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Nanomaterials for toxic dye absorption & its applications- A Comprehensive Review

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Abstract:

Significant levels of synthetic dyes are present in wastewater from a variety of businesses, most notably the textile sector, which presents health and environmental hazards. Dyes are classified as Acidic dyes, Reactive dyes, Disperse dyes, Cationic dyes, Vat dyes and Direct dyes which are present in waste water and makes waterbodies hazardous.SO, these waste water must be treated for the removal of dyes, There are different methods for the removal of dyes, those are Electro coagulation, Electro oxidation, Photocatalysis, Membrane filtration and Adsorption. These all methods having there own pros and cons in dye removal. Adsorption is an excellent dye removal technique since it is easy to use, efficient, and economical. Many adsorbents have been studied for their greater ability to remove dyes from wastewater, including natural materials and activated carbon. This approach is notable for being a workable way to alleviate the problems of environmental contamination brought on by industrial dyes. In dye adsorption, nanomaterials such as metal oxides, graphene, carbon nanotubes, and nanoparticles are very effective because of their active binding sites, increased surface area, and improved porosity. The method is efficient and economical because of their tiny size and magnetic qualities, which make separation from water simple. Adsorption capacities are improved by doped nanomaterials like Fe_3O_4, TiO_2, and ZnO, which increase surface area, improve porosity, and provide active sites for dye binding. In order to maximize the efficiency of dye adsorption, these nanomaterials are created using techniques such as Solgel Method, Co – Precipitation, Laser Ablation, Combustion, Chemical Precipitation, Hydro thermal process. This study explores about the synthesis of doped nanomaterials, Advantage of Adsorption method in dye removal over other methods.

1.Introduction:

1.1.Nanomaterials:

The field of nanotechnology has grown significantly over the past century. Furthermore, nanotechnology is directly or indirectly related to a wide range of research topics now a days. The creation, synthesis, characterization, and use of materials and devices by altering their size and shape at the nanoscale is known as nanotechnology. The prefix “nano” is used as a keyword in every stream, including product advertising. Actually, the word “nanos” which means “dwarf” or the Greek word "nanos". It combines the fields of solid state, chemistry, physics, material science, and biosciences. Nanotechnology is being used in practically every field of science and technology.

Nanoscience and nanotechnology are different in that the former provides information about the arrangement of atoms and their fundamental properties at nanoscale, while the latter uses technology to control matter at the atomic level in order to create new nanomaterials with distinct properties. Nanotechnology is receiving attention in practically engineering field, but the general public is unaware of its existence in everyday life. Despite this, its applications in medicine, engineering, the environment, electronics, defence, and security are still growing.

As a result, this sparks interest in the topic and generates conversation about the fundamental and important aspects of nanotechnology. The fundamental and essential components of nanotechnology are known as "nanomaterials." Materials that are smaller than 100 nm in at least one dimension are called nanomaterials. They are therefore much smaller than microscales. [1]

The nanomaterials typically have a size of 10^{-9} nm, which is one billionth of a meter. Nanomaterials exhibit distinct physiochemical characteristics from bulk materials, which are inevitably influenced by their size and shape. By altering their size and shape at the nanoscale level, nanomaterials surprisingly produce unique properties with new features and capabilities. Nanomaterials can take various forms, such as nanorods, nanoparticles, or nanosheets, which are distinguished by their dimensionality. Two dimensional nanomaterials are typically films and layers of type one, one-dimensional nanoparticles. These are mostly classified for the single isolated nanomaterials. Their physical characteristics will change when two or more particles interact. Bulk three -dimensional nanomaterials are these particles of various constituents according to the nanoscale (less than 100 nm) dimensions, they are classified as follows:

1.2.Classification of Nanomaterials:

1.2.1.Zero Dimensional Nanomaterials:

Zero dimensional nano materials are the materials in which all the dimensions are measured within the range of nanoscale, there is no dimensions are the larger than 100 nm. So basically 0D Nanomaterials are called as nano particles. Which includes Quantum dots, Nanosphere Fullerenes, Gold nanoparticles, Silver nanoparticles etc., They are shown in Fig1, Fig 2 and Fig 3.

- Gold Nanoparticles:

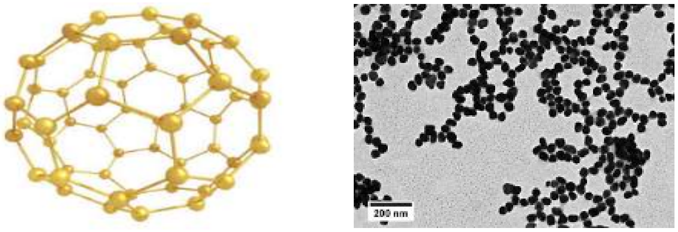

Fig 1: Schematic and TEM Diagrams of 0D Nano Particles

- Silver Nanoparticles:

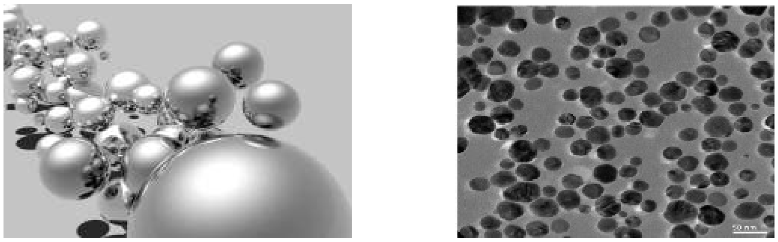

Fig 2: Schematic and TEM images of 0D Silver Nano Particles

- Quantum Dots:

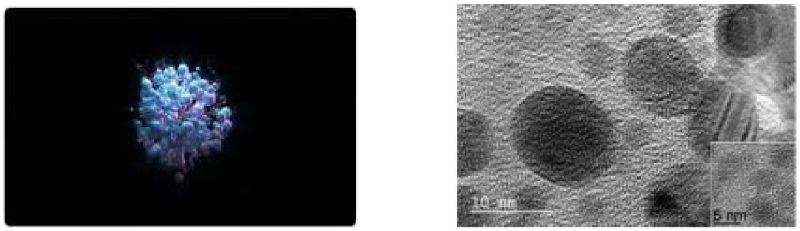

Fig 3: Schematic and TEM images of 0D Quantum dots

1.2.2.One Dimensional Nanomaterials:

One dimension nanomaterials are the materials in which one dimension is outside of the nanoscale, 1D nanomaterials will be visible whenever turn the material until a large side of them are visible like long tubes, includes nano tubes(carbon nanotubes), nanorods, nanofiber, nano wires(silicon) etc., They are shown in Fig 4 and Fig 5.

- Carbon Nanotubes:

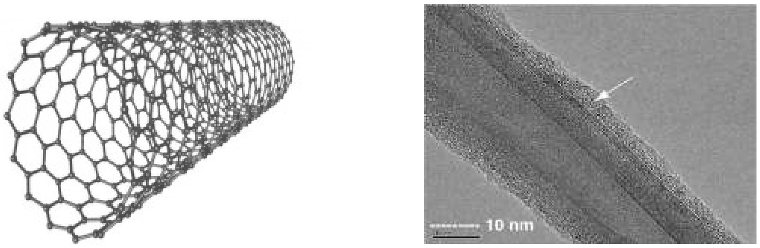

Fig 4: Schematic and TEM images of 1D Carbon Nanotubes

- Silicon Nano wires:

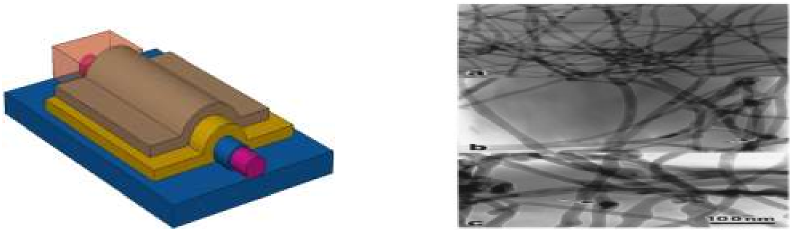

Fig 5: Schematic and TEM images of 1D Silicon Nano wires

1.2.3.Two Dimensional Nanomaterials:

Two dimension nanomaterials are the materials in which two dimensions are outside of the nanoscale, this class exhibit plate like structures, these are the thin films whose thickness is very small, which includes graphene, nanofilms, nanolayers, nano coatings, nano sheets, nano plates etc., Graphene sheets are shown in Fig 6.

- Graphene sheets:

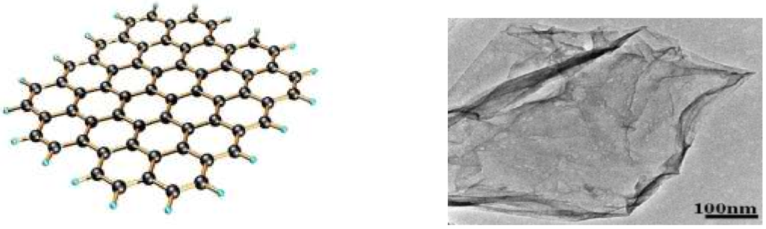

Fig 6: Schematic and TEM images of 2D Graphene Sheets

1.2.4.Three Dimensional Nanomaterials:

Three dimensional nanomaterials are the materials that are not confined to the nanoscale in any dimension, this class can contain bulk powders, dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multi-nano layers. Porous siliicon shown in Fig 7.

- Porous Silicon:

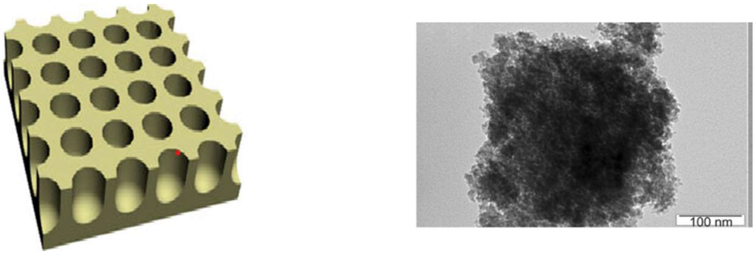

Fig 7: Schematic and TEM image of 3D Porous Silicon Nanoparticles

1.3.Sources of Nanomaterials:

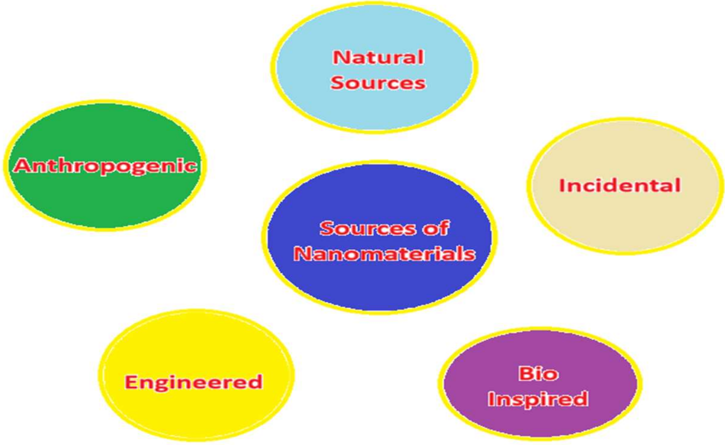

Fig 8: Sources of Nanomaterials

The different sources of Nanomaterials including Natural, Incidental, Bio-Inspired, Engineered and Anthropogenic sources are illustrated in Fig 8.

1.3.1.Natural Sources:

Natural processes such as photochemical reactions, volcanic eruptions, forest fires, and simple erosion, as well as plant and animal shedding of skin and hair, produce nanoparticles, which are widely distributed in nature.

1.Dust Storms: The biggest single source of environmental nanoparticles seems to be dust storms. Recent years have seen a great deal of research into the long-distance movement of both anthropogenic pollutants and mineral dust from the major continents. Minerals from the deserts make up about half of the troposphere's atmospheric aerosol particles. 68 One third to half of the dust mass is smaller than 2.5 m, and the size of the particles created during a dust storm ranges from 100 nm to several microns. 65, 68 Concentrations of particles between 100 and 200 nm can reach 1500 particles/cm3.

2.Forest Fires: Lightning strikes and human activity are the main causes of forest fires and grass fires, which have long existed in Earth's natural history. Large fires can produce more particulate matter, including nanoparticles, than ambient air quality standards and spread smoke and ash over thousands of square miles.

3.Volcanic eruption: As a volcano erupts, ash and gases that contain particles as small as nanoscales or microns are launched high into the atmosphere, sometimes as high as 18,000 meters. There are a lot of particles released into the atmosphere; up to 30 106 tons of ash can be ejected in a single volcanic eruption. The two lowest layers of the atmosphere, the stratosphere and the upper troposphere, are where volcanic ash can travel globally and have a long-lasting impact on every region of the planet. One of the main effects of upper atmospheric particulate matter is that it scatters and blocks solar radiation. Particles made of heavy metals are one particularly dangerous volcanic product because they are known to be toxic to humans.

4.Ocean and Water Evaporation: Around the world, seas and oceans release a significant amount of sea salt aerosols. These aerosols are created when water vapor evaporates and water droplets created by waves are released into the atmosphere. They are between 100 nm and several microns in size. Additionally, evaporation and temperature fluctuations can cause precipitation, which is another way that nanoparticles can form in bodies of water. Lake Michigan, which sits in a limestone basin with high calcium carbonate levels, is an illustration of this phenomenon. The calcium carbonate stays dissolved in cold water for the majority of the year, but as summer draws to a close, the water temperature rises and the calcium carbonate becomes less soluble.

5.Organisms: Numerous organisms are smaller than a few microns, such as some bacteria that range in size from 30 nm to 700 nm and viruses that scale from 10 to 400 nm. What we refer to as "particles," such as microparticles or nanoparticles, should be clearly distinguished from nano organisms or their constituent parts, such as bacteria, viruses, cells, and their organelles. Self-organizing, self-replicating, dissipative structures with a shorter structural lifetime than inorganic solids are found in cells, bacteria, and viruses. Generally speaking, nano organisms dissipate when their energy source runs out. On the other hand, nanoparticles are usually inorganic solids that don't need an energy source to stay stable. They react chemically with their surroundings to interact, dissipate, or change.

1.3.2.Incidental Sources:

These nanoparticles and nanostructured materials are inadvertently created by anthropogenic (such as mechanical or industrial) processes or direct or indirect human influences, such as combustion during cooking, welding fumes, vehicle exhaust gases, and solid fuel heating (home heaters). Unintentionally created during a purposeful process, incidental atmospheric nanomaterials could contribute to air pollution. Forest fires produce a variety of nanomaterials, such as cement, pigments, and fumed silica. When humans first began producing incidental nanoparticles is difficult to determine, but it was most likely when they began controlling fire. The sizes and shapes of incidental nanomaterials, which are byproducts of human activity, are typically poorly controlled. In contrast to engineered nanomaterials, incidental nanomaterials have significant environmental impacts and need to be taken into account.

1.3.3.Bio-Inspired materials:

These are artificial nanomaterials that have characteristics similar to those of living things or natural nanomaterials. By altering their structures, numerous bioinspired nanomaterials with particular uses can be created using cutting-edge nanofabrication technologies. When fighting or courting, for instance, chameleons can quickly change their colours from a camouflaged to a highly visible state. The lattice of guanine nanocrystals inside iridophore cells is actively tuned to produce this colour shift. In order to replicate the photonic structure of chameleon iridophore cells, mechanochromic elastomers have been developed. Rigid silica nanocrystals are embedded in an elastomer matrix to create non-close-packed crystals in these sensors. When stretched, these sensors show a red to blue colour shift, and when compressed, they show a red to green colour shift.

1.3.4.Engineered Material Source:

Nanoparticles and nanostructured materials that are engineered are made for particular uses according to their dimensionality and unique properties (e.g., nanostructured medical implants). To lessen or minimize these nanomaterials' unforeseen negative effects, they need to be thoroughly characterized. In the 1940s, aerosol (fumed silica) was created to create the first commercial nanomaterials. In this instance, aqueous solutions were used to create the first silica nanospheres in the 1960s. The shapes of natural and incidental nanoparticles can be irregular or regular. Typically, engineered nanoparticles are shaped like tubes, spheres, rings, and so on. Graphene, fullerenes, and carbon nanotubes are examples of engineered carbon nanostructures that have a more regular shape and structure than carbon soot (Incidental Nanomaterials).

1.3.5.Anthropogenic Materials Source:

Both incidental and engineered nanomaterials are included in this term. Anthropogenic nanomaterials intentional and unintentional releases into the environment are growing to be significant public concerns.[2]

2.Doping of Nanomaterials:

2.1.Doping:

Doping is the process in which impurities are added intentionally to the material to alter its properties to enhance its efficiency. doping can alter the properties like optical activity, electrical conductivity, or catalytic properties of a material to make the material effective. In doping metals (Iron, Zn, Ag, Cu, Mn),nonmetals(N,S,B,O)polymers(Polyaniline,Polyethyleneimine,Chitosan),magneticsubstances(MagnetieCobalt ferrite), and functional groups(Amino groups, Carboxyl groups, Sulfonic groups) are used as the dopant materials which can enhance the adsorption capacity of a material in a dye removal by increasing the surface area, pore structure, functional group availability, the choice of dopant materials depends on the type of dye being targeted and the desired properties of the adsorbent, such as adsorption capacity, selectivity and recoverability.[3]

2.2.Methods of doping nanomaterials:

Numerous techniques have been used to dope nanoparticles on different substrates. Numerous physical, biological, and chemical methods have been employed to produce doped nanoparticles. The top-down strategy, which breaks down more prominent precursors into smaller units, and the bottom-up approach, which builds up smaller units to form nanosized materials, are the two main techniques for creating nanosized materials. While the bottom-up approach uses solvothermal techniques, the top-down strategy uses decomposition techniques. Numerous techniques have been employed, including sol-gel, combustion, chemical breakdown, sonication, dip-coating, arch discharge, laser ablation, and others. Due to its ease of use, product purity, and other advantages, the sol-gel technique has grown to be the most widely used technology.

1. Solgel Method
2. Co – Precipitation
3. Laser Ablation
4. Combustion
5. Chemical Precipitation

1.Solgel method:

Process:

A flexible way for creating doped materials for uses such as dye removal is the sol-gel doping process. This method involves dissolving the precursors of the host material and the dopant (such as metal ions) in a solvent to create a sol, or colloidal solution of particles. This sol progressively changes into a gel—a semi-solid matrix with the dopant evenly distributed—through hydrolysis and condensation processes. After drying, the gel is frequently calcined to provide a stable, highly surface-area, porous doped substance that is perfect for removing dye molecules from wastewater. General representation of Solgel method shown in Fig 9.

Case study:

Spinel ZnCrO4 nanoparticles were created by thermally decomposing Zn-Cr gel using the sol-gel process, with oxalic acid acting as a chelator. The findings demonstrate that $ZnCr_2O_4$ nanoparticles successfully remove high amounts of RB5 dye molecules.[4]

SnO_2 nanoparticles were successfully produced using a sol-gel technique. Several techniques were used to characterize the as-prepared SnO_2, including TG-SM, XRD, and SEM. The results says the Synthesized SnO_2 nanoparticles successfully removed the congo red azo dye.[5]

Fig 9: General represantation of Solgel method

2. Co – Precipitation:

Process:

The co-precipitation approach is frequently used for doping materials because it allows for exact control over their physical or chemical characteristics. This method entails dissolving ions from both the host and dopant materials in a solution, then adding a precipitating agent (e.g., ammonia) to cause simultaneous precipitation. Under regulated temperature and pH conditions, dopant ions are distributed uniformly inside the host material, resulting in a co-precipitate. The precipitate is aged to promote crystallization, then separated, washed to remove impurities, dried, and calcined to stabilize the doped structure. Co-precipitation is popular because it is simple, cost-effective, and scalable, allowing exact modifications in material characteristics for applications in catalysis, energy storage, and electronics. Manufacture of Fe3O4 NPs are shown in Fig. 10.

Case study:

Chemical co-precipitation was used to manufacture Fe_3O_4 nanoparticles with diameters ranging from 5-20 nm and a saturation magnetic of 89.46 emu g-1, indicating superparamagnetic characteristics. Fe_3O_4 nanoparticles are effective for removing dye from water using a simple magnetic separation method.[6]

Copper nitrate was used as the precursor in the co-precipitation process to create the nanoparticles.. EDTA and the EDTA-Silane complex were successfully added to the precursor to functionalize CuO NPs. FT-IR and SEM methods were used to characterize the functionalized CuO. [7]

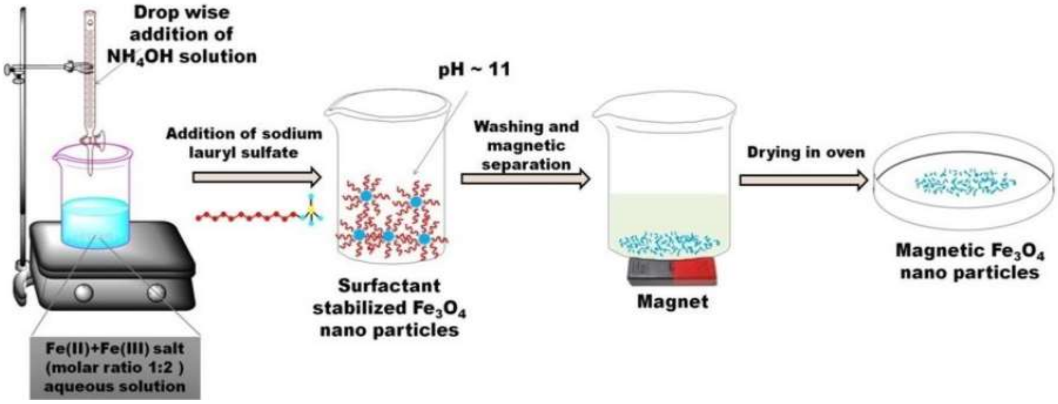

Fig 10: Mnufacture of Fe3O4 Nanoparticles using Co-Precipitation Method

3.Laser Ablation:

Process:

Laser ablation is a high-precision doping technique where intense laser pulses remove material from a target, creating a plasma plume that deposits atoms onto a substrate, forming a doped thin film. By controlling laser parameters like pulse duration, intensity, and wavelength, manufacturers can achieve precise dopant concentration and distribution. This method allows for high purity and tailored dopant integration, often used to enhance optical, electronic, and magnetic properties in materials. Laser ablation is commonly used in semiconductor and thin-film industries due to its ability to handle various materials with minimal contamination. General representation of Laser-Ablation Method is shown in Fig 11.

Case study:

NiO nanoparticles were prepared and decorated in a single step using the pulsed laser ablation process, leaving no byproducts. The nanocomposite was evaluated using several analytical methods, including FT-IR, TEM, XRD, Raman spectroscopy, XPS, and EDX.[8]

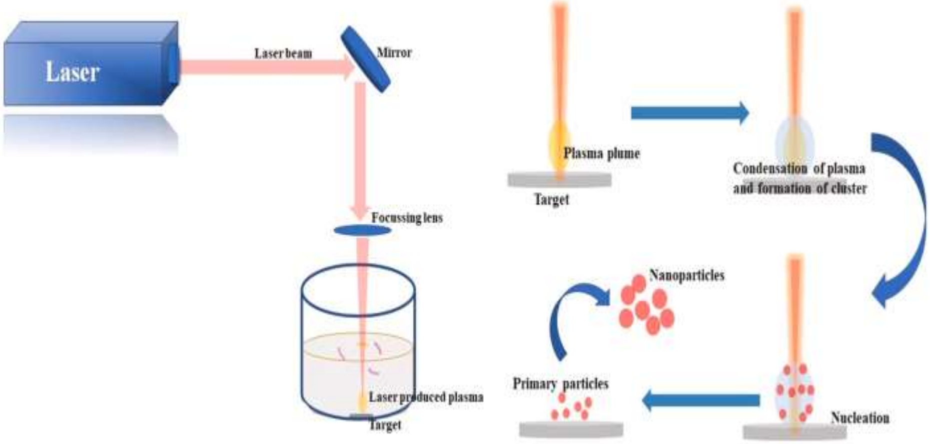

Fig 11: General representation of Laser-Ablation Method

4.Combustion:

Process:

Combustion doping involves introducing dopant ions into a material by high-temperature combustion processes, which frequently result in nanocrystalline formations. The process normally begins by combining a fuel (such as urea, glycine, or citric acid) with metal precursors containing both host and dopant ions. When the exothermic process ignites, it releases energy and rapidly heats the mixture, causing combustion. This causes dopant ions to crystallize while also being incorporated into the host lattice. Combustion doping is popular because it is simple, inexpensive, and can create doped materials with high purity and uniform particle dispersion. This approach is frequently utilized to generate improved materials for applications in catalysis, sensors, and luminescent devices. Controlled doping boosts qualities like conductivity, magnetism, or optical characteristics. General representation of Combustion method is shown in Fig 12.

Case study:

ZnO nanoparticles (NPs) were created by a simple combustion method. $Zn(CH_3COO)_2$ precursors were migrated to the top of a burning lampwick using alcoholic fuel. Chemical reactions happened at the lampwick's solvent-air interface, resulting in ZnO NPs. [9]

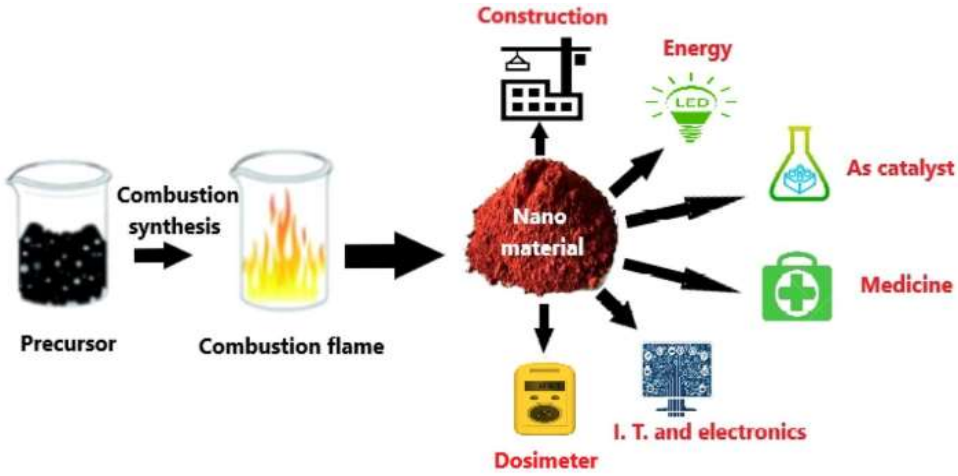

Fig 12: General representation of Combustion method

5.Chemical Precipitation Method:

Process:

One method for adding dopants to host materials to improve their capacity to remove pollutants is chemical precipitation. Making solutions with the host material and dopant ions (such as metal salts) is the first step in this procedure. To encourage dopant ions to stick to the host material, precipitation is started by adjusting the pH with a base after the solutions have been mixed. The precipitate becomes more uniform as it ages, stabilizing the particles. The host-dopant link is then strengthened by separating the doped material, washing it to get rid of any residues, drying it, and calcining it. Because of its improved adsorption capabilities, this finished doped product is useful for eliminating dyes and other contaminants from wastewater. Manufacture of Mn doped ZnO NPs by Chemical Precipitation Method is shown in Fig 13.

Case study:

A wet chemical precipitation approach was used to effectively prepare hydroxyapatite nanopowder, and AuNPs were then impregnated into the hydroxyapatite nanopowder matrix. The XRD analysis's findings verified that AuNPs and hydroxyapatite nanopowder had formed.[10]

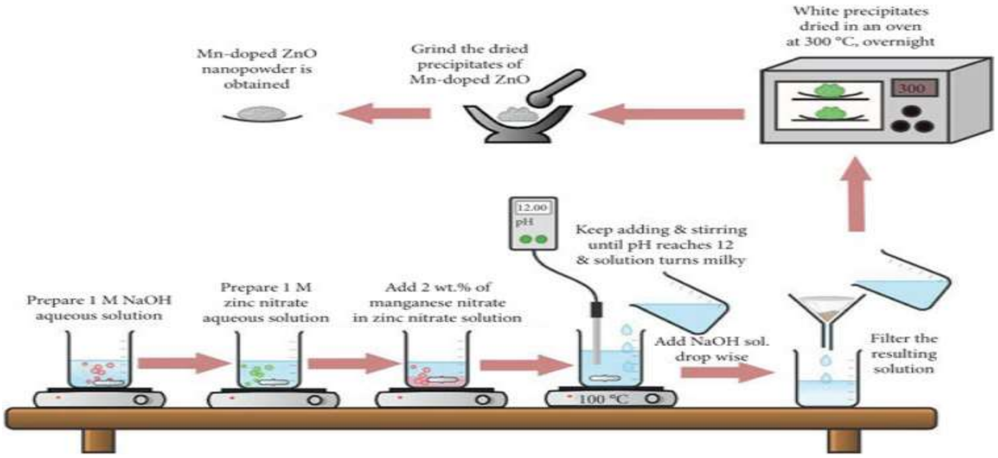

Fig 13: Manufacture of Mn doped ZnO NPs by Chemical Precipitation Method

3.Characterization of Nanomaterials:

Understanding the characteristics, structure, and behavior of nanoparticles is crucial for a variety of applications, including electronics, medicine, and environmental cleanup. Important methods for characterizing nanoparticles include.

3.1. Particle size and distribution:

- SEM-EDX: SEM-EDX, or scanning electron microscopy with energy dispersive X-ray spectroscopy, is a potent analytical method that blends elemental analysis and high-resolution imaging. By passing a concentrated electron beam over the sample and identifying secondary electrons released from its surface, SEM creates fine-grained surface pictures that provide information about topography and morphology. By examining X-rays released from the sample as a result of electron interactions, EDX enhances SEM by enabling the identification of the elemental composition at certain locations. SEM-EDX is perfect for both imaging and compositional analysis since it is widely used in materials science, nanotechnology, and geology to investigate surface structure, particle size, and elemental distribution. SEM-EDX image for Mg doped Fe NPs are shown in Fig 14.[38,39]

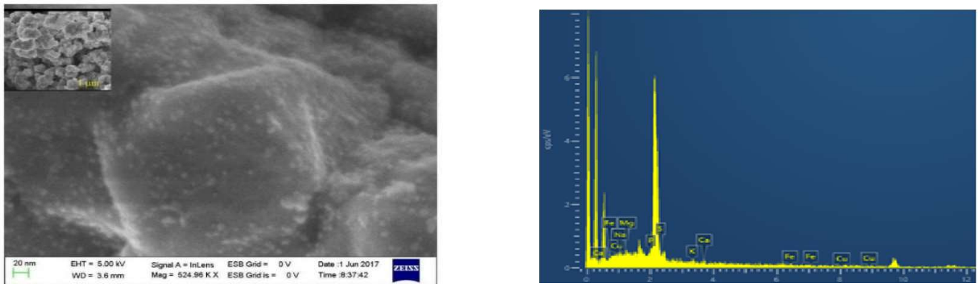

Fig 14: SEM-EDX image for Mg doped Fe NPs

- TEM:

  A high-resolution imaging method called transmission electron microscopy (TEM) makes it possible to see the atomic-scale interior structure and shape of materials. A concentrated electron beam travels through an extremely thin sample in a transmission electron microscope (TEM), creating a picture that displays minute structural features. TEM is useful for examining biological specimens, crystalline materials, and nanoparticles because it offers vital information on particle size, shape, crystallinity, and lattice structure. TEM is crucial for cutting-edge research in nanotechnology, materials science, and biology because it may be used in conjunction with methods like Selected Area Electron Diffraction (SAED) to discover crystallographic structures. TEM image for Mg doped ZnO NPs is shown in Fig 15.[40]

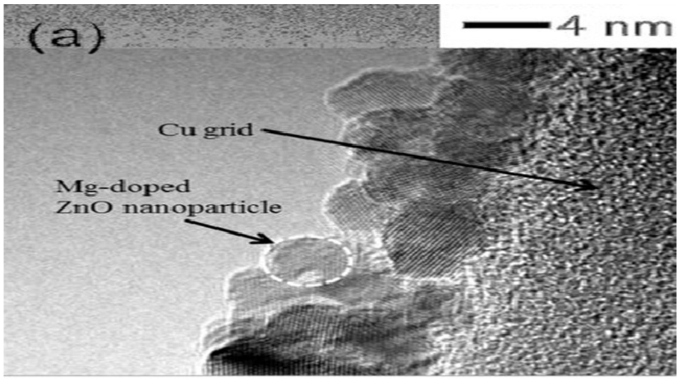

Fig15: TEM image for Mg doped ZnO NPs

- XRD:

  One analytical method for figuring out a material's crystalline structure is X-ray diffraction (XRD). XRD examines the angles and intensities of diffracted beams, which are determined by the arrangement of atoms in a material, by shining X-rays upon a sample. The crystal structure and lattice are shown by this diffraction pattern. XRD Image for MgO NPs is shown in Fig16.[38]

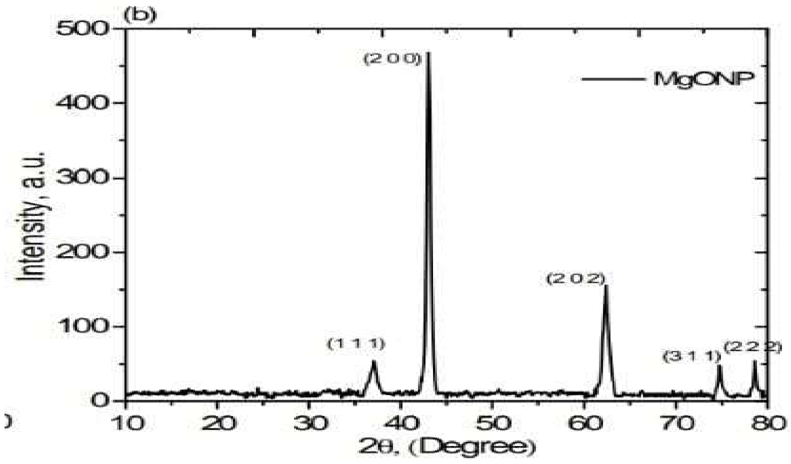

Fig 16: XRD Image for MgO NPs

3.2. Surface Properties:

- Zeta-Potential:

  The electric charge on the surface of suspended particles is measured by their zeta potential, which indicates how stable they are. It measures the potential difference between the particle's stationary fluid layer and the dispersion medium. Strong particle repulsion, indicated by a high zeta potential (positive or negative), predicts stable colloids, whereas a tendency to assemble is suggested by a low zeta potential. Zeta potential is used in nanoparticle research to evaluate dispersion stability, which is crucial in domains such as material science, wastewater treatment, and medicines. Electrophoretic light scattering is commonly used to measure it, providing information on surface characteristics and possible interactions. Zeta Potential Image for MgO NPs is shown in Fig 17. [38]

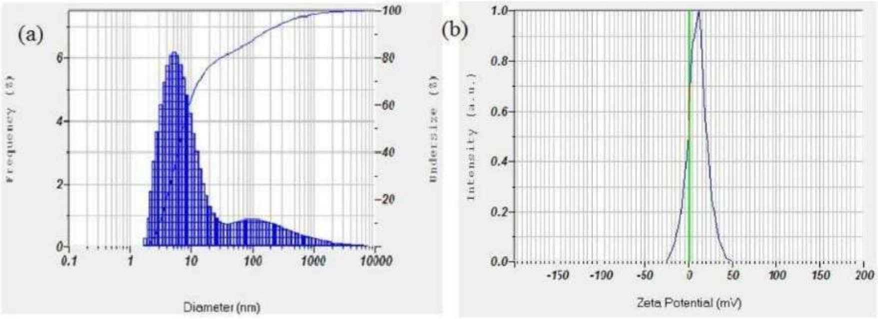

Fig 17: Zeta Potential Image for MgO NPs

3.3. Chemical Composition and Functional group:

- FTIR:

  An analytical method called Fourier-transform infrared spectroscopy (FTIR) uses molecular vibrations to identify organic, polymeric, and inorganic materials. By measuring the way molecules absorb infrared light at different wavelengths, FTIR creates a spectrum that shows the distinctive "fingerprint" of chemical connections in a sample. Because of its ability to detect functional groups and chemical bonds, FTIR is useful for structural characterisation, purity analysis, and material identification. A non-destructive technique for analyzing solid and liquid samples, FTIR is widely used in chemistry, pharmacology, and materials research to provide quick, accurate information on molecular interactions and composition. FTIR Image for MgO NPs is shown in Fig 18.[38]

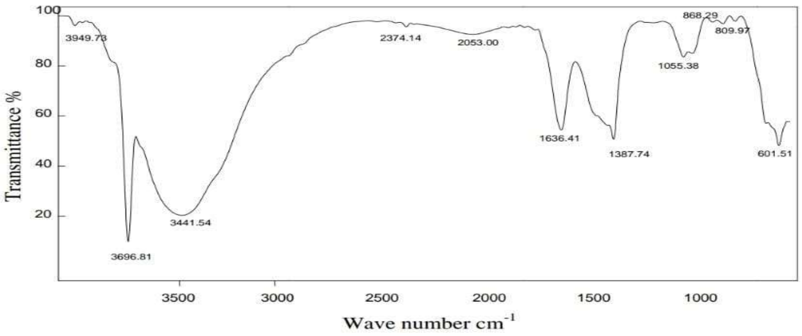

Fig.18: FTIR Image for MgO NPs

- XPS:
  X-ray A surface-sensitive quantitative spectroscopic method for determining a material's elemental makeup and chemical state is called photoelectron spectroscopy (XPS). It entails exposing a sample to X-ray radiation, which results in the emission of photoelectrons. XPS determines the binding energies of the constituent elements by measuring the kinetic energy of these released electrons, which enables the identification of certain chemical states. In several disciplines, such as materials science, chemistry, and surface engineering, this method is frequently used to characterize coatings, thin films, and nanostructures as well as to investigate contamination and surface interactions. XPS Image for MgO NPs is shown in Fig 19.[38]

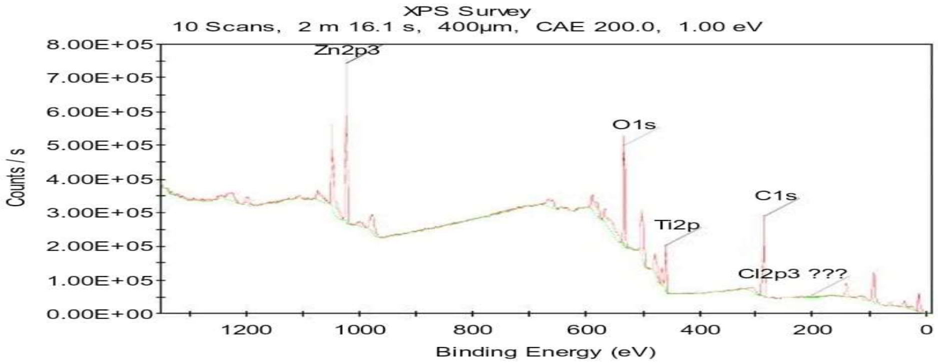

Fig 19: XPS Image for MgO NPs

3.4. Optical Properties:

- UV-Visible Spectroscopy:
  An analytical method for determining how much ultraviolet and visible light a sample absorbs or transmits is called UV-visible spectroscopy. Certain wavelengths of visible (400–700 nm) or ultraviolet (200–400 nm) light are absorbed by a sample, leading to electronic changes in molecules. A spectrum created by this absorption aids in chemical identification and concentration analysis. In chemistry, biology, and environmental research, UV-Vis spectroscopy is frequently used to measure analytes, evaluate purity, and examine the structure of organic molecules. It is prized for its ease of use, rapidity, and precision in analyzing both liquid and solid materials. UV-Visible Spectroscopy image for MgO NPs is shown in Fig 20.[38]

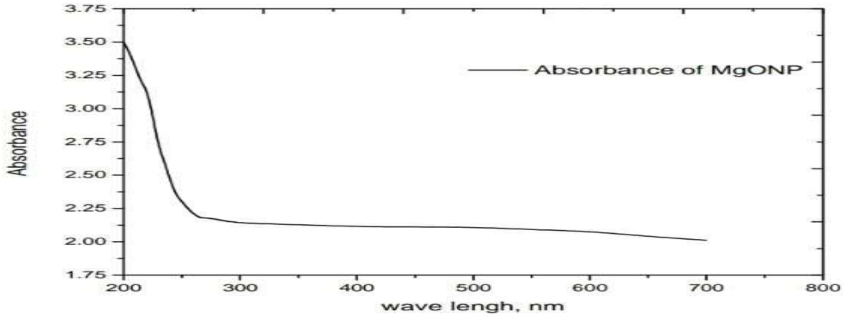

Fig 20: UV-Visible Spectroscopy image for MgO NPs

3.5. Thermal Stability:

- TGA:

  A method called thermogravimetric analysis (TGA) is used to quantify how much a substance weighs when heated over time. It offers information about composition, degradation patterns, and temperature stability. In TGA, a sample is heated progressively in a controlled setting, usually with air or nitrogen, and the weight loss (or gain) that results is noted. Moisture content, volatile chemicals, and thermal degradation temperatures are all determined with the use of this data. TGA is often used to evaluate material characteristics, quality control, and compositional analysis, especially for polymers, composites, and complex materials, in the fields of material science, polymer analysis, medicines, and environmental research. TGA image for MgO NPs is shown in Fig 21.[38]S

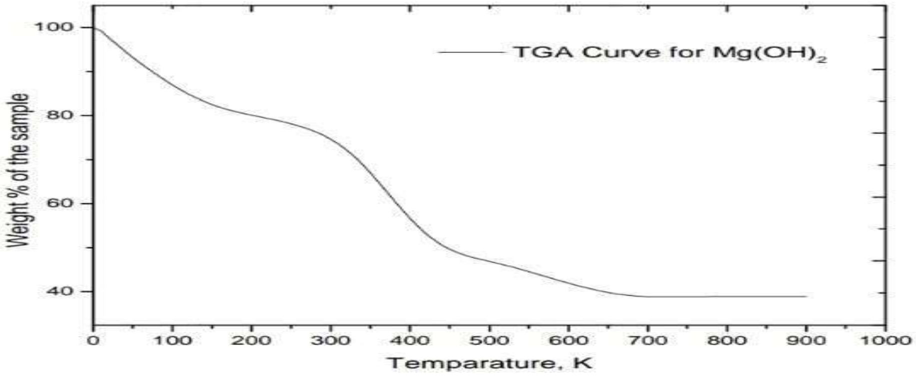

Fig 21: TGA image for MgO NPs

4.Dyes:

For thousands of years, dyes have been widely used in paint, pigment, textile tile, and numerous other applications. Nowadays, dyes are essential to the textile, paint, and pigment manufacturing industries, and there are currently at least 100,000 different types of dyes on the market. It is estimated that 1.6 million tons of dyes are produced annually to meet industrial demand, with 10% to 15% of this volume being discarded as wastewater. Dye is a major water pollutant as a result. Over exposure to dyes can lead to respiratory issues, skin irritation, and, in some cases, an increased risk of cancer in humans. Furthermore, the presence of dyes in wastewater results in a bad odour and increases the demand for chemical oxidation. Therefore, it is crucial to remove dyes from wastewater in an efficient manner to guarantee the safe release of treated liquid effluent into waterways.

4.1. Types of dyes:

Dyes are categorized as natural dyes and synthetic dyes. Natural dyes are comes from the nature such as plant source(Indigo, Saffron, Turmeric, Tea, Fustic), animal source(Lac, Tyrian purple, Cochineal), insects source(Cochineal insect-red, Lac insect-red, violet, Murex snail-purple, indigo blue, Octopus-sepia brown) and mineral sources, as they are extracted from the nature natural dyes are environment friendly, bio degradable and they does not causes any harm. Synthetic dyes are made from the chemicals and they are differentiated according to the ionic and non-ionic nature. Ionic dyes are cationic and anionic(acid, reactive, direct) dyes, non-ionic dyes are vat dyes and disperse dyes. These synthetic dyes are not biodegradable and act as pollutants in the environment. Since then, the dyeing industries have relied on synthetic dyes and have begun to grow internationally, producing close to 8 × 105 tons of synthetic dyes annually. Notably, the textile industry uses about 10,000 different dyes to print and/or colour various types of fabrics, and it holds about 75% of the global dyestuff market.

The majority of synthetic dyes come from petrochemical compounds and are sold in liquid powder, paste, and granule form. They possess multiple potentialities. such as quick and uniform colouring with various classes of manufacturers as listed in the previous section, a large selection of colour pigments and shades, ease of manipulation, stability against a number of external factors, and economical energy use. As a result, most synthetic dyes have negative effects when released into the environment in untreated or partially treated forms. According to a number of reports, the processes involved in textile dyeing (dying, fixing, washing, etc.) use a significant amount of water, and up to 15% of applied dyes escape the textile fibers and end up in wastewater. As a result, an enormous amount of improper discharge is consistently rejected. Chlorinated compounds, heavy metals, sulphur, nitrates, napthol, soaps, and chromium compounds are among the many organic and inorganic pollutants foundin dye effluents, which also have high biological and chemical oxygen demands (BOD and COD). dyes, pigments, and formaldehyde benzine sequestering agents.

Coagulation-flocculation, aerobic and anaerobic treatment, electrochemical treatment, membrane filtration, and adsorption are the usual methods used to treat wastewater. Adsorption is the most widely used of these techniques because of its effectiveness and ease of use. Commercial activated carbon for dye removal is frequently used in dye manufacturing facilities because of its high porosity and large surface area (500–2000m2/g). However, due to high production costs, commercial activated carbon is rather pricey. Activated carbon regeneration also necessitates a high-pressure stream, which raises the system's operating costs. This high price has spurred the hunt for less expensive and more effective alternative adsorbents for removal.

Nanomaterials, also known as nanoparticles, are particles that range in size from 1 to 100 nm. Well-known nanomaterials are generally prized for their low mass, high strength, and highly active sites. Current research focuses on the development of nanomaterials for optical data storage, sensors, and durable and lightweight construction materials in addition to wastewater treatment. Some nanomaterials have two main advantages over activated carbon as adsorbents, despite the fact that both have relatively large surface areas: they can be readily synthesized at a lower cost, and smaller quantities are needed for efficient pollutant removal. Therefore, it is anticipated that for adsorption applications, nanomaterials will become more cost-effective than activated carbon.[11]. Types of dyes with its properties and applications has shown in Table 1.

Table 1:Types of dyes with its properties and applications:

Dye type	Examples	Prperties	Applications	Hazourdous
Cationic	Methylene Blue Jaanus Green Basic Voilet 5 Basic Green 5	Water soluble, Releasing coloured Cations in solution. Some dyes show biological activity	Paper, polyacrylonitrile, modified polyesters, modified nylons, and antiseptics used in medicine	carcinogenic (both malignant and benign tumors)
	Methyl Orange Acid Red183 Acid Red 73		P	

Acidic	Acid Red 18 Acid Orange10 Acid Orange 12 Acid Orange 8 Acid Green 27 Amido Black 10B Indigo Carmine	Soluble in water Anionic	aper, leather, wool, silk, nylon, and inkjet printing	carcinogenic (both malignant and benign tumors)
Reactive	Reactive Black 5 Reactive Green 19 Reactive Blue 4 Reactive Red 198 Reactive Blue 19 Reactive Red 120	Brighter dyeing than direct dyes and extremely high wash fastness because of the covalent bond formed with the fiber	Textiles made of cotton, wool, nylon, and inkjet printing	Occupational asthma, rhinitis, allergic conjunctivitis, and dermatitis
Direct	Cango Red Direct Red 23 Direct Orange 39 Direct Blue 86	Water soluble, anionic, and enhances wash fastness through chelation with metal salts	Leather, paper, cotton, and regenerated cellulose	Bladder Cancer
Vat	Vat Blue 4 Vat Green 11 Vat Yellow 20 Vat Orange 28 Vat Orange 15	Use soluble leuco salts in an alkaline bath (NaOH)following reduction.	The cellulosic fibers	-
Disperse	Disperse Orange 3 Disperse Red 1 Disperse Yellow 1	Non-ionic and insoluble in water; for hydrophobic aqueous dispersion	Cellulose, cellulose acetate, polyester, nylon, and acrylic fibers	Skin-allergic and carcinogenic

4.2. Methods Used for the dye removal :

4.2.1.Adsorption:

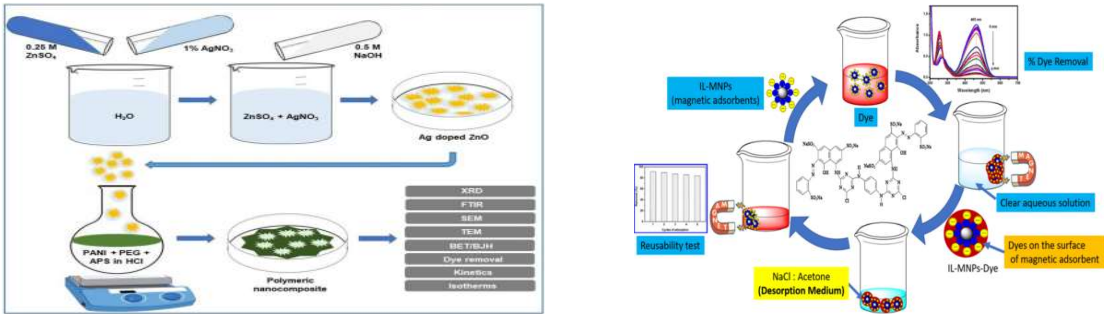

Fig 22: General representation of Adsorption

The adsorption of colors from wastewater is one of the most effective uses of nanotechnology in the field of environmental remediation. Nanomaterials' special qualities, namely their large surface area, adjustable pore size, and increased reactivity, make them incredibly powerful adsorbents. The several nanomaterials utilized in dye removal adsorption techniques are examined in this research along with their benefits, mechanisms, and most recent developments.[12]. General representation of Adsorption Is shown in Fig 22.

Nanomaterials used for the dye adsorption:

1.Natural Nanomaterials:

Because of their natural abundance, biodegradability, and environmental friendliness, natural nanomaterials such as chitosan, clay, and biochar are becoming more and more appreciated in environmental applications. The cationic properties of chitosan, the layered structure of clay, and the porous surface of biochar make them all very efficient and long-lasting adsorbents for the removal of pollutants from water.

- Chitosan and chitosan based adsorbents:

  A natural polysaccharide that is present in relatively large amounts on Earth (such as in the shells of crayfish, crabs, etc.), chitosan can be obtained from food processing by-products and used for a variety of purposes, such as the removal of hazardous pollutants from water. This practice promotes sustainable development and benefits the environment. The fact that chitosan-based materials are far less expensive than other well-known and widely used adsorbents, such activated carbon, is another significant benefit. Because of chitosan's many benefits, such as its adsorption capabilities, accessibility, adaptability, and affordability, scientists are becoming more interested in chitosan-based adsorption materials. As a result, numerous innovative and efficient adsorption techniques have been developed to remove particular pollutants from various kinds of water solutions.[13]

- Biochar:

  In wastewater treatment, biochar—a carbon-rich substance made from biomass pyrolysis—has shown promise as an environmentally benign adsorbent for dye removal. The effective adsorption of different dye molecules is made possible by its vast surface area and high porosity. Furthermore, biochar may be thermally or chemically altered to increase its adsorption capacity, which will improve its interactions with both anionic and cationic dyes. It is the perfect substitute for traditional adsorbents in sustainable water treatment due to its low cost of manufacture, renewability, and biodegradability.[14]

2.Carbon based Nanomaterials:

Because of their vast surface area and porous architectures, which improve their capacity to collect pollutants, carbon-based materials including activated carbon, graphene, and carbon nanotubes (CNTs) are well known for their effectiveness as adsorbents. Because of their high adsorption capacity and adjustable characteristics, these materials are very useful in environmental applications, such as the removal of pollutants and dyes.

- Activated Carbon:

  Activated carbon is the oldest known adsorbent and is often made from wood, lignite, coal, coconut shells, and other materials. It has a huge surface area of 500–2000 m2 g1 and an extremely porous structure . Since van der Waals forces cause adsorption on activated carbon, it has been discovered that this process is typically not selective. Charcoal's capacity to eliminate flavor and odor was noted millennia ago.In addition to removing various colors, activated carbons employed as adsorbents also eliminate metal ions, chlorinated hydrocarbons, and organic chemicals that give off an unpleasant taste or odor. It is commonly recognized that the removal of color and other contaminants from textile and dye wastes may be accomplished economically and effectively through the use of activated carbon adsorption.using Filtrasorb-type activated carbon to remove acidic, basic, disperse, and direct dyes; it was found to be quite effective at removing all colors except direct ones.Three reactive dyes used in the textile industry were adsorbed onto Filtrasorb 400 activated carbons. Additional research was conducted on different activated carbons for the removal of cationic dyes (methylene blue) and anionic dyes (reactive black), and the results showed a positive correlation between the performance of activated carbons and the capacity/surface area of methylene blue.[15]

- Graphene and Graphene Oxide:

Because of its special structural and chemical characteristics, graphene oxide (GO) is a remarkable adsorbent for wastewater treatment dye removal. Its oxygen-containing functional groups, such as hydroxyl, carboxyl, and epoxy groups, increase its hydrophilicity and affinity for a variety of contaminants, and its broad surface area offers a wide range of locations for interactions with dye molecules. These functional groups enable a variety of adsorption processes, such as hydrogen bonding, electrostatic interactions, and π-π stacking, which enable GO to efficiently attract and bind both cationic and anionic dyes.Chemical changes can enhance GO's strong adsorption capability, making it even more efficient and selective for particular dye types, according to studies. Moreover, GO is easily separated after treatment, stable in water, and regenerable for further usage. These characteristics make it a sustainable and viable material for environmental remediation applications, especially when treating industrial wastewater that contains dyes.

- Carbon Nanotubes:

Because of their special mechanical and structural characteristics, carbon nanotubes (CNTs) make excellent dye adsorption materials. Their tubular form and high aspect ratio provide a large surface area that makes it easier for dye molecules to adsorb. The total removal effectiveness is increased by the wide surface area, which enables a large number of dye molecules to interact with the CNTs. Furthermore, CNTs have exceptional thermal stability and mechanical strength, which makes them appropriate for a range of environmental uses, including wastewater treatment. Through a variety of processes, including electrostatic attractions, van der Waals forces, and π-π stacking interactions, CNTs' special qualities allow them to efficiently adsorb both cationic and anionic dyes. Additionally, CNTs' capacity to intercalate dye molecules inside their tubular structure enhances the adsorbent-dye interaction, leading to quicker and more effective adsorption. Because of these qualities, carbon nanotubes (CNTs) are a good option for treating wastewater dye contamination.[16]

3.Metal oxide nanoparticles:

A metallic element is one of the constituents of metallic nanomaterials. To date, dye adsorption has been investigated for one pure metal nanomaterial, nano-zero-valent iron (nZVI), nano-zinc oxide (nano-ZnO), nano-magnesium oxide (nano-MgO), and nano titanium dioxide (nano-TiO2). These metals have quite diverse adsorption methods, physical and chemical characteristics, and belong to various periodic table groups. Adsorption of dyes is mostly a physical process in some adsorbents, including nano-TiO2, which rely on structural and physical morphology. Adsorbents like nZVI, on the other hand, primarily use chemical adsorption to adsorb colors via an oxidation-reduction reaction. The next sections will cover the mechanism of these nanomaterials in adsorption.

- Titanium Dioxide:

TiO_2, or titanium dioxide, is a common material because of its photocatalytic qualities, which can accelerate the destruction of dyes when exposed to ultraviolet light. To increase its capability for dye adsorption, its surface can be altered. For example, it has been demonstrated that doping TiO_2 with metals such as gold or silver increases its photocatalytic effectiveness, enabling the simultaneous adsorption and degradation of dyes. Because of its photocatalytic properties, which can hasten the degradation of dyes when exposed to UV light, titanium dioxide, or TiO_2, is a common substance. Its surface may be changed to improve its dye adsorption capacity. For instance, it has been shown that doping TiO_2 with metals like gold or silver boosts its photocatalytic efficiency and permits dye adsorption and degradation to occur simultaneously.

- Nano magnesium Oxide:

Nano magnesium oxide, or nano-MgO, has been employed for ten years as an antibacterial nanomaterial, a destructive adsorbent for several harmful chemical agents, and an adsorbent for the treatment of wastewater containing dyes since 2009. Crucially, because it may be readily synthesized from a variety of naturally occurring alkaline minerals, the cost of manufacture is minimal. Congored, reactive blue 19, and reactive red 198 are eliminated using MgO nanoplates. Because of their strong basic surface sites, magnesium oxide nanoparticles have a high surface area (150–200 m2/g), which contributes to their comparatively high adsorption capabilities and quick removal of these dyes. Nano-MgO is therefore highly suited for adsorbing anionic dyes by electrostatic attraction since the zeropoint charge occurs at pH 12.4.[17]

Mechanism of Adsorption:

1.Physical adsorption:

Weak van der Waals forces and hydrogen bonds hold dye molecules to an adsorbent surface during the process of physical adsorption, also known as physisorption. Since no chemical bonds are formed during these interactions, the adsorption process is often quick and frequently reversible. The adsorbent may be able to regenerate because dye molecules may readily desorb from the surface due to the weak nature of the forces. Larger areas and porosity increase the adsorption capacity. Physical adsorption usually takes place at low temperatures and is dependent on pore size and surface area.[18]

2.Chemical Adsorption:

The process by which dye molecules create robust chemical connections with the adsorbent surface—typically via covalent or ionic interactions—is known as chemical adsorption, or chemisorption. Chemisorption, as opposed to physical adsorption, entails the sharing or transfer of electrons, strengthening the connection and frequently making it irreversible. Because it takes more energy to create chemical connections, this process is slower than physisorption and often takes place at higher temperatures. Adsorbents can more safely hold onto adsorbed molecules due to the strength of chemisorption, which makes it more stable and selective. The efficacy of chemisorption depends on how well the surface of the adsorbent and the particular dye molecules mix chemically.[18]

3.Electrostatic Attraction:

When the adsorbent and dye molecules have opposing charges, electrostatic attraction—which is the attraction of oppositely charged ions—works very well in dye adsorption. For instance, anionic dyes attach to positively charged surfaces, whereas cationic dyes are drawn to negatively charged adsorbent surfaces. Adsorption is made more effective by this attraction as the charged adsorbent surface generates an electric field that attracts and holds dye ions. The pH of the solution influences electrostatic interactions, which in turn impacts the adsorbent's surface charge and may be modified to maximize dye removal.[19]

Advantages:

Advantages of Adsorption in Nano technology for the dye removal:

- High Adsorption Capacity: Nanomaterials can adsorb huge amounts of dye molecules, even at trace concentrations, thanks to their enormous surface area and many active sites, which improves the efficacy of purification.

- Fast Removal: Nanoadsorbents enable quicker dye removal, improving treatment procedures, because of their tiny size and surface reactivity.
- Enhanced Selectivity: Chemical groups can be added to nanomaterials to functionalize them, increasing their selectivity for specific dye types and enabling more focused and effective adsorption.
- Reusability and regeneration: A large number of nanoadsorbents are stable and reusable, which lowers waste and total operating expenses.
- Multifunctionality: By enabling simultaneous dye adsorption and breakdown, nanomaterials such as ZnO or TiO_2 provide dual adsorption and photocatalytic degradation, enhancing treatment effectiveness.[20]

4.2.2. Photocatalysis:

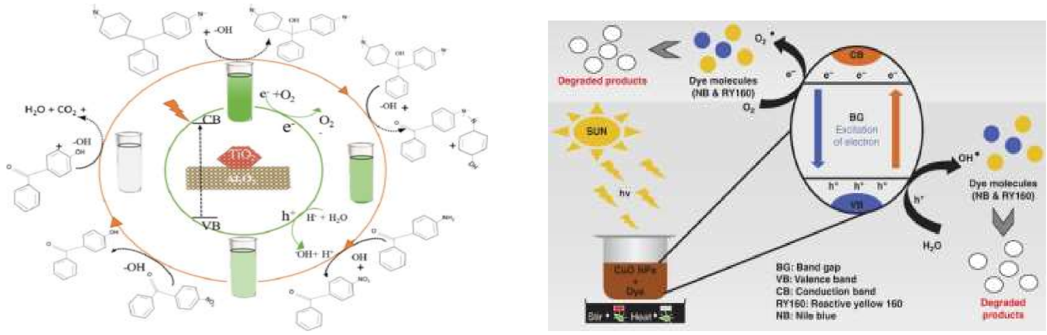

Fig 23: General representation of Photocatalysis

Photocatalysis has emerged as a possible remedy to the growing environmental effect of industrial dye pollution, particularly in wastewater. Complex dye molecules may be efficiently broken down by photocatalysis into non-toxic byproducts, in contrast to conventional chemical treatments. Because of the special qualities of nanomaterials—such as their large surface area, optical characteristics, and improved reactivity—which support robust dye adsorption and ease reactions under light exposure, nanotechnology increases the effectiveness of photocatalysis.[21]. General representation of Photocatalysis is shown in Fig 23.

Nanomaterials used for Photocatalysis:

1.Titanium dioxide:

Titanium dioxide(TiO_2) is widely recognized as a photocatalyst for dye removal in wastewater treatment due to its high photocatalytic efficiency, stability, and low toxicity. Primarily effective under UV light, TiO_2's performance can be extended to the visible spectrum through specific modifications, broadening its application range. Nanostructured TiO_2, like nanotubes and nanoparticles, offers a high surface area, facilitating enhanced dye adsorption and degradation, which significantly improves purification results[22,23]

2. Zinc Oxide:

Because of its excellent photocatalytic activity, chemical stability, and high UV absorption, zinc oxide (ZnO) is a useful photocatalyst for dye removal. ZnO functions well in ultraviolet light, much like titanium dioxide, but it may be modified to increase its activity in the visible range. Large surface areas provided by its nanoscale forms, such as ZnO nanoparticles and nanorods, improve dye adsorption and degradation, making them ideal for wastewater treatment applications.[24]

3.Silver Nanoparticles:

Because of their special optical and antibacterial qualities, silver nanoparticles (AgNPs) are frequently utilized in dye removal procedures. AgNPs boost light absorption by producing localized surface plasmon resonance (LSPR), which increases photocatalytic activity, especially in the visible range. AgNPs are useful for environmental and wastewater treatment applications because they increase electron transfer when paired with photocatalysts like TiO_2 or ZnO, which lowers electron-hole pair recombination rates and increases dye degradation efficiency.[25]

4.Metal Organic Frameworks:

Made of metal ions and organic linkers, metal-organic frameworks (MOFs) are very porous materials that are prized for their large surface area and adaptable structure. These characteristics enable MOFs to capture a range of dye molecules in their pores, making them efficient adsorbents for dye removal in water treatment. Additionally, MOFs can be functionalized or combined with photocatalysts to improve dye degradation, offering a productive and sustainable method of purifying wastewater.[26]

Mechanism of Photocatalysis:

In photocatalysis, photons from light energy—usually UV or visible light—are absorbed by a semiconductor photocatalyst, such as zinc oxide (ZnO) or titanium dioxide (TiO_2). Electrons in the valence band (VB) of the semiconductor are stimulated to the conduction band (CB) by radiation, forming electron-hole pairs (e^-/h^+). These electrons and holes have the ability to react with oxygen or water molecules on the photocatalyst's surface, generating reactive oxygen species (ROS) such hydrogen peroxide ($H2O_2$), superoxide anions ($\bullet O_2^-$), and hydroxyl radicals (•OH). Due to their potent oxidizing ability, these radicals convert pigment molecules into simpler, frequently non-toxic byproducts like CO_2 and H_2O.

Advantages of photocatalysis in Nano technology for the dye removal:

- Complete Mineralization:

  In contrast to physical adsorption, which only traps dye molecules, complete mineralization in photocatalysis breaks them down into simple, non-toxic byproducts like CO_2 and H_2O. This guarantees that dangerous substances are completely removed from wastewater, resulting in a more comprehensive and ecologically friendly treatment.

- High Efficiency:

  Because of their extraordinarily large surface areas, nanomaterials like zinc oxide (ZnO) and titanium dioxide (TiO_2) enhance the number of contact sites that dye molecules may make contact with. In wastewater treatment procedures, this increases the rates of adsorption and photocatalytic degradation, making them extremely effective in dissolving colors.

- Dual Adsorption and Degradation:

  The capacity of photocatalytic nanomaterials to simultaneously adsorb dye molecules onto their surfaces and destroy them when exposed to light is known as dual adsorption and degradation. Because pollutants are efficiently caught and transformed into innocuous byproducts in a single process, this integrated technique improves dye removal efficiency overall.

- Renewable Energy Source:

  Photocatalysis is the process of driving chemical processes for dye degradation using renewable energy sources, mainly sunshine. In addition to lowering operating expenses, this dependence on solar energy lessens the environmental effect of traditional energy sources. Consequently, photocatalytic technologies help create environmentally safe and sustainable wastewater treatment methods.

4.2.3. Membrane Filtration:

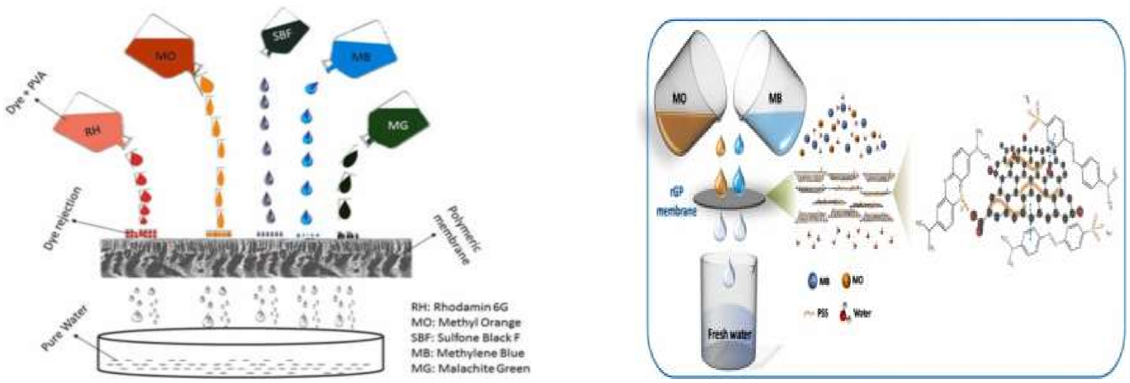

Fig 24: General representation of Membrane Filtration

Significant environmental problems are caused by dye contamination from industrial effluent, especially in textiles, paints, and printing. These persistent pollutants are sometimes difficult to adequately remove using traditional wastewater treatment techniques. Nanotechnology provides creative ways to improve the effectiveness of color removal, especially through the creation of sophisticated membrane filtering systems. [27]. General representation of Membrane Filtration is shown in Fig 24.

Nanomaterial used for the Membrane filtration:

1.Polymeric Membrane:

Because polymeric membranes are versatile, inexpensive, and simple to fabricate, they are frequently used in membrane filtering procedures. These membranes, which are made of different polymers, may be designed to target certain pollutants, such as dyes in wastewater treatment. By adding nanoparticles, their performance may be greatly improved, leading to nanocomposite membranes with better permeability, mechanical strength, and selectivity. For successful dye removal and general water purification in a variety of industrial applications, polymeric membranes can be modified by adding nanoparticles of materials like graphene oxide or titanium dioxide, which can improve photocatalytic activity and fouling resistance.

- Nano composite membranes:

  Advanced materials called nanocomposite membranes are made by incorporating nanoparticles into polymer matrices, such as zinc oxide (ZnO) or titanium dioxide (TiO_2). The features of the membranes are improved by this integration, especially their photocatalytic activity, which is essential for wastewater treatment's dye removal process.The imbedded nanoparticles in these membranes become active and produce reactive species, including superoxide anions and hydroxyl radicals, when they are exposed to UV radiation. The breakdown of dye molecules adsorbed onto the membrane surface is aided by these reactive species. Nanocomposite membranes are a very effective way to deal with dye pollution because they combine adsorption and photocatalytic degradation to remove colors from wastewater efficiently in a single step.[28]

- Graphene Oxide Membrane:

Graphene oxide membranes are novel filtering materials made from graphene oxide that have functional groups that contain oxygen to improve their characteristics. These membranes have outstanding heat stability, strong mechanical strength, and flexibility. Larger dye molecules and impurities are successfully rejected by their adjustable pore diameters, which also enable accurate molecular separation and good water permeability. Furthermore, other materials may be added to graphene oxide membranes to enhance their adsorption capacity and photocatalytic activity, allowing dye adsorption and degradation to occur simultaneously. Because of these characteristics, graphene oxide membranes are very good in treating wastewater and effectively and sustainably addressing dye pollution.[29]

2.Inorganic Membranes:

Materials like ceramics, metals, or composites are used to create inorganic membranes, which have remarkable mechanical, chemical, and thermal durability. These membranes' resistance to fouling and deterioration makes them perfect for wastewater treatment, especially for the removal of dyes. For example, consistent pore structures seen in ceramic membranes allow for efficient dye separation while preserving high flux rates. The adsorption capacity and selectivity of inorganic membranes can also be improved by adding nanomaterials, such as silica nanoparticles or metal-organic frameworks (MOFs). Their longevity and effectiveness reduce the need for chemical additions in wastewater treatment systems, making them more sustainable and efficient.

- Silica Nanoparticles:

  Because of their large surface area, adjustable porosity, and superior durability, silica nanoparticles are useful for a variety of processes, including the removal of dyes from wastewater. Sol-gel techniques may be used to create these nanoparticles, giving exact control over their surface characteristics and size. Because of their enormous surface area, which offers a wealth of active sites for interaction with pollutants, silica nanoparticles can efficiently adsorb dye molecules in the context of dye removal.Additionally, silica nanoparticles can be functionalized with various chemical groups to improve their adsorption ability and selectivity for particular dye types. To increase overall filtration efficiency and fouling resistance, they can also be added to membrane systems or hybrid materials. Because of its biocompatibility and non-toxicity, silica nanoparticles are a sustainable choice for environmental applications. All things considered, their special qualities allow for effective color removal while encouraging environmentally acceptable wastewater treatment methods.[30]

- Metal Organic Frameworks:

  Metal-organic frameworks (MOFs) are very porous materials made up of a three-dimensional network of metal ions bonded to organic ligands. Their remarkable surface area and adjustable pore sizes have earned them a reputation as very efficient adsorbents for a range of uses, including the removal of dyes in wastewater treatment. Because of their adaptable architectures, MOFs may selectively trap dye molecules, enabling the targeted removal of certain pollutants. Furthermore, their high porosity promotes quick adsorption kinetics, which raises removal efficiency overall. Because MOFs may be functionalized, their efficacy is further increased, giving them a viable option for the effective and sustainable treatment of dye wastewater.[31]

Principles of Membrane Filtration:

- Micro Filtration:

  Microfiltration membranes work well in pre-treatment procedures to clear liquids and safeguard finer filtration systems later on by removing particles bigger than 0.1 micrometers, such as suspended particulates and some microorganisms.

- Ultra Filtration:

  Ultrafiltration captures bigger organic molecules, viruses, and colloids by focusing on particles that are between 1 and 100 nanometers in size. It is frequently employed in biomolecule separation, water purification, and water preparation for further filtration steps.
- Nano Filtration:

  Nanofiltration membranes efficiently capture tiny organic molecules and divalent ions by filtering molecules with a diameter of 1–10 nanometers. When treating wastewater containing dyes, NF is perfect for softening the water and partially eliminating dissolved chemicals.
- Reverse Osmosis:

  Reverse osmosis membranes remove organic molecules and dissolved salts to provide high purity by filtering ions, molecules, and bigger particles. For desalination and complete color removal in wastewater treatment applications, RO is widely utilized.

Applications:

- Textile Industry and Waste water treatment:

  One of the main sources of dye pollution is the textile sector. Nanotechnology combined with membrane filtration has shown promise in the treatment of wastewater from textiles. For example, hybrid systems that combine photocatalytic membranes and nanofiltration have been developed to improve dye removal rates, with over 90% removal efficiency for reactive dyes.

- Dye Recovery and Reuse:

  Additionally, dye recovery from wastewater can be facilitated by advanced membrane technology, enabling the reuse of precious dye ingredients. For instance, studies have demonstrated that membranes modified with silver nanoparticles and polydopamine may selectively absorb colors while preserving high flux rates, allowing for dye recovery and recycling in the textile sector.

- Integrated Membrane System:

  Overall dye removal can be improved by combining membrane filtration with other treatment techniques like adsorption or biological processes. Because the membrane acts as a pre-treatment step to lessen the strain on downstream processes, hybrid systems that combine membrane filtration with activated carbon or biosorbents, for example, show enhanced removal efficiency.

4.2.4. Electro Chemical treatment:

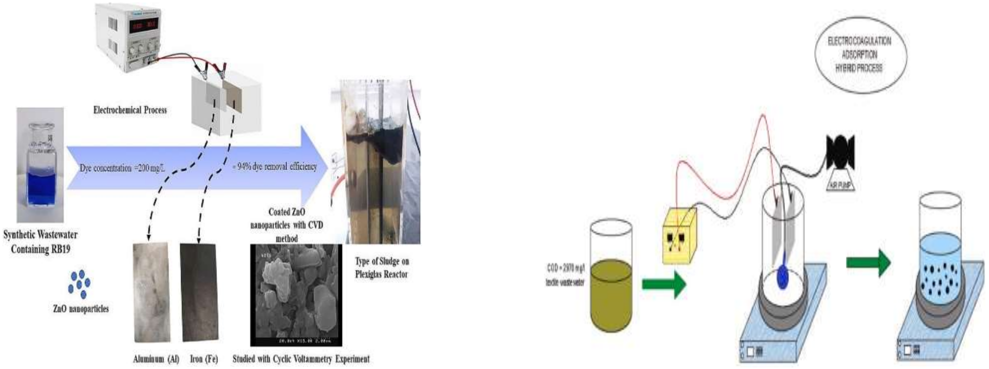

Fig 25: General representation of Electrocoagulation

The process of electrochemical treatment uses electrical energy to propel chemical processes that break down wastewater contaminants. Because of its strong selectivity and capacity to generate hydroxyl radicals, potent oxidizing agents that may degrade complex colour molecules, it is especially useful for treating organic dyes. Processes for electrochemical treatment fall into a number of types.[32]. General representation of Electrocoagulation is shown in Fig 25.

- Electrocoagulation:

  Electrocoagulation is a successful water treatment method that releases coagulant ions into wastewater using metal electrodes, usually made of aluminium or iron. These ions coagulate into bigger particles that settle or are easily filtered out when an electric current is applied. This reaction occurs with dye molecules and other contaminants. By eliminating pollutants, reducing turbidity, and removing colours, electrocoagulation is a flexible and effective wastewater treatment method.[32]

- Electro-Oxidation:

  An electrochemical process called electro-oxidation involves oxidizing organic contaminants, including dye molecules, at the anode. Reactive species such as hydroxyl radicals, which are potent oxidants that degrade complex dye molecules into simpler, non-toxic byproducts, are produced during this process. Wastewater's color and pollutant load are successfully decreased by this treatment. Electro-oxidation is a useful method for treating industrial wastewater because of its effectiveness and adaptability.[33]

- Electro- Fenton Process:

  The Electro-Fenton process is a sophisticated electrochemical technique that breaks down pollutants by combining Fenton's reagent (iron ions and hydrogen peroxide) with electrochemical oxidation. This technique involves reducing oxygen and then reacting with iron ions to produce hydroxyl radicals in situ at the cathode. Because of their great reactivity, these hydroxyl radicals effectively cleanse wastewater by dissolving dye molecules and other organic pollutants into simpler, non-toxic chemicals.[32,34]

- Electro Chemical Reduction:

  An electrochemical cell's cathode reduces dye molecules and other contaminants as part of the wastewater treatment process known as electrochemical reduction. Because azo dyes have nitrogen double bonds that are hard to break down, this approach works very well for them. Electrochemical reduction reduces wastewater's colour and toxicity by converting complex contaminants into simpler, frequently less harmful chemicals by transferring electrons to the dye molecules.[32,35]

Nano materials used in Electrochemical treatment:

- Metal Oxides:

  Zinc oxide (ZnO) and titanium dioxide (TiO_2) are two examples of metal oxide nanoparticles that are commonly employed because of their superior photocatalytic and electrochemical capabilities. In the Electro-Fenton process or as anode coatings, they encourage the generation of hydroxyl radicals when a voltage is applied. For instance, under UV radiation, TiO_2 exhibits great stability and reactivity, efficiently oxidizing colour molecules. Especially when it comes to dye degradation, ZnO nanoparticles are also quite effective in producing reactive species.[36,37]

- Carbon based Nanomaterials:

  High electrical conductivity, a huge surface area, and chemical stability are characteristics of carbon-based nanomaterials like graphene and carbon nanotubes (CNTs). By increasing electron transfer rates, graphene-based electrodes can promote effective dye degradation via electrochemical processes. Because of their tubular shape, CNTs also increase the electrodes surface area and conductivity, which promotes dye molecule adsorption and degradation.[38]

- Noble metal Nanoparticles:

  In electrochemical systems, noble metal nanoparticles such as platinum (Pt), gold (Au), and silver (Ag) are frequently employed as catalysts. By improving dye removal rates, these nanoparticles can raise the electrodes' catalytic efficiency. They work especially well in the electro-oxidation process because of their catalytic activity, which speeds up the production of reactive oxygen species.[39]

- Metal Organic Frameworks:

  MOFs are appropriate for dye adsorption and catalysis because they are porous materials with large surface areas and adjustable pore diameters. MOFs can be coated on electrodes or mixed with other materials to enhance their adsorption and catalytic properties in electrochemical applications. They are therefore useful substances for dye removal procedures, especially where specific dye adsorption is needed. [40]

Applications:

- Textile waste water treatment:

  One of the biggest contributors to dye pollution is the textile sector. Textile effluent frequently contains complicated colour combinations, which can be effectively treated by electrochemical systems augmented by nanotechnology. TiO_2-coated electrodes, for instance, may efficiently break down dyes when exposed to UV radiation, but electrodes enhanced with graphene increase the rate of electron transfer, hence increasing treatment effectiveness.

- Industrial Dye removal system:

  The creation of small and effective industrial wastewater treatment systems is made possible by nanotechnology. Integrated electrochemical cells using nanomaterials such as CNTs and noble metals may be made to run continuously, which makes them appropriate for large-scale dye removal in a variety of sectors, such as pharmaceuticals, cosmetics, and polymers.

- Portable dye removal devices:

  Portable electrochemical devices for on-site dye removal can be created with the help of nanotechnology developments. By treating small-scale dye pollution from artisanal dyeing, these devices which have electrodes based on nanomaterials ensure that even smaller sources of pollution may be efficiently controlled.

- Hybrid Electrochemical system:

  It has showed promise for improved dye removal to combine electrochemical treatment with other nanotechnology-based techniques like adsorption or membrane filtering. For example, integrating graphene-oxide membranes with electrochemical oxidation produces a dual function of adsorption and degradation, increasing the efficiency of dye removal in a single step.

5.Comparing Adsorption with other dye removal Methods:

Comparing the Adsorption with other dye removal methods like Photocatalysis, Membrane Filtration, Electrochemical treatment

5.1.Effectiveness and Efficiency:

- Adsorption: Adsorption, especially for stable dye molecules, produces significant dye removal efficiency across a broad concentration range. For instance, a research that used coconut shell-derived activated carbon removed almost 95% of the dye from industrial effluent in just 60 minutes.
- Photocatalysis: Although photocatalysis may efficiently break down dyes, particularly when exposed to UV light, it frequently necessitates extended exposure periods and certain lighting conditions. Depending on the light intensity, a case study published in the Journal of Hazardous Materials showed that TiO_2-based photocatalysis destroyed dye by around 90% after a few hours.
- Membrane Filtration: Although membrane filtration is effective at removing large amounts of dye for certain particle sizes, it suffers from fouling, which is a buildup of dye molecules on the membrane surface that lowers efficiency. According to a research that used nanofiltration, fouling caused efficiency to decrease over repeated cycles even while dye rejection rates were above 90%.
- Electrochemical treatment: High dye removal efficiency is attained by electro treatment, particularly for resistant dyes like azo dyes. However, variables like dye concentration, current density, and pH control affect efficacy. For instance, electrocoagulation removed 85% of the dye after 90 minutes, but results differed depending on the dye concentration.

5.2.Energy Consumption Cost:

- Adsorption: Adsorption is economical for large-scale applications due to its energy efficiency and little requirement for agitation or pumping. Some adsorbents, like activated carbon, are regenerative, which further lowers long-term expenses.

- Photocatalysis: Although photocatalysis can be less expensive when sunlight is used, it is energy-intensive if UV radiation is needed. Unfortunately, photocatalysis is less effective in natural light, which makes it a more costly and energy-intensive solution, particularly in areas with little sunshine.

- Membrane Filtration: Membrane filtration requires pressurizing the system, which might result in significant operating expenses. Maintenance costs are also greatly increased by the periodic cleaning or replacement of membranes to address fouling, particularly when processing dye-laden effluents.

- Electrochemical treatment: The electric current must be maintained continuously during electrochemical treatment, and electrode deterioration over time raises the expense of replacement. Even while electrochemical treatment works well for small-scale applications, it is typically more expensive for big amounts of industrial wastewater.

5.3. Environmental Impact and Sustainability:

- Adsorption: Adsorption is ecologically beneficial since it makes use of sustainable resources like biochar made from agricultural waste. Adsorption procedures produce little secondary contaminants, and regenerative adsorbents minimize waste creation.

- Photocatalysis: Although photocatalysis can provide ecologically safe byproducts, it necessitates certain catalyst materials, and if nanoparticles like TiO_2 are discharged into the environment without adequate containment, they might pose health hazards.

- Membrane Filtration: Intensive dye sludge from membrane filtration needs to be disposed of carefully. Membranes themselves need to be disposed of or recycled safely since they have a finite lifespan.

- Electrochemical treatment: Metal sludge produced by electrochemical treatment presents disposal issues. Additionally, the procedure adds metal ions to wastewater, which calls for additional treatment to prevent pollution of the environment.

5.4.Simplicity and Operational Control:

- Adsorption: Adsorption is appropriate for smaller operations or decentralized treatment facilities since it is simple to deploy and needs little technical know-how.
- Photocatalysis: Because photocatalysis needs UV light and regulated reaction conditions (such as pH and catalyst concentration), it becomes more complicated to operate and might not be feasible in all places.
- Membrane Filtration: In order to regulate fouling, pressure, and flow rates, membrane filtration systems require routine monitoring, which can be resource-intensive and technically complex.

- Electrochemical treatment: Electrochemical treatment is a technically demanding process that requires constant monitoring of parameters such as current, pH, and electrode state. Comparison of the Adsorption with other methods is shown in Table 2.

5.5.Comparison Table:

Table2: Comparing the Adsorption with other methods.

Parameter	**Adsorption**	**Photocatalysis**	**Membrane Filtration**	**Electrochemical Treatment**
Efficiency	High	Moderately High	High	Moderately High
Operational Cost	Low	Moderate	High	High
Energy Requirements	Low	Moderately High	Moderate	High
By product Generation	None	Non-Toxic	None	None
Scalability	High	Moderate	High	Moderate
Maintenance	Moderately Low	Moderate	High	High

6.Conclusion:

In the context of wastewater dye removal, this study shows that each treatment technique—adsorption, photocatalysis, membrane filtering, and electrochemical treatment—has particular advantages and disadvantages. Adsorption is preferred due to its ease of use and affordability, although photocatalysis has the benefit of mineralizing colours into non-toxic byproducts. Although it is more expensive, electrochemical treatment shows promise in producing reactive species for dye degradation, whereas membrane filtration excels in separation efficiency but has drawbacks such fouling. Economic factors, treatment objectives, and particular wastewater properties all play a role in choosing the best approach.

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