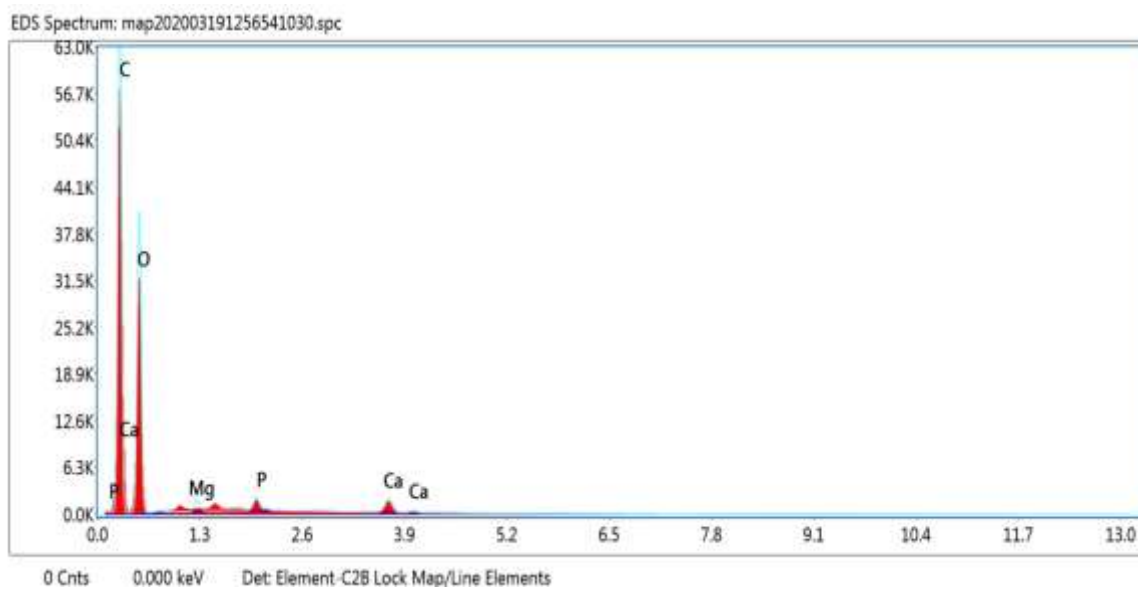


Figure-3.8 EDAX spectrum of fabricated PVA/HA nanofiber

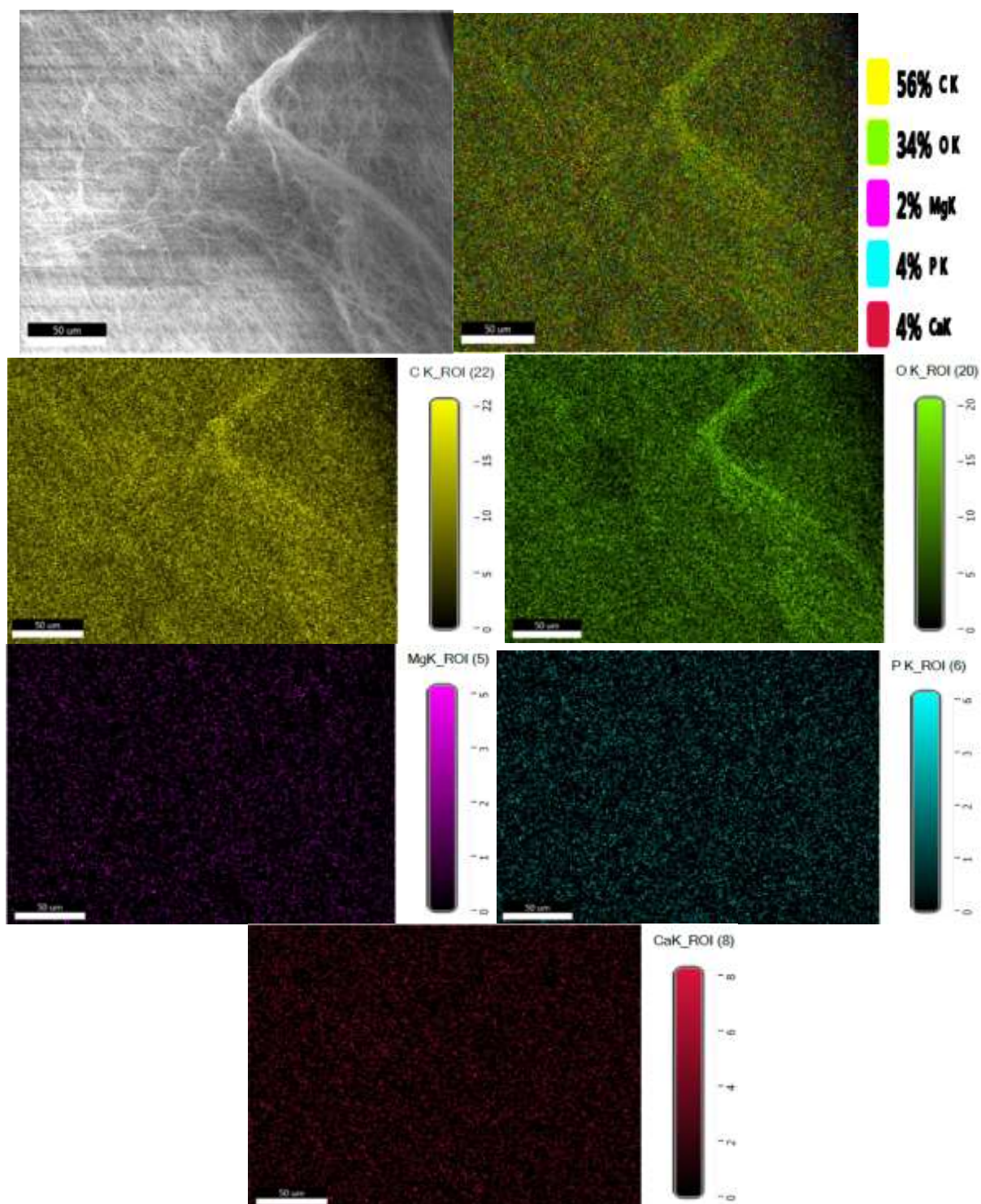


Figure-3.9 Elemental mapping of PVA/HA composite nanofiber

PVA/AL/HA composite nanofiber

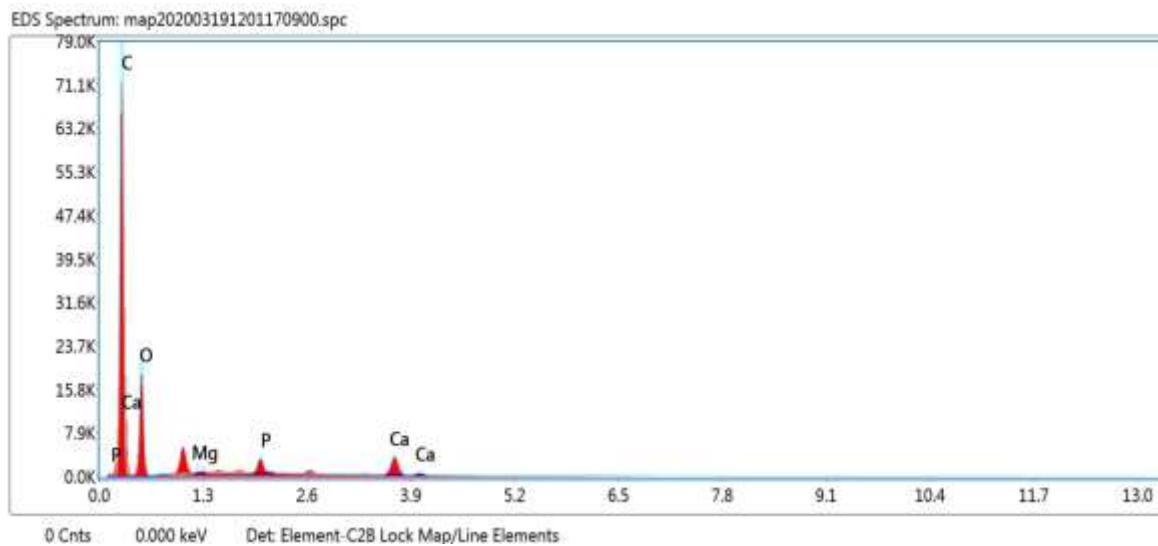
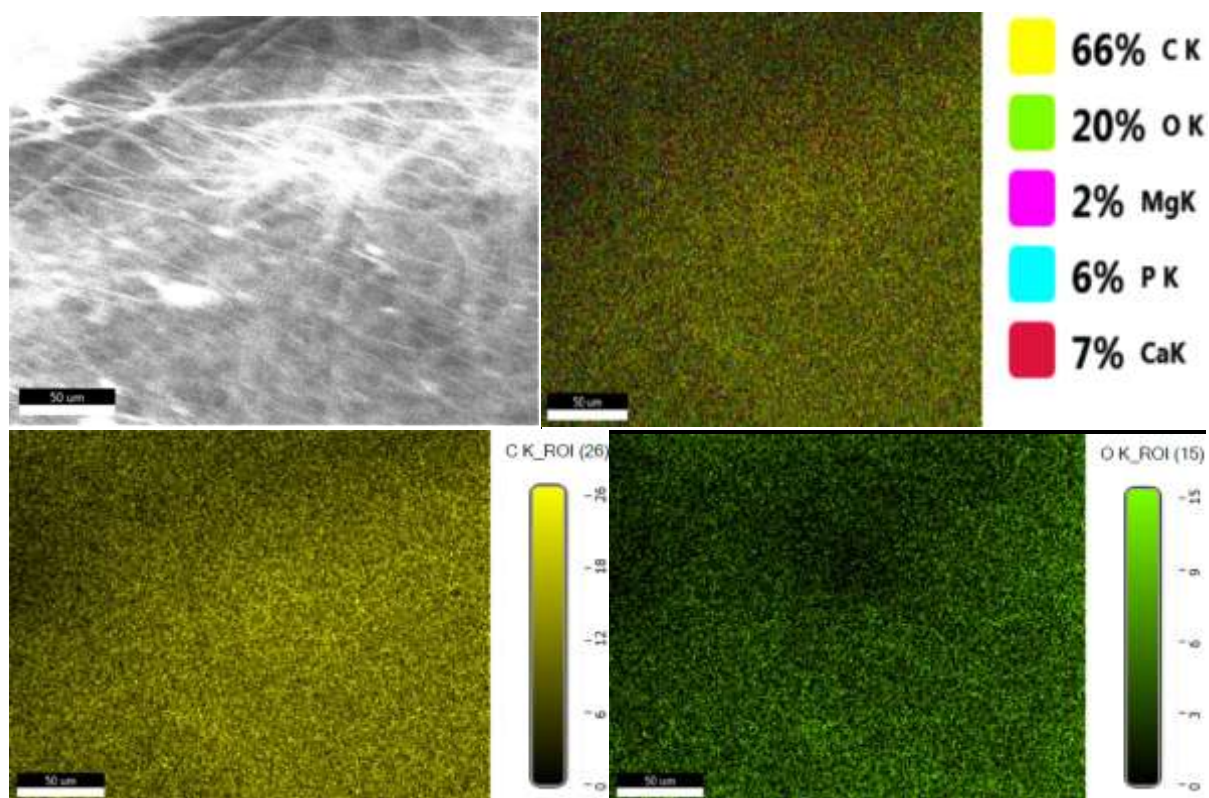


Figure-3.10 EDAX spectrum of fabricated PVA/AL/HA nanofiber



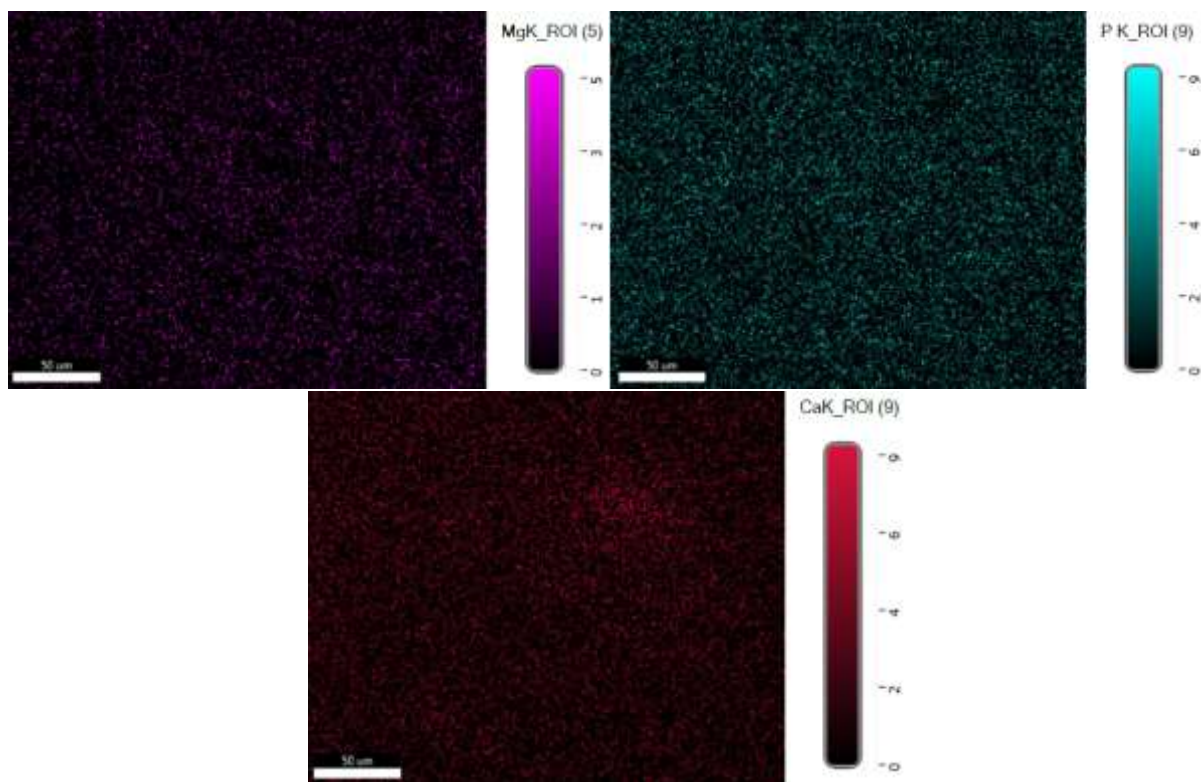


Figure-3.11 Elemental mapping of PVA/AL/HA composite nanofiber

3.5 DYE ADSORPTION ANALYSIS

The adsorption experiment was conducted for different reaction time for the three samples ceramic HA, PVA/HA composite nanofiber and PVA/AL/HA composite nanofiber. The adsorbent dosage of 30 mg of each samples with adsorbate volume of 10 ml of dye solution of adsorbate dosage 50 mg/l was analyzed by batch equilibrium method. The adsorption efficiency of the adsorbents was studied by UV-Visible spectroscopy analysis. The absorbance value were obtained at the visible region wavelength of 673 nm.

The image shows the dye adsorption by HA, PVA/HA composite and PVA/AL/HA composite in figure 3.12.

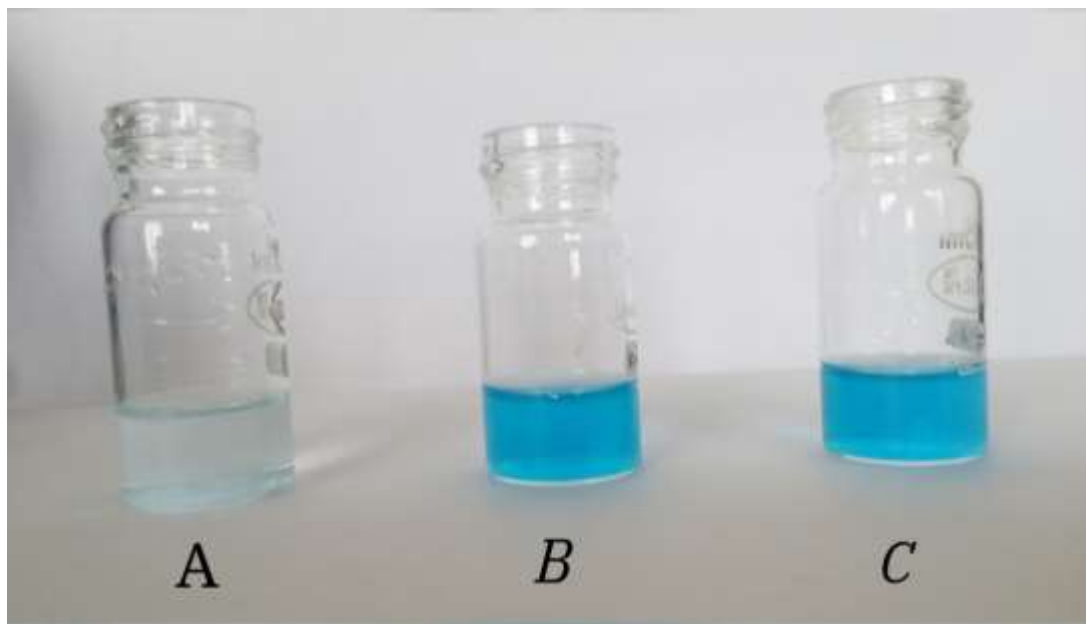


Figure-3.12 Optical image of dye solution after adsorption at 24 hours by A) HA, B) PVA/HA composite nanofiber & C) PVA/AL/HA composite nanofiber

From the experimental observations it is observed that the polymer-composite fiber membranes of PVA/HA and PVA/AL/HA when stirred in dye solution it dissolves completely due to the hydrophilic nature of the polymer. As the nanofiber membranes is not stable in its composition with high surface to volume ratio its property of adsorption is limited.

The HA is an ideal adsorptive material for long-term contaminants because of its high sorption capacity for actinides and heavy metals, low water solubility, high stability under reducing and oxidizing conditions, availability, and low cost, the adsorption takes place effectively. The nanofibers have a high efficiency in dye removal processes, where it could be recovered and reused during the successive treatment processes.

The fabricated composite nanofibers have greater PVA composition. PVA is a synthetic water soluble hydrophilic polymer. The basic properties of PVA are dependent on the degree of polymerization or on the degree of hydrolysis. It has been widely used in adhesives, emulsificants, and the textile and paper industry applications and in the attainment of amphiphilic membranes for enzyme immobilization where properties can be improved, such as mechanical, thermal and chemical stability. The application of PVA for adsorption is

limited by its hydrophilicity, as the PVA dissolves in dye solution. The chemical cross-linking could improve its stability in aqueous media.

CONCLUSION

In the present study the dye sorption capacity of the as synthesized HA by wet chemical precipitation method and electrospun nanofibers of hydroxyapatite-polymer composite has been investigated. The hydroxyapatite nanoparticles doped electrospun polymer-ceramic composites of PVA-HA and PVA-AL-HA nanofibrous mat was successfully fabricated. The electrospun nanofibres naturally form a non-woven mat with a large surface to volume ratio and high porosity, making it useful as an adsorption medium.

The removal of reactive blue dye from aqueous solution using adsorbents PVA/HA composite nanofibres, PVA/AL/HA composite nanofibers and as synthesized HA has been investigated. The adsorbents were characterized using XRD, FTIR, SEM, EDAX and UV-Visible spectrometer. The crystalline phase of HA and semi-crystalline phase of the polymers were characterized by XRD analysis. The functional groups of the adsorbents were characterized by FTIR analysis. The SEM and EDX images showed the morphology of HA and successful encapsulation of HA nanoparticles into the polymer nanofibers matrix. The efficiency of the adsorbents towards reactive blue dye from aqueous solution was analyzed under experiments by batch equilibrium method for different adsorbent dosage and reaction time. The addition of polymer with the HA helps in the effective regeneration of adsorbent over many cycles but the composite nanofiber membrane dissolves completely couldn't act as effective adsorbent.

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