CHAPTER-1

General Introduction

Chapter 1: Introduction

Living on Earth is a tough challenge nowadays; the basic requirements for living are air, water, and the properties of soil. It is a natural gift for us, but these are all gifts becoming hazardous, polluted day by day. The reasons for the hazards and pollution of these areas are human development. Development should be going on, but taking into consideration of future global environmental impact on humans and other living organisms. In the United States of America, total water intake for men and women is 1.7–7.9 and 1.3–6.1 L/24hours, respectively[1]. In this chapter, we will discuss water pollution with its need, and its uses. The remediation or treatment of the water will also be covered, with an emphasis on the methods by which it is being contaminated. By discussing the merits and demerits of the various approaches, we will clarify why the best approach is required to acknowledge the problem of water pollution quickly and affordably.

1.1. Water and Its Sources:

All life on Earth depends on water, and people specifically need fresh water for drinking, cooking, bathing, and washing. The most significant use of both surface and groundwater is in the agricultural and industrial fields. Because of the presence of water, seasonal natural phenomena occur. In terms of precipitation, condensation, evaporation, and melting of water, they are hydrologically interconnected, which maintains the balance of the ecosystem with water. America, Asia, Europe, and Africa each have a 45, 28, 15.5, and 9 per cent share of the estimated 43,750 km^3/year total water resource. Additionally, this survey found that the proportion of water resources per person in America, Europe, Africa, and Asia was 24,000, 9300, 5000, and 3400 m^3/year, respectively [2]. Since the ocean covers 70% of the planet, there is already water on the ground, in rivers, and on the surface, but as daily pollution on land rises, so does the demand for it. According to WHO/UNICEF (2004), 1.1 billion people do not have access to safe water supplies, and over 2.6 billion people do not have basic sanitation. Water remains liquid between 0°C and 100°C. Oceans cover 71% of the planet and hold 97.5% of all water. 2.5 per cent of all water is available on land. A significant portion of water (1.9% of the total) is available in glaciers and ice caps. The remaining 0.6% of the total support's life as a whole. It is known as fresh water (water that contains less than 0.5 per cent salt). Over 90 % of this freshwater is located underground as groundwater. The resume 10 % of freshwater comes from soil, water vapour in the atmosphere, and surface water from lakes, ponds, rivers, and dams [3, 4].

1.1.1. Ground Water:

Essential elements of the natural hydrological cycle that support life on Earth are groundwater and surface water supplies. Both natural and man-made processes have caused them to undergo significant alterations in the last few decades [5] . The holy Ganga River in northern India rises from the Himalayan Gangotri glaciers and flows for around 2525 km before emptying into the Bay of Bengal. Approximately 26.2 % of India's total land area is made up of the Ganga River basin, one of the greatest alluvial systems, which forms massive multi-aquifer groundwater reservoirs that reach depths of over 2000 meters [6]**.** In the rainy season, groundwater level increases, and in states like Gujarat, Rajasthan, people collect harvested water for their daily needs. It has various advantages, including helping to control floods, runoff loss, and soil erosion, as well as collecting rainwater and directing it into subterranean aquifers, thereby replenishing groundwater.

1.1.2. Fresh Water:

Freshwater on Earth makes up 2.5 per cent. Three primary reservoirs can be formed by further breaking down this freshwater. The cryosphere, which is mostly kept in ice sheets and glaciers, makes up over 68.5 % of all freshwater on Earth. The remaining freshwater (around 31 %) is largely found in aquifers, which are underground water sources, but it is also found in land reservoirs as surface water and soil moisture. At just 0.1% of the total freshwater on Earth, the atmosphere is the smallest freshwater reservoir. 99.9% of this water is in the form of vapour, with the remaining 0.1% of the atmosphere consisting of suspended liquid and solid water in clouds [7]. Our lives depend heavily on water, a natural resource that is becoming more and more limited as a result of bad rainfall, population growth, and industrial and agricultural activity. While India is home to 16% of the world's population, it only has access to 2.5% of the world's land area and 4% of its water resources. Water is a precious resource for more than 60% of the world's population, and 36% of the fresh water reserves are found in Asia. Africa is in a better position than Asia, with 11% of its fresh water reserves accessible to 13% of its population. South America, with 6% of the world's population and 26% of its fresh water reserves, is followed by North and Central America, with 8% of the population and 15% of its fresh water reserves, and Australia and the Ocean, with 1% of its population and 5% of its fresh water reserves [8].

1.2. Various Water Pollution Sources

Water pollution sources are in two forms: point and non-point sources [9]. Groundwater is the most commonly used drinking water source in rural areas [10]. Human activities such as the widespread applicability of pesticides, herbicides, fertilizers, fuel leaks, chemical tanks, industrial chemical spills, household chemical drainage, poorly managed landfills, etc., can contaminate groundwater [11]. In various developing nations, the problems of drinking contaminated water and experiencing sanitation difficulties are growing daily as a result of urbanization and industrialisation. Unsanitary and tainted drinking water is closely linked to common illnesses, including cholera, diarrhoea, dysentery, hepatitis A, etc. Over 842,000 individuals worldwide are thought to pass away from diarrhoea each year[12]. There are several water wastewater pollution sources, which also arise from point and non-point sources, but they can be discussed in terms of various water pollution occurrences in the environment, like domestic, agricultural and industrial.

1.2.1. Domestic Water Pollution:

This type of water pollution arises from areas where people reside, including their living, eating, bathing, and cooking systems. These include a restaurant, shops, laundries, households, commercial buildings, and confectioneries. Various types of waste are generated here, which can pollute both the surface and groundwater, including soap solutions, oil spillage, cosmetic materials, and daily-use cleaning chemicals, as well as other grease-type materials. Plastics are used in homes instead of biodegradable bags, which take a long time to break down and can lead to cancer-causing amounts of water in surface and groundwater. These domestic pollutants damage the parameters of water quality like odour and taste, pH, BOD, COD level, and pathogenic problems [13]. In some cases, collected water samples were analysed from various households, and further analysis in the lab confirmed the presence of threats causing antibiotics[14]. If treatment is not received, the wastewater produced by restaurants' cooking, cleaning, and other operations, which include high levels of suspended solids, BOD, COD, and fat, oil, and grease, could seriously endanger both human health and the environment. In our daily lives, the use of soaps and detergents for cleaning and washing tasks in restaurants is so widespread that the repercussions are occasionally disregarded. A significant number of xenobiotic chemicals are being moved into the environment as a result of the widespread and haphazard application of detergents [15]. The manufacturing of ethoxylated surfactants and other raw chemicals, which are frequently found in consumer goods, including shampoo, body wash, dish soap, and laundry detergent, produces 1,4-dioxane as a contaminant. This chemical is known to be a probable carcinogen and is mobile and persistent. Among the many ways that people might be exposed to 1,4-dioxane are through the use of drinking water and the use of products [16]. Various personal care products, chemical excreted, used in households, can cause water pollution. These may be from deodorants, diaper creams, lotions, oils, shampoos, skin cleansers, hair care products, lotions, nail paints, and perfumes etc. Personal care items are increasingly being loaded into wastewater systems and, subsequently, the environment as a result of the growing variety and availability of personal care products from retail stores. As a result, the inactive and physiologically active components of personal care products are continuously and persistently leaking into the atmosphere. Municipal wastewater is the main way that personal care items are exposed [17].

1.2.2. Agricultural Water Pollution:

As the population increases, the field work for food and corps requirements is also being increased. Several agro products as chemical materials are being used to fulfil the climate as well as crop requirements, which are day to day decreasing the soil fertility. Agrochemicals, such as fertilizers and biocides, are hazardous substances that are purposefully used to maximize their toxic properties. When levels increase, they become water contaminants [18]. Nearly all agro-developing nations permit the use of nitrogen fertilizers; nevertheless, from the point of production to the site of use, the fertilizers leave behind nitrogen oxides, such as nitrate, in the soil, which can lead to soil erosion and groundwater contamination. Given all of these concerns about nitrogen fertilizers, it is imperative to prevent water pollution from these sources [19]. The leaching of fertilizer has two major disadvantages. First of all, leaching causes fertilizer loss. Second, the leached material can contaminate subsurface water, which is frequently used untreated for drinking. Regretfully, it is yet unknown how much nitrates from agriculture contribute to water bodies. For instance, pesticides used in agriculture, such as herbicides, fungicides, and insecticides, have contaminated groundwater and surface water. Water supplies may experience eutrophication, algal blooms, and other negative consequences from the overuse of chemical fertilizers and pesticides. Although insecticides are typically utilized through spraying in fields and crops to prevent the growth of pests that damage them, it has been noted that these sprays also kill pollinators and other beneficial insects. It was a loss, but it wasn't the end because these chemicals were carried by the rinsed water from agricultural land that was transferred to canals and rivers, causing health issues when the sprayed food was consumed. It subsequently entered human bodies for drinking and was once more utilized to produce plants, beginning an endless cycle in the food chain [20] [21]. Sometimes, metal-containing herbicides or pesticides pose some threats in agriculture when used. When lead or mercury-based agrochemicals are used can harm the health of humans through agricultural pathways to drinking water sources. When these pollutants rise, they will create an algal bloom in the surface water, which will cause the organisms to lack oxygen and die. This will also cause animals on the surface to die from a lack of oxygen in their drinking water, and the entire ecosystem will be impacted by the runoff of contaminated water from agricultural sources [22]. Population growth, climate change, and other patterns of consumption are the main causes of agricultural water pollution, while increased use of pesticides, agrochemicals, antibiotics, and other animal feed ingredients is the secondary cause. These components enhance the load of nitrogen, phosphorus, BOD, and other salts and increase the likelihood of low surface runoff of water in agricultural fields. A contaminant of growing concern that arose from agriculture is animal excrement, which is handled, used, and stored in an improper way when certain pesticides are used [23]. As the fertilizer use in all developing countries will increase, agricultural water pollution will increase. In a country like China increasing population pose a challenge to the agricultural field to grow a high number of foodstuffs by using fertilizers due to which water pollution also increasing. Due to environmental degradation, the agriculture industry in emerging countries is also focusing on adaptation. This includes constructing dams, improving crop tolerance to drought, producing stronger seeds, and growing crops that are adapted to acid rain. To achieve short-term benefits in place of long-term benefits, countries are receiving subsidies, and due to long-term environmental pollution, such as water pollution, comes into effect [24].

1.2.3. Industrial Water Pollution

There are several industries worldwide working in different fields of production and synthesis on a commercial level, but the side products left out by the industries are directly going into the surface and groundwater. By this activity, flora and fauna became in a dangerous zone when they drink or use this polluted water. There are several inorganic and organic types of hazardous waste entering water to make it wastewater. Out of all these, some are carcinogenic, and some have long-term effects on the body. Industries release various types of heavy metals, organic fluids, trace inorganic and organic matter, polychlorinated biphenyls, pesticides, detergents, and dyes etc. These materials are toxic, carcinogenic, and unhealthy to biota as well as to humans [25]. The quality of crops grown can be seriously harmed by the negligent handling of industrial wastewater disposal used for crop irrigation, which can go into the food chain as well. Various diseases such as diarrhoea, cancer, jaundice, hepatitis, typhoid, and giardiasis can be impacted by industrial polluted water [26 27]. The type of plant and the industry illustrate the kind of toxins found in industrial wastewater. Examples of industries that generate wastewater include the mining field, steel and iron manufacturing facilities, industrial laundry facilities, power sectors, oil and gas fracking operations, metal finishers, and the food and beverage industry. Treatment of wastewater from industries is often challenging since each setup and treatment facility must be examined separately on an industry-by-industry basis. Filter presses are therefore used on the site for the operation of effluents in wastewater to address this [28 29].

Heavy metals such as chromium, iron, molybdenum, zinc, mercury, lead, bismuth, and arsenic are found in industrial wastewater [30]. Oil refineries, drug synthetic materials from industries release phenol and phenolic compounds into the water body. Wastewater carries a variety of poorly biodegradable refractory pollutants observed by the petrochemical industries, containing hydrocarbons, naphthalenic acid, olefins, nitrobenzene, sulfides, and aniline [31]. Water is applied in numerous manufacturing operations in the dyeing and printing industries, which produce urea, ammonium nitrogen, and other nitrogenous and phosphorus wastes. Because perfluoroalkyl acids have great stability, strong surface properties, and oil-water repelling properties, they are employed as surface protectors. But two perfluoroalkyl acids that may pose health hazards are perfluorooctanoic acid and perfluorooctane sulfonate [32 33]

1.3. Industrial Dyes Water Pollution

To colour fabrics, leathers, hair, fur and plastics materials, dye materials are required, which are synthesized in industries, basically in the textiles industry. Over 95 million workers in India are working in the textiles industry, which is the third-largest producer of textiles worldwide [34]. Dyes are classified in various categories based on chromophoric group: Azo dyes (-N=N-), Nitro dyes (-NO_2), Triphenyl methyl dyes, Indigoid dyes, Phthalein dyes, Anthraquinone dyes, and Nitroso dyes. In all of these, 70 % of dyes belong to azo dyes like monoazo, diazo, etc. They are widely used in the food, paper, paint, pharmaceutical, cosmetic, leather, and textile fields. These dyes, when released into the water body, do not degrade themselves, and if degraded, they leave their moiety residue as toxic by-products. Various physicochemical impacts occur when dyes are mixed into water: The total suspended solid concentration increases, BOD and COD values change, pH and odour of water vary, and total dissolved solid concentration increases [35].

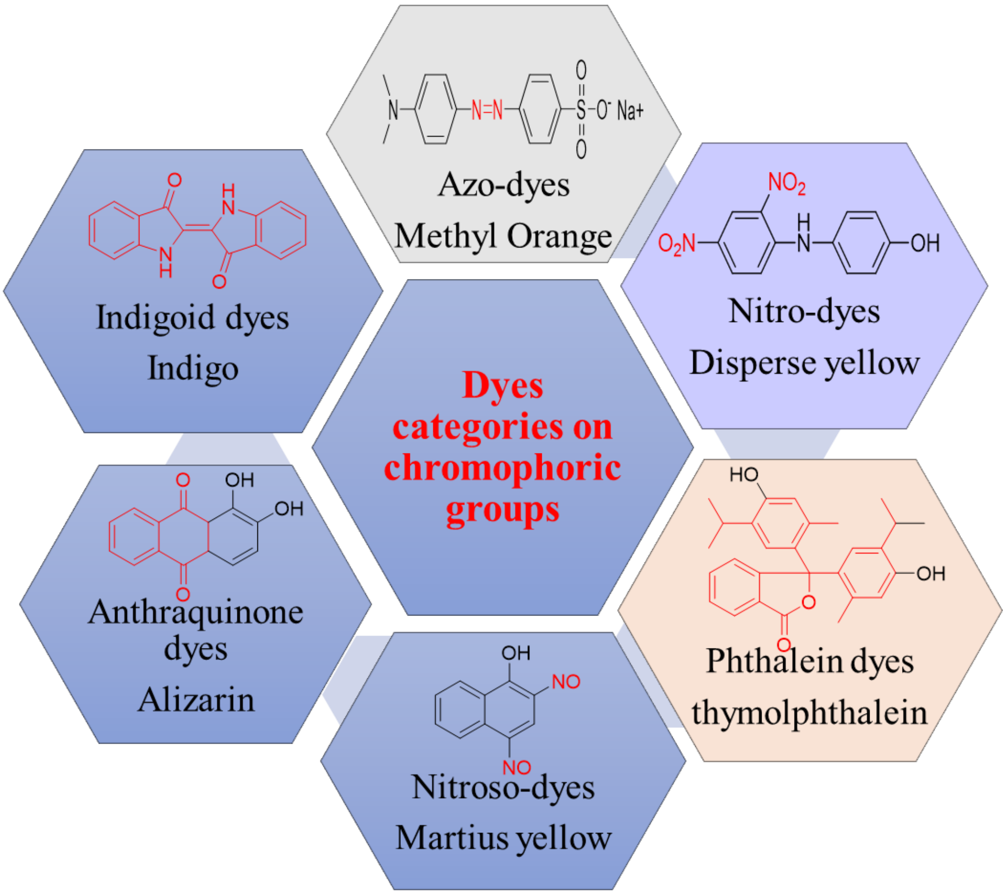

Figure 1-1. Various chromophoric categories of dyes with structure.

Some other types of dyes exist based on industrial utilization, like vat dyes, basic dyes, acidic dyes, direct dyes, disperse dyes, Sulphur dyes, and reactive dyes. When the concentration of all the above-discussed physicochemical parameters increased, the health risk possibility increased after accumulation in water, like cancer, skin infection, respiratory problems, etc. A higher number of ionic dyes are water soluble. Textiles and the paper industry mostly use the cellulosic fiber dyes for colorization, and they are all reactive [36]. It is observed that seventeen to twenty per cent of water pollution is achieved through industrial textiles dyeing and fiber finishing processes [37]. Almost 2,80000 tons of dyes effluents are globally discharged into the water as waste, and seven lakh tons are produced for commercial purposes yearly. In European countries, eels are an endangered species due to the existence of these toxic dyes, especially in the muscle tissue of eels [38]. The dye industry releases toxic gases such as Sulfur, formaldehyde, nitrogen oxides, volatile compounds, particulate matter, and dusts, all of which have an unpleasant odour. Negative health risks arise when chemical dye effluent and its byproducts are found in wastewater media or dust from the textile areas. For example, methylene blue dye hinders the inhibition of the growth of microalgae, disperse yellow 3 has a carcinogenic impact with liver damage and development of hepatocellular tumours. Rhodamine B has a reverse mutation in some stains of Salmonella that makes it mutagenic. Crystal violet dye may cause skin irritation due to inhaling, and is dangerous for the lungs. Reactive red 120 is generally hazardous for aquatic flora and fauna [39–41]. Many textile producers utilised methylene blue, a significant cationic dye that emits aromatic amines like benzidine and methylene and may cause cancer.

1.3.1. Literature survey on water pollution by dyes and their removal

In literature, various industries use organic synthetic dyes like azo, reactive, acidic and basic dyes. Higher numbers of synthetic dyes are illustrated to be carcinogenic, mutagenic, and toxic to microorganisms and human health. From aquatic systems, the removal of these hazardous dyes was investigated by various authors using various sources of materials and methodologies. Generally, three major approaches, that is, physical, chemical and biological, are used in the literature to decontaminate these pollutants from dye containing water bodies. These are adsorption, coagulation, ion-exchange, and membrane separations (physical approach), photochemical degradation, Fenton's reagents utilisation, electrochemical approach and ozonation (chemical approach), and by use of microorganisms, enzymes and other biological approaches [42,43]. Physical methods are upfront methods and generally use the principle of mass transfer [44].

1.3.1.1.1. Removal of dyes by biological, chemical and physical approaches:

1.3.1.1.2. Using microbial biomass

In this biological approach, bacteria, fungi, yeast or algae are utilised for the decontamination of textile dye effluents from wastewater. The interaction of the cell wall and dye described a bigger role during the decontamination steps. Two different types of bacteria can play a role in removal, which are gram-positive and gram-negative. In the case of fungi, filamentous types are very effective in removal. This approach of dye removal has some disadvantages, like sludge formation, poor regeneration, and a slow start-up time [45]. Some approaches for dye removal are discussed here.

1.3.1.1.3. Enzyme Degradation

The dye effluents using biological enzymes can be degraded. Enzymes have good selectivity for the removal of dyes. The fungi Phanerochaete and Trametes, which cause white rot, will be primarily responsible for the outcomes; however, enzymes from both anaerobic and aerobic systems are efficient in decolourising the dyes. The percentages at which bacterial enzymes, specifically laccase, peroxidase, and azoreductase, can break down azo dye are encouraging [46,47]. It also has some disadvantages, like being challenging for an industrial setup, selective enzymes for the selective dye issue, and toxic waste generation after degradation [48].

1.3.1.1.4. Advanced oxidation approach

The basic theory of this process is to completely degrade the dyes or organic pollutants from the wastewater stream. It uses a free radical mechanism approach for degradation. These radicals may be hydroxyl, peroxide, peroxyl, carbonate or sulfate radicals. These can be generated through chemical, photochemical, Sono chemical, or electrochemical approaches. It has disadvantages like the generation of nitro radicals after the maximum degradation steps; it is only applicable to lab scale, perfectly, and during specific radical generation, some other radical ions are generated, which is problematic [48].

1.3.1.1.5. Electrochemical approach

This method includes the use of an electrode based on the reduction and oxidation of dyes through electrons. Electrode production is generally done with graphite, metals, diamond electrodes, and a chlorinated electrode system to decompose the dye solution in a wastewater system. It has several disadvantages, like high cost for electrode preparations, chlorinated by-products, pH adjustments, and monitoring [49,50].

1.3.1.1.6. Photochemical Method

Photocatalyst degradation is a method where, in the presence of light, a photocatalyst active material degrades the dye effluent. Catalyst must have a band gap within the semiconducting range to cause this degradation. Various researchers have utilised different photocatalysts, like graphite-nitride, titanium oxide, zinc oxide, and CdS. There are two approaches to photodegradation: one is the homogeneous way, and another is the heterogeneous way. Heterogeneous photodegradation is better than homogeneous because of no leaching of catalyst into the water system [51]. There are a few disadvantages of this method, like a particular wavelength of light is required, making it high-cost, and the selection of an improper catalyst [52].

1.3.1.1.7. Coagulation-Flocculation Approach

Coagulation is used to neutralize the charge dye by using a salt material in the wastewater system. These may be aluminium sulfate or the chlorides of metals. When neutralization happens, a polymer is added to flocculate the dye solution, through which the mass of particles increases, and finally, the sedimentation of the dye solution is achieved. It is applicable for a large amount of dye solution in a water system. but out of all these, it has some disadvantages like sludge formation during the coagulation step in large quantities, and it is not applicable for all types of dyes [53].

1.3.1.1.8. Irradiation method

This approach uses electron beam radiation to adsorb dye molecules. Materials, including microgel, hydrogel, polymers, adsorbents, and photocatalysts, are made by electron beam irradiation. These materials made with electron beam have superior chemical and mechanical qualities. The produced material is utilized for the adsorption and photodegradation of textile effluent dyes. Acid blue 80 dye was adsorbed by electron beam irradiation at a flow rate of 5 cm^3 with a capacity of 194 mg/g [54]. So, the direct and indirect approach of using of chemical electron beam method can be varied for dye adsorption removal. Several shortcomings of this method are that the electron beam generation is costly, produces toxic by-products, and non-selective approach [55].

1.3.1.1.9. Membrane Filtration

This is a very interesting method for low molecular weight pollutants from wastewater. Mostly conventional and commercial composite thin film membranes (synthetic) are utilised for separation. Which is further modified by polyether sulfone, Polysulfone, and Polyamide based on size requirements. Separation of dyes based on concentration, pressure and electrical potential gradients. On pressure gradients nature of the process, membrane filtration is indexed as microfiltration, ultrafiltration, reverse osmosis, and nanofiltration. The particle size above 0.1 micrometre can be applied for removal [56]. Nowadays, various other graphene oxide-based membrane is used for dye removal. Which has shown good performance in the decontamination of above 98 % of the dye solution from the water system [57]. Air or liquid can move from one side of the membrane to the other at a certain pressure because of the membrane's specific surface area, denser pore distribution, and capacity for selective penetration. This method has some disadvantages, like membrane fouling limits the effectiveness of reverse osmosis membranes by lowering flow, shortening membrane life, and affecting toxin sensitivity in membrane separation techniques [58].

1.3.1.1.10. Adsorption Process

Adsorption which not only a method but also a procedure for the excretion of different hazardous products like heavy metals, antibiotics, pesticides, herbicides, textile dyes, etc. The adsorption method refers to the attachment of adsorbate molecules on the adsorbent surface through weak or strong bonding. There are two types of adsorptions, which are chemisorption and physisorption. Dyes which are large in molecular structure and weight are easier to remove using the adsorption phenomenon. Adsorption can be attributed to four primary mechanisms: diffusion/convection, diffusion over a diffusion boundary layer, diffusion from the surface into the inner part of the adsorbent material, and diffusion from the surface into the interior portion of the adsorbent material [59]. Adsorption is inexpensive, simple, time-efficient, and has a high capacity for regeneration. Out of all other methods, it is far better suited for dye removal due to these properties and the absence of sludge production or any toxic side products entering the water body during removal. Adsorption of dyes by non-carbonaceous adsorbents is less likely to be effective than by carbonaceous adsorbents. Various physico-chemical properties of an adsorbent have shown desired results in the case of decontamination of dyes [60]. In the field of adsorption removal of dyes by metal oxides and their composites has been applied. These are like gamma-alumina for acid red 27, humic acid-iron oxide for malachite green, iron oxide-cerium oxide composite for acid black 210, magnetic graphene oxide for orange G and methylene blue, ionic liquid grafted nanoparticles for reactive black 5, and magnetic silica nanocomposite-immobilised pseudomonas fluorescens for rhodamine B [61–66]. Various metal-organic frameworks (MOF) have also been employed for dye removal, like porous MOF material based on chromium-benzene dicarboxylate for methyl orange removal, Zeolitic imidazolate framework (ZIF) with carbon nanotubes and graphene oxide for malachite green removal, and zirconium-based metal-organic framework for crystal violet and rhodamine B removal [67–69]. Polymeric composites have also been used, like polyaniline with reduced graphene oxide for methylene blue, polyaniline/silver, polyaniline/alumina, polyaniline/nickel ferrite for the adsorption of reactive red, acid blue 62, direct blue 199, and methylene blue [70–73]. Many natural and artificial clays are commonly utilized as adsorbents for decontamination of dyes from aqueous solutions due to their easy availability, low cost, high porosity, high potential for ion exchange, and non-toxicity. For instance, methylene blue was eliminated from coal-bearing kaolinite treated with sulfuric acid. Good adsorption removal from the waste stream was demonstrated for rhodamine B on sodium montmorillonite clay [74,75]. Agricultural waste materials have also been used for dye removal. Such as corn cob maize, rice husk, coffee ground powders, and other tree residue byproducts as waste [76]. All of the adsorbents mentioned above have lower adsorption capacities, slower adsorption kinetics, higher prices, or regeneration challenges. The economic boom of this modern era led to the consideration of criteria other than the scientific ones (pH, kinetics, capacity, etc.). The efficiency of removing dye from textile effluent using inexpensive activated carbons made from different solid wastes is thus being studied. The first option was to use inexpensive, practical materials. There are situations in which leftover colour in wastewater may be successfully removed using activated carbons made from solid waste. Activated carbons made from various biomass sources have varying levels of efficacy in removing dyes, depending on their physicochemical characteristics [77]. Activated carbon is outstanding because of its well-developed porosity and high affinity for a variety of compounds. Although microporous activated carbons are currently the commonly used, their application is restricted to low-molecular-weight compounds. Consequently, porous materials that are effective in removing bigger molecular dyes from the paper and textile sectors are needed. These days, researchers are concentrating on mesoporous activated carbon, a type of activated carbon with pores that span from 2 to 50 nm [78–80]. Adsorption processes are mainly done in two modes: Batch mode and Column mode. Continuous column adsorption is more advantageous than batch adsorption because it is easier to use, the adsorption process is finished faster, and scaling up is less complicated. In contrast, scientists prefer to use batch adsorption since it uses less material and takes less time overall when conducting laboratory-scale research. Nevertheless, whereas batch adsorption works well for small-scale research, it is inappropriate for larger-scale applications. Before an adsorbent is utilised on a larger scale, its performance can be predicted by the research of adsorption in batch mode [81]. We have utilised the batch mode study across all the studies done. The novelty is that, in literature, the adsorption removal capacity, reusability impact of these dyes in various works is discussed. Still, it is quite low compared to other biomass-derived activated carbon. So, there was a requirement to fill this gap to improve it very well and innovative. It is described in the research gap section below clearly with strong articulation.

1.4. Research Gap on Mesoporous Carbon-based Dye Removals:

A widespread biomass has been utilized to prepare nano-mesoporous activated carbon in literature for dyes removal, basically cationic and anionic dye removal. But preparation steps, times, chemical utilization, biomass to chemical activation ratio optimization, and temperature with the rate of temperature per minute are not very clearly focused. When these optimizations are done for mesoporous carbon synthesis from precursors, it gives very high adsorption decontamination of cationic and anionic dyes from wastewaters. In addition to acting as channels for diffusion into the micropores, mesoporous carbon can adsorb organic and large molecules. Lastly, although macropores have little effect on adsorption capacity, they can help molecules reach a solid's interior surface. Thermostability, chemical inertness, biocompatibility, large specific surface area, uniform and tuneable pore size, and periodically arranged monodisperse mesopore space are some of the characteristics that have recently drawn attention to mesoporous carbons because microporous carbon materials have significant mass transfer limitations. These characteristics are just a few of what make this kind of porous material desirable for research and use [82,83]. Various researchers have prepared mesoporous carbon through the physical approach, the hydrothermal approach, hard-soft template approach, but the chemical approach is far better and energy efficient. This chemical approach utilises a chemical for the treatment of biomass precursor for days to hours, and then activation through heating is performed, which gives good tunability, stability, regeneration ability, and high specific surface area base nano-mesoporous activated carbon which suitable best for larger dye removal like Rhodamine B, Orange G, and Crystal Violet [84–86]. Adsorption capacity of dye removal refers to the maximum adhesion of adsorbate onto the surface of adsorbents. Polyaniline/almond and walnut shell adsorbent is prepared by Imgharn et al. in 2021, to remove orange G dye, but the removal capacity was not too high because of the lower surface area and porosity of the absorbents [87]. Baloo et al., in 2021, prepared the activated carbon from empty fruit bunches, and they didn't get too much adsorption capacity for orange G removal [88]. Similarly, Activated Carbon prepared from stalk corn was prepared by Mousavi et al., 2023, for rhodamine B removal, but the removal capacity was very low. Further, W. Wu et al., 2023 prepared the activated carbon from potassium carbonate using bamboo shoot as precursor to remove rhodamine B, adsorption capacity achieved around 53.9 mg/g [89]. Using avocado pear seed activated carbon, crystal violet dye is removed, but the adsorption capacity is much lower, making it not a good adsorbent. Similarly, flower-based activated carbon was observed to have a low crystal violet dye removal from wastewater. Researchers have also shown that an activated carbon based on chitosan can remove a significant amount of crystal violet dye, but it only reaches about 12.5 mg/g [90,91 92]. Adsorption capacity is not only a parameter through which we can fill the research gap; there are some other limitations, like pH variation in dye removal, adsorbent regeneration, removal percentage, concentrations, economic sensitivity for adsorbent synthesis, and time duration for decontamination of dyes. These limitations in the study are addressed and covered to overcome the problems. In many research adsorption capacities is high, but time requirements are high for removal; somewhere, both are good, but regeneration ability is low or used by hazardous chemicals. To synthesize a novel adsorbent for future perspective, the precursor of the products should be cheaper and easily available during the seasons. Various biomass is used, like oil seeds, mango peel, orange peel and date stone powder for dye removal, but they do not have enough regaining property to hold the dye onto their surface once again after a single removal. Mesoporous carbon from cheaper biomass sources in less time can be synthesised within a nitrogen atmosphere chemically, over other methods. Biomass like wood sawdust, corn husk, luffa sponge, and other tectona grandis seed material can be cheaper alternative to synthesize the activated carbon in a good nano-mesoporous range for crystal violet, rhodamine B and orange G types of cationic and anionic dye removal with good porosity and specific surface area using chemical activator like phosphoric acid, KOH, sulfuric acid, and zinc chloride at moderate temperature within 1 to 3 hours of reaction time [93]. If the mesoporous carbon does not remove itself, there are several ways to change it, for as by combining it with metal oxide to increase the rate of removal. During the dye removal steps, the water should be collected from waste sites; otherwise, it will be made in the laboratory using distilled water. The buffer solution should set the dyes' pH range. Some dyes are light sensitive, so they should be kept in the dark. To fill these gaps in future, we should select the biomass available on the earth in large amounts and not only are side uses going on. In 2019, Banerjee et. al worked with nano alumina to remove orange G dye, and the adsorption capacity is 93 mg/g. Further, the desorption study states that they used a stronger acid ($HClO_4$), which has shown 91 per cent regeneration. The use of stronger acid can be harmful, so it should be avoided. A less harmful solvent can be utilised to recover the adsorbent for reusability in future studies [94]. So, these research gaps, after concluding, led us to focus on these issues regarding the synthesis of mesoporous carbon and dye removal with their regeneration steps, use of chemical, economic viability, biomass selection, and time of removal for dyes.

1.5. Research Objectives:

The Research objective is to fill the gap described above in detail while considering all the parameters of the study. To produce the mesoporous carbon and its composite is done in the thesis, with their physico-chemical properties, to remove hazardous dyes like Crystal Violet, Rhodamine B, and Orange G. The following bullet points illustrate the objectives of the study:

- Using Tectona Grandis sawdust as an easily available feedstock, the production of mesoporous carbon is attained by utilising zinc chloride as a chemical activating agent.

- Synthesis of gamma-alumina using aluminium nitrate precursor with urea to using the solution combustion method.
- Hydrothermal approach to the synthesis of gamma-alumina decorated mesoporous activated carbon (MAC@Al) adsorbent.
- Removal study of crystal violet (CV) staining dye from aqueous solution at lab scale.
- Regeneration study of the MAC@Al adsorbent using chemical-sonication approach.
- Characterization of MAC@Al adsorbent and removal study of CV dye with other co-adsorbents comparison.
- MAC and MAC@Al, Bare activated carbon (BAC), and gamma-alumina decorated Bare activated carbon (BAC@Al) used for crystal violet removal study comparison.
- Interference study to check the adsorption removal limitations using metal salts like Ca^{2+}, Mg^{2+}, Cr^{3+}, and As^{5+}.
- Further selection of Corn Husk biomass from agricultural sources to synthesize mesoporous carbon chemically using orthophosphoric acid as a chemical activating agent in a nitrogen atmosphere.
- The corn husk and chemical activating agent w/w impregnation investigation for obtaining a better mesoporous carbon adsorbent.
- Characterization study of corn husk-based mesoporous activated carbon (CHMAC) using XRD, FTIR, BET, HR-TEM, SEM and XPS analysis.
- Two carcinogenic dyes, Rhodamine B and Orange G, removal investigation using CHMAC adsorbent at different temperatures.
- Kinetic, Isotherm and Regeneration study of rhodamine B and OG dye removal by CHMAC.
- Overall comparison study with other studies of these dyes using these adsorbents over other studies in the literature.
- Conclusion of these results in the way of what we wanted and what we got.