# Chapter 1

## Introduction

## *Introduction*

Environmental pollution is one of the most persistent global topics affecting ecosystems and human health. Among the various forms of pollution, water pollution has arisen as a critical concern due to its direct influence on the availability of clean water, a vital resource for life. The contamination of water bodies such as lakes, rivers, and oceans by harmful substances including heavy metals, organic pollutants, industrial effluents, agricultural runoff, and microplastics causes substantial hazards to both aquatic life and humans. Rapid industrialization, urbanization, and agricultural practices have exacerbated water pollution, making it a persistent challenge that requires innovative solutions for remediation, Siddiqua et al. (2022).

In response to the escalating problem of water pollution, several chemical and material-based treatment strategies have been developed to eliminate contaminants from polluted water sources. Traditional methods for example sedimentation and filtration, while effective to some extent, often fail to address the complexity of modern pollutants. Therefore, advanced materials and chemicals, including polymer adsorbents, hydrogels, and flocculants, have added noteworthy consideration due to their enhanced capacity for pollutant removal and water treatment, Manisalidis et al. (2020).

This thesis aims to explore the application of these advanced materials—polymer-based composite and sugarcane bagasse adsorbents in the treatment of water pollution. By evaluating their effectiveness, mechanisms of action, and potential for large-scale implementation, this study seeks to assist to the development of more efficient and sustainable water treatment techniques. The results of this study will provide valuable perceptions that how innovative chemical and material-based solutions can address the growing challenge of water contamination and contribute to environmental protection.

## 1.1. Pollution

Pollution is defined as the introduction of harmful contaminants into the natural environment, leading to adverse changes that render life on Earth increasingly unsustainable, Perera (2017). It has far-reaching influences on the environment and human health, causing severe disruptions to ecosystems, wildlife, and human populations, Siddiqua et al. (2022). Pollution displays in several types, such as air, water, soil, and noise pollution, all presenting distinct challenges and sources. The accumulation of waste constituents in the atmosphere and on land has reached critical levels, prompting the need for urgent interventions to mitigate its consequences and protecting the planet for upcoming generations, Kibria et al. (2023).

## 1.2 Water Pollution

Water pollution is a critical environmental topic that causes noteworthy threats to ecosystems and human health. Among the various pollutants, synthetic dyes and antibiotics are of particular concern because of extensive use and accumulation in the environment, Al-Tohamy et al. (2022). Synthetic dyes, prevalent in industries like textiles, leather, paper, and antibiotics, widely used in medical treatments and agriculture, contribute to severe ecological and health impacts when released into aquatic system, Mishra et al. (2023). These include toxicity to aquatic life, disruption of photosynthesis, and the emergence of antibiotic-resistant bacteria, Maghsodian et al. (2022).

Water pollution arises from the release of four primary categories of substances: traditional organic waste, industrial waste, agricultural chemicals, and silt from degraded catchments, Ardila-Leal et al. (2021). Traditional organic waste, such as sewage and food processing byproducts, depletes oxygen in water bodies, harming aquatic ecosystems. Industrial activities introduce hazardous chemicals like heavy metals and toxic compounds into waterways, Aziz et al. (2023). Agricultural runoff, laden with fertilizers and pesticides, contributes nitrates, phosphates, and harmful chemicals, fostering eutrophication and degrading aquatic habitats, Bala et al. (2022). Silt from degraded catchments, caused by deforestation and poor land management, leads to sedimentation, further harming water quality and aquatic environments, Khatri & Tyagi, (2014).

Pollutants responsible for water contamination classified as physical, chemical, biological, and radioactive categories. Physical pollutants, such as debris, block waterways and damage aquatic ecosystems, Kumar et al. (2021). Chemical pollutants include a wide variety of substances like heavy metals, toxic industrial chemicals, and synthetic compounds (e.g., pesticides and fertilizers). Biological pollutants consist of pathogens like bacteria, viruses, and parasites, which causes health risks to together humans and animals, Singh et al. (2022). Radioactive pollutants, originating from nuclear waste or accidental releases, tend to lasting water contamination, Adil et al. (2023). Additionally, heat from industrial discharges alters water temperatures, affecting aquatic organisms' metabolism and reproductive cycles, Mahaveerchand & Salam (2024).

Mitigating water pollution requires concerted efforts, including stricter regulation of waste disposal practices, the promotion of cleaner industrial production methods, and the adoption of environmentally friendly agricultural practices, Yadav et al. (2024). A. Public education and awareness campaigns can further reduce pollution by encouraging proper disposal of household chemicals and reducing waste, Kumar et al. (2023). Moreover, investing in advanced water treatment technologies is essential for addressing existing pollutants and providing cleaner water for human consumption and environmental health, Hajam et al. (2023).

Color is a highly visible pollutant in wastewater, particularly from textile dyes, and its removal is crucial for preventing aesthetic, ecological, and health issues, Castillo-Suarez et al. (2023). Unlike colorless organic compounds, which primarily increase biochemical oxygen demand (BOD), colored compounds pose significant risks by impeding light penetration, disrupting photosynthesis, and destabilizing aquatic ecosystems, Azanaw et al. (2022). Effective and cost-efficient methods for color removal from wastewater are necessary to protect the environment and meet regulatory requirements Periyasamy et al. (2024).

## 1.3 Dyes

A dye is generally defined a colored constituent that exhibits an affinity for the substrate to which it is applied. Dyes are typically used in aqueous solutions and may need a mordant to advance the fastness of the dye on fibers, A. Kumar et al. (2021). Both dyes and pigments appear colored due to their capability to absorb specific wavelengths of light. However, unlike dyes, pigments are typically insoluble and lack affinity for the substrate, Ayele et al. (2021). Certain dyes can be precipitated with an inert salt to form lake pigments, which are categorization based on the kind of salt used, such as aluminum, calcium, or barium lake pigments, Horobin et al. (2019). The advent of synthetic dyes began in 1856 with the discovery of mauveine by William Henry Perkin, which rapidly replaced traditional natural dyes. This discovery marked the onset of a new era in dye manufacturing, giving rise to a diverse range of synthetic dyes, Tamburini et al. (2024). Today, synthetic dyes are extensively utilized across various industries because of their vibrant colors, consistency, and cost-effectiveness, Sandstrom et al. (2023).

## 1.4 Components and Chemical Structure of Dyes

Dyes are organic compounds that have been used for centuries to impart color to various materials, including textiles, paper, plastics and leather industries. The ability of dyes to produce vibrant, long-lasting colors is closely related to their chemical composition and structure. A dye's effectiveness depends on its molecular structure, which lets it to absorb light of specific wavelengths, leading to the appearance of color. Chemical structures of dyes designed to interact with the substrate—such as fabrics or fibers—to ensure strong adhesion, durability, and resistance to external factors like washing or exposure to sunlight. The fundamental component of any dye molecule is the chromophore, a chemical group accountable for the dye's color. Chromophores contain unsaturated bonds, particularly conjugated double bonds, which interact with light in the visible spectrum, resulting in the absorption of certain wavelengths and the reflection of others, thereby producing color. As well to chromophores, many dyes also comprise auxochromes, functional groups that enhance the color intensity and increase the solubility and binding properties of the dye to the substrate. These include groups such as $–OH$, $–NH_2$, and $–SO_3H$, which modify the electronic structure of the chromophore, enabling the dye to bind more effectively to fibers and other materials, Alegbe and Uthman (2024).

Dyes can be broadly categorized based on their chemical structure, which directly influences their application and performance. Common types of dyes comprise azo dyes, anthraquinone dyes, and indigo dyes, each with distinctive molecular features. For example, azo dyes, characterized by the presence of one or more azo groups ($–N=N–$), are the most widely used category of synthetic dyes due to their broad range of colors and stability, Wu et al. (2021). Anthraquinone dyes derive their color from the anthraquinone structure, which is known for its exceptional lightfastness, making it ideal for outdoor applications, Soriano-Souza et al.

(2019). Indigo dyes, derived from the indigoid structure, are used extensively in the dyeing of denim and other textiles due to their unique blue hue and durability, Juzsakova et al. (2023). Some of the dyes and antibiotic which are used in this thesis such as methylene blue, methyl orange, neutral red and doxycycline, Rauf et al. (2008), .

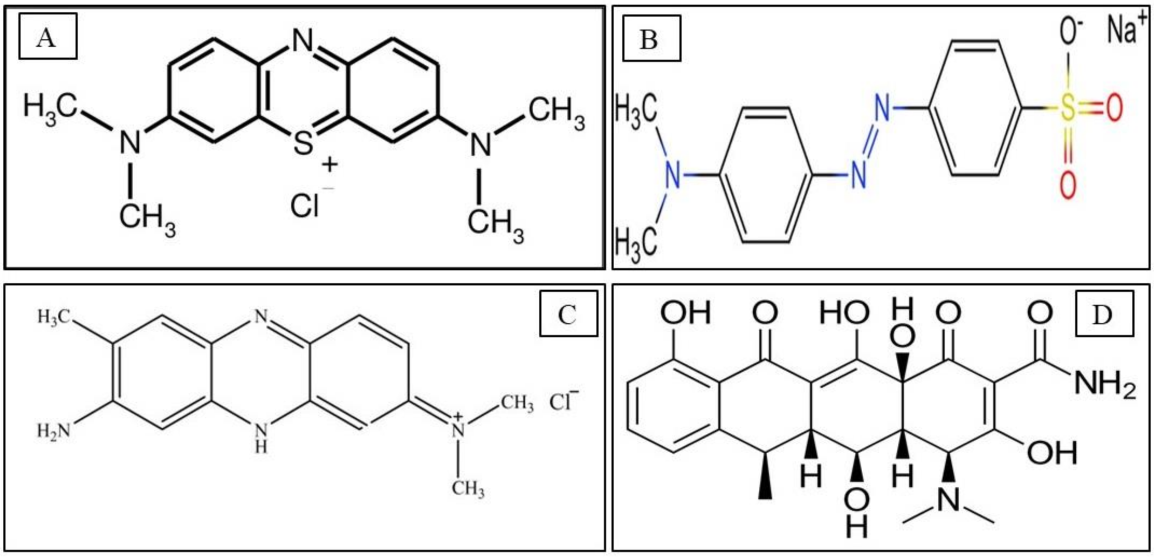

**Fig. 1.1** Structure of Dyes and antibiotic (A) MB, (B) MO, (C) NR, (D) DXN

In addition to the chromophores and auxochromes, the overall chemical structure of dyes may include additional functional groups that affect their behavior in various applications, like solubility in water or organic solvents, reactivity with mordants, or resistance to fading. The molecular architecture of dyes also determines their classification into groups like reactive dyes, vat dyes, disperse dyes, and direct dyes, each tailored for specific materials and uses.

## Chromophores

Chromophores are the components of dye molecules responsible for producing color by visible spectrum absorbing light, which tends to the emission of a specific color, Yan et al. (2023).

The structure of chromophores generally includes conjugated double bonds and aromatic rings, which facilitate this light absorption and subsequent color generation, Alsukaibi et al. (2022).

**Auxochromes**

Auxochromes remain functional groups attached to chromophores that has a central role in enhancing the dye's solubility and affinity for the substrate. Additionally, auxochromes can modify the intensity and shade of the color produced by the chromophores. Common auxochromes include hydroxyl (-OH), amino ($-NH_2$), and carboxyl (-COOH) groups.

## 1.5 Classification of Dyes

Dyes are classified based on their chemical structure, application method, or the type of fibers they are used to color. One of the most general classifications are depend on chemical structure, which includes classes such as azo dyes, anthraquinone dyes, and indigo dyes. Azo dyes which most widely used and are characterized by the occurrence of one or more azo groups (-N=N-), offering a broad spectrum of vibrant colors. Anthraquinone dyes derive their colors from the anthraquinone structure, known for its excellent lightfastness and durability, while indigo dyes, popular in the textile industry, are valued for their deep blue hues, Benkhaya et al. (2020).

Dyes can also be classified based on application method, such as reactive dyes, vat dyes, direct dyes and disperse dyes. Reactive dyes comprise a covalent bond with fibers, confirming excellent wash fastness, and are commonly applied for cellulosic fibers like cotton. Vat dyes are water-insoluble dyes that are first reduced to a soluble form and then oxidised back to an insoluble form before being applied to the fibre. This process produces colours that are vivid and long-lasting, especially on cotton. Direct dyes are used in an aqueous solution and adhere to the fabric without requiring a binder, though they generally offer lower fastness. Disperse dyes are primarily used for synthetic fibers like polyester, where the dye molecules are finely dispersed in water and absorbed by the fibers through high temperature, Berradi et al. (2019).

Another important classification of dyes is based on their origin—natural and synthetic dyes. Natural dyes, derived from plants, animals, and minerals, were traditionally used but have been largely replaced by synthetic dyes, which offer greater color variety, consistency, and ease of production. Synthetic dyes, introduced with the discovery of mauveine in 1856, dominate modern industries due to their improved colorfastness, affordability, and versatility. Each class of dye has its own unique characteristics, making them appropriate for different applications and substrates, Shrwardi et al. (2023).

### Vat Dyes

Vat dyes are water-insoluble dyes that necessitate a reduction process to convert them into a water-soluble form prior to application, Glogar et al. (2023). Following the dyeing process, these dyes are oxidized back to their insoluble form, which results in excellent color fastness. Vat dyes are commonly employed for dyeing cellulose fibers such as cotton, Kabish et al. (2023).

### Disperse Dyes

Disperse dyes, originally developed for acetate fibers, are water-insoluble but can be dispersed in water. They are primarily utilized for dyeing synthetic fibers such as polyester and nylon, Ketema & Worku (2020).

### Sulfur Dyes

Direct dyes are applied in a manner like vat dyes but are generally less expensive. They are primarily used for dyeing cellulose fibers and offer good wash fastness; however, they may fade upon exposure to sunlight, Nguyen & Juang (2013).

### Reactive Dyes

Reactive dyes make covalent bonds with the fiber, which result high colorfastness. They are commonly utilized for dyeing cellulose fibers and, to a lesser extent, wool and nylon, Chakraborty et al. (2010).

### Acid Dyes

Acid dyes are soluble in water and are primarily applied for dyeing protein fibers such as wool, silk, and nylon. They called acid dyes because they are applied in an acidic dye bath, Sharma et al. (2024).

### Basic Dyes

Basic dyes, also stated to as cationic dyes, are utilized for dyeing acrylic fibers, certain nylons, and polyester blends. They are recognized for their brightness and high tinctorial strength, Ingrassia et al. (2023).

### Direct Dyes

Direct dyes applied directly to the fabric as of an aqueous solution without the necessity of a mordant. They are primarily used for dyeing cellulose fibers and are valued for their simplicity and ease of application, Rapo & Tonk (2021).

### Mordant Dyes

Mordant dyes require a mordant—a substance that aids in fixing the dye to the fiber—to enhance color fastness. Mordants, such as alum, are utilized to treat the fabric before, during, or after the dyeing process, Repon et al. (2024).

**Other Dyes**

Numerous other types of dyes exist, such as azoic dyes, which are formed directly on the fabric through the reaction of diazo components with coupling components. Additionally, metal complex dyes contain metal atoms that enhance the stability and colorfastness of the dye, Maliyappa et al. (2022).

## 1.6 Applications of Synthetic Dyes

Synthetic dyes have become integral to a multitude of industries, revolutionizing the way materials are colored and enhancing the aesthetic appeal of products across various sectors. Unlike their natural counterparts, synthetic dyes offer superior color consistency, vibrancy, and versatility, making them the preferred choice for manufacturers. The ability to produce a vast array of colors on demand and the advancements in dye technology have led to the widespread adoption of synthetic dyes in textiles, plastics, paper, cosmetics, and food, among other usages.

In the textile industry, synthetic dyes dominate due to their ability to create vivid colors that withstand washing and exposure to light. They are utilized to dye a variety of fabrics, including cotton, wool, polyester, and nylon, with specific types of dyes selected based on the fiber type and desired properties. Reactive dyes, for example, form covalent bonds with cellulose fibers, resulting in high colorfastness, while disperse dyes are employed for synthetic fibers, providing bright hues and excellent stability.

Beyond textiles, synthetic dyes find applications in the plastics industry, where they are used to enhance the color of plastic products ranging from household items to automotive parts. In the paper industry, synthetic dyes are utilized to produce vibrant shades for printed materials, packaging, and stationery. Moreover, the cosmetics sector leverages synthetic dyes to create an array of colors for makeup and personal care products, ensuring both aesthetic appeal and compliance with safety regulations. In the food industry, synthetic dyes are used to improve the visual appeal of food products, playing a significant role in marketing and consumer acceptance. Regulatory agencies closely monitor the use of synthetic food dyes to ensure safety and compliance with health standards, resulting in a spectrum of colors that can enhance the appearance of beverages, candies, and processed foods, Dey & Nagababu (2022).

Despite their extensive applications, the use of synthetic dyes is not without challenges. Concerns regarding their environmental impact and potential health hazards have prompted research into safer alternatives and improved dyeing processes. Innovations in dye chemistry, such as the development of eco-friendly dyes and sustainable dyeing methods, are vital for addressing these issues while maintaining the benefits that synthetic dyes provide. Synthetic dyes are extensively applied in various industries because of their vibrant colors, consistency, and economy, Lellis et al. (2019).

### Textile Industry

Textile industry is the major consumer of synthetic dyes, applying them to color fabrics and garments made from natural and synthetic fibers. The industry relies on different types of dyes to achieve a huge variety of colors and fastness properties, Mabuza et al. (2023).

### Paper Industry

Dyes are used in the paper industry to produce colored paper and to add color to products such as packaging materials, tissues and cardboard, Mertoglu-Elmas (2017).

### Pharmaceutical Industry

In the pharmaceutical industry, dyes are used to color medications and capsules to differentiate between various drugs and dosages, Fahad et al. (2024).

### Leather Industry

Synthetic dyes are applied to color leather products, including shoes, bags, and furniture. The dyes used in this industry need to have good penetration and fastness properties, Maina et al. (2019).

**Cosmetics Industry:** Dyes are used in cosmetics to provide color to products like lipsticks, eye shadows and nail polishes, Guerra et al. (2018).

**Food Processing Industry:** Certain synthetic dyes are approved for use in food products to enhance their appearance and make them more appealing to consumers.

**Printing Industry:** The printing industry uses dyes in inks for printing on paper, textiles, and other materials.

**Rubber and Plastic Industry:** Dyes are used to color rubber and plastic products, including toys, household items, and automotive components.

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A new class of pollutants has emerged because of the pharmaceutical industry's extensive usage of antibiotics in recent years. Antibiotics can be released into the environment directly from a variety of sources, including human waste, urine, animal faeces, manure containing unmetabolized medications, and waste from the manufacture and use of pharmaceuticals. The majority of antibiotics are recognised for their metabolic characteristics, environmental buildup, and non-degradation, Sharma et al. (2022). Antibiotic residues can be found in certain soils, surface water, groundwater, agricultural runoff, and the final effluent and sludge of urban sewage treatment facilities, Polianciuc et al. (2020). The ecosystem may suffer greatly if antibiotics are found in the natural environment. Additionally, this may result in the emergence of organisms that are resistant to these medicines. Tetracyclines are among the most widely used antibiotics in both human and animal medicine, as well as in some agricultural fields. Tetracycline residues have been found in the aquatic environment, much like those of other antibiotics, Ahmad et al. (2021). Antibiotics like tetracyclines should thus be eliminated from the effluent as much as possible before it is released into receiving sources, Manyi-Loh et al. (2018). Since they can successfully cure bacterial illnesses, antibiotics are essential to modern medicine and have saved many lives. However, their use also comes with significant drawbacks for both the human body and the environment, Manyi-Loh et al. (2018).

## 1.7 Antibiotics

Antibiotics, widely use for medicine and agriculture, arisen as significant environmental pollutants because of their extensive application and improper disposal. These medications frequently get up in soil and water bodies because of wastewater from hospitals, pharmaceutical manufacturing sites, and agricultural runoff. The presence of antibiotics in natural ecosystems poses a substantial risk, as they can disrupt microbial communities and result to the formation of antibiotic-resistant bacteria, which poses a serious hazard to public health, Polianciuc et al. (2020).

The remediation of antibiotic pollution is crucial to mitigating these risks and restoring environmental health. Various strategies continue to developed for addressing these issue, including advanced wastewater remediation technologies, bioremediation and the use of adsorbents. These methods aim to reduce antibiotic concentrations in wastewater and stop their release into the environment. Additionally, the implementation of strict regulations regarding pharmaceutical waste management and public awareness campaigns can further enhance efforts to combat antibiotic pollution. Through a combination of technological innovation and regulatory measures, it is possible to effectively manage antibiotic pollution and protect both human health and ecosystems.

## 1.8 Application of Antibiotics

### Treatment of Infections

The main purpose of antibiotics is to cure bacterial infections, which include skin infections, urinary tract infections, pneumonia, and many more. They function by either eliminating germs or preventing their development, which enables the immune system to successfully eradicate the illness, Patangia et al. (2022).

### Surgical Prophylaxis

Antibiotics are often administered before surgeries to prevent post-operative infections.

### Chronic Conditions

Some chronic conditions, like acne and periodontal disease, require long-term antibiotic therapy to manage symptoms and prevent complications, Habteweld et al. (2023).

## 1.9 Drawbacks of Antibiotics

### 1.9.1 Human Body

### Antibiotic Resistance

The emergence of antibiotic resistance is one of the biggest disadvantages. Through mutations or the acquisition of resistance genes from other bacteria, bacteria can adapt and develop an antibiotic resistance. This can result in infections that are challenging to cure and lessens the efficacy of medications, T. M. Uddin et al. (2021).

### Disruption of Normal Flora

Antibiotics not only kill harmful bacteria but also disrupt the body's natural microbiota (good bacteria). This disturbance can lead to conditions like antibiotic-associated diarrhea or yeast infections, Tegegne and Kebede (2022).

### Allergic Reactions

Some individuals may be allergic to certain antibiotics, which can range from mild skin rashes to severe anaphylactic reactions (Blumenthal et al. (2019).

### Side Effects

Common side effects of antibiotics include gastrointestinal upset (nausea, vomiting, diarrhea), dizziness, and photosensitivity (increased sensitivity to sunlight). Long-term use of certain antibiotics can also lead to liver or kidney damage, Aliabadi et al. (2022).

## 1.10 Methods of pollutants Removal in Wastewater

Numerous methods have been developed and employed to eliminate textile dyes and pharmaceutical waste from aqueous system. These methods can be broadly classified into physical, chemical, and biological processes. Every method possess its benefits and limits, and often a combination of methods is required to achieve effective decolorization and antibiotics removal, Tripathi et al. (2023).

### 1.10.1 Physical Methods

### Membrane Filtration

Techniques likes microfiltration, ultrafiltration, nanofiltration and reverse osmosis can effectively remove dyes from wastewater, Othman et al. (2021). Membrane filtration stands efficient but can be expensive due to high operational costs and membrane fouling issues, Ahmed et al. (2022).

### Adsorption

Activated carbon is a commonly utilized for adsorbent of dye antibiotics remediation. Other materials such as biochar, clay minerals, and polymer-based adsorbents are also employed. Adsorption is highly effective and versatile but remain expensive if the adsorbent materials are not regenerated and recycled, S. Khan et al. (2023).

### Ion Exchange

This procedure comprises exchanging ions in the wastewater with ions attached to an exchange resin. It is effective for removing ionic dyes but may not be suitable for non-ionic or complex dye structures, Barman et al. (2023).

## 1.10.2 Chemical Methods

### Coagulation/Flocculation

Chemical coagulants like aluminum sulfate, ferric chloride, and organic polymers aggregate dye molecules into larger particles removed through sedimentation or filtration. This method is cost-effective but may yield huge amount of sludge that require further treatment, Badawi et al. (2023).

### Precipitation

Chemicals are added to wastewater to produce insoluble precipitates with dye molecules, which can then be remediate by sedimentation, Pohl (2020). This method is effective but can generate secondary pollution, Meng et al. (2022).

### Advanced Oxidation Processes (AOPs)

Methods like ozonation, Fenton’s reagent, and photocatalysis use strong oxidizing agents to degrade dye molecules. AOPs are highly useful for large variety of dyes but can be expensive due to the cost of reagents and energy requirements, Khader et al. (2024).

### Chemical Reduction

Reducing agents like sodium dithionite and iron salts can break down dye molecules. This method is effective for specific dyes but may need cautious regulation of reaction conditions and can produce secondary pollutants, Li et al. (2022).

## 1.10.2 Biological Methods

### Biosorption

Certain bacteria, fungi, and algae can adsorb dyes from wastewater. Biosorption is may be low cost and environmentally friendly but may need extensive biomass processing, Tripathi, Singh, Singh, et al. (2023).

### Biodegradation

Microbial degradation of dyes involves using bacteria or fungi to metabolize dye molecules in aerobic, anaerobic, or combined anaerobic/aerobic conditions, Mishra et al. (2022). While biodegradation is sustainable and cost-effective, it can be slow and may not completely decolorize wastewater, A. Moyo et al. (2022).

## 1.11 Economic Considerations and Combined Approaches

While numerous methods exist for the elimination of dyes and antibiotics from wastewater, it is essential to consider the economic feasibility of these processes, Collivignarelli et al. (2019). High operational and maintenance costs can render certain methods impractical for large-scale applications. Consequently, the advancement of cost-effective and efficient treatment methods are crucial, Chien & Ganesan, (2024).

### Combining Methods

Often, a single treatment method is insufficient for complete decolorization. Combining physical, chemical, and biological processes can enhance overall efficiency. For instance, combining coagulation/flocculation with biological treatment can reduce sludge volume and improve dye removal efficiency, Su et al. (2016).

### Optimizing Conditions

Costs can be greatly decreased and treatment effectiveness increased by optimising operating factors including pH, temperature, and reagent dose. Maintaining ideal conditions can be facilitated by putting in place real-time monitoring and control systems, Reza et al. (2024).

### Reuse and Recycling

Developing methods to regenerate and reuse adsorbents, as well as recovering valuable by-products from wastewater, can make the treatment process more economical. For example, regenerating activated carbon or biochar can reduce material costs, Ngeno et al. (2022).

### Innovative Materials and Technologies

More economical and efficient treatment alternatives may result from research into low-cost adsorbents such biochar made from agricultural waste and sophisticated oxidation catalysts. Furthermore, the effectiveness of biological therapies can be improved by scientific breakthroughs such genetically modified microbes, Satyam and Patra (2024).

## 1.12 Adsorbents

The adsorbent, which absorbs selected compounds from a solution, is crucial in wastewater treatment. Its physicochemical properties significantly influence the removal of toxic substances. Large surface area with active sites, particular functional groups, porosity, chemical and thermal stability, structural flaws, distinctive shape, ease of functionalisation, and mechanical strength are all necessary for an efficient adsorbent, Rathi & Kumar (2021). Numerous ingredients have been evaluated as adsorbents for cleaning contaminated water. Generally, nanomaterials are preferred over bulk materials because of their high surface area and active sites, Bagheri et al. (2020). At the nanoscale, the surface-to-volume ratio surges, laterally heightened surface energy, thereby enhancing sites available for adsorbing water contaminants, Benettayeb et al. (2023).

### Types of adsorbents

In wastewater treatment, both synthetic and natural adsorbents play vital roles in removing contaminants effectively, each offering distinct advantages and applications. Synthetic adsorbents, engineered with precise control over their physical and chemical properties, are often preferred because of their high surface area and customizable surface chemistry, Dehghani et al. (2023). Activated carbon most common and widely used synthetic adsorbents due to its exceptional adsorption capacity across a broad spectrum of pollutants, including organic compounds, heavy metals, and even certain pathogens, Al-Gethami et al. (2024). Its extensive porous structure and high surface area offer sufficient sites for adsorbing contaminants from water, making it suitable for both industrial and municipal wastewater treatment, Mariana et al. (2021). Another example is zeolites, which possess well-defined pore structures and ion-exchange capabilities, enabling them to selectively remove specific ions and molecules from water. Synthetic polymers like polymeric resins are also employed for their capability to selectively adsorb pollutants based on tailored functional groups integrated into their structure, offering versatility in addressing diverse water quality challenges, Sheraz et al. (2024).

Natural adsorbents, derived from renewable resources, offer sustainable alternatives in wastewater treatment, Lukum et al. (2020). Biochar, produced from biomass such as agricultural residues or wood through pyrolysis, is recognized for its porous structure and high adsorption capacity for organic pollutants, heavy metals, and even pharmaceuticals, Olugbenga et al. (2024). Its carbon-rich composition enhances its effectiveness in removing contaminants from water while promoting carbon sequestration and waste valorization, Jagadeesh and Sundaram (2023). Chitosan, derived from chitin found in crustacean shells, is another notable natural adsorbent known for its biocompatibility and capability to adsorb heavy metals and dyes through ion exchange and complexation mechanisms, Muthu et al. (2021). Its sustainable sourcing and biodegradability make it an attractive option for both environmental remediation and water purification applications, Pang et al. (2021).

Polyaniline/sand composites are used for the removal of dyes and antibiotics, making polyaniline (PANI) an important material in environmental applications. Among conducting polymers, PANI is one of the most extensively studied due to its easy synthesis, environmental stability, and straightforward doping/dedoping chemistry. PANI is well-documented in the literature for its wide range of applications, and its status as the oldest and most researched conducting polymer has drawn increased interest. This attention is largely due to PANI's low cost, simple synthesis, and its versatile electrical, electrochemical, electrochromic, and optical properties. PANI is insoluble in common solvents and does not diffuse when melted, although it has been found that doping PANI with organic dopants enables its dissolution in organic solvents. The history of PANI traces back to the oxidation of aniline by F. Ferdinand Runge in

1834, and it was initially known as "aniline black" in 1835, referring to products formed under acidic conditions through aniline oxidation. In 1862, Henry Letheby reported the electrochemical oxidation of aniline for the first time, though its electrical properties were not measured. Further developments occurred in the early 1860s, leading to polyaniline being widely recognized. PANI is a p-type semiconducting polymer composed of benzenoid and quinoid rings, as well as nitrogen atoms that can exist in imine or amine forms. Based on the relative composition of these nitrogen forms and their quaternization states, PANI exists in three distinguishable and isolable oxidation states, either in its base or salt forms.

(a) Leucoemeraldine: the fully reduced form

(b) Pernigraniline: the fully oxidized form

(c) Emeraldine: the partial oxidized (the ratio –N-/-N= is 0.5)

Polyaniline (PANI) exhibits variable oxidation states, with the degree of oxidation ranging from 0 to 100. During doping, the base form of polyaniline is converted into its salt form, with the emeraldine salt being the only conductive variant. The chemical structure of PANI is influenced by its protonation level and oxidation state, which change with pH and redox potential. The protonation/deprotonation equilibrium determines the electrical conductivity and colour of polyaniline. Protonic acid doping induces an insulator-to-conductor transition by converting emeraldine base to emeraldine salt without altering the number of π-electrons. In contrast, oxidative doping transforms leucoemeraldine into emeraldine salt through electron exchange. When PANI is doped with an acid, both polaron and bipolaron structures contribute to electrical conduction. In the polaron structure, a positive charge on a nitrogen atom acts as a hole, enabling nearby nitrogen electrons to jump into the hole, resulting in charge mobility along the polymer chain. However, in the bipolaron structure, charge movement is restricted because two adjacent holes prevent electron mobility. The primary structure of PANI is a linear arrangement of benzoid and quinoid units, the secondary structure involves compact coil formations, and the tertiary structure features an amorphous architecture, Beygisangchin et al. (2021).

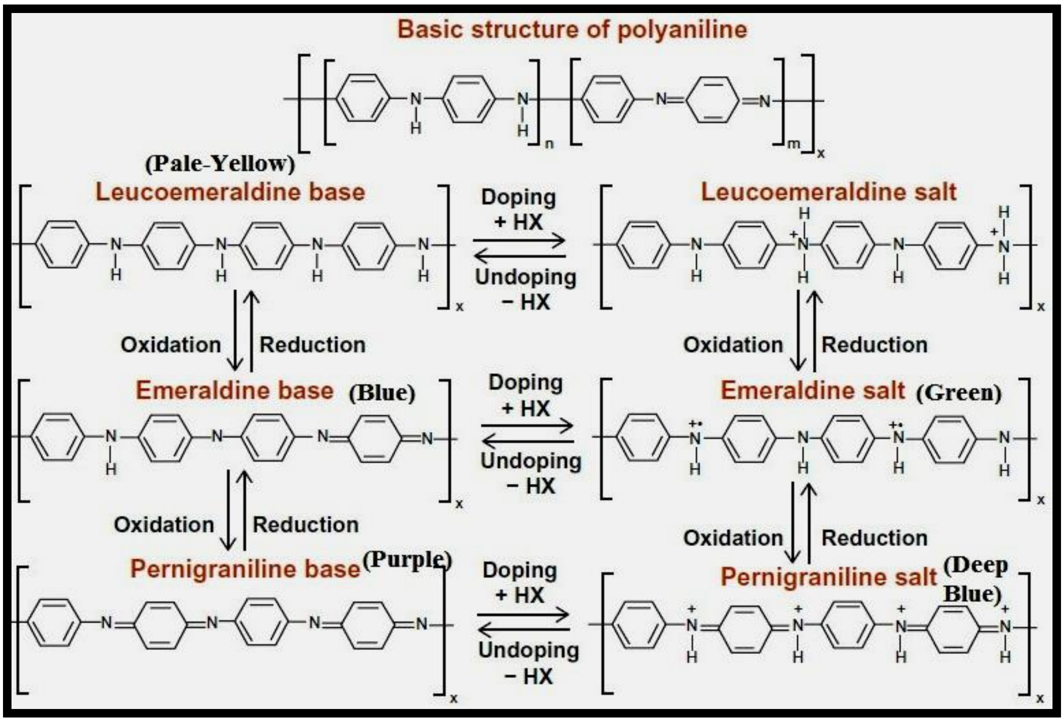

**Fig. 1.2** Structures of different forms of Polyaniline, Malhotra et al. (2015)

Sand, easily available ceramic material, varies in its mineral constituents and rock particles, depending upon its source. Sand based composite material can be utilize for low-cost adsorbent for the elimination of pollutants from effluent water especially in the developing countries. The main attraction of sand based composite material is easy and abundant availability of sand and its higher density compared to agro-based low-cost adsorbents (which float in solution phase and hence are difficult to separate from liquid phase). Higher density of sand makes it settle down very rapidly in stagnant water so we need not pay extra attention for separation of sand from effluent water.

Sugarcane bagasse (SCB), a by-product of the sugarcane industry, is comprise of cellulose, hemicellulose, lignin, and small quantities of wax, Vu et al. (2024). Approximately 40-50% of SCB is cellulose, a glucose polymer that serves as a primary structural component, Mahmud and Anannya (2021). The remaining constituents include hemicellulose, lignin, and wax. Cellulose from SCB can be processed and utilized in numerous ways, including the production of paper, nanocellulose, and bioethanol, Arni (2018). The extraction process for cellulose typically involves pre-treatment, delignification, and purification to remove impurities and isolate high-purity cellulose. This makes SCB a valuable raw material for producing sustainable and renewable products, reducing the reliance on traditional resources, Casanova et al. (2023). Hemicellulose and lignin, which together make up a significant portion of SCB, also have valuable applications, Barciela et al. (2023). Hemicellulose can be hydrolyzed into fermentable sugars, which can be transformed into bioethanol or xylitol, a low-calorie sweetener. Lignin, on the other hand, is often extracted through chemical processes and can be used in the production of biofuels, bioplastics, and various aromatic chemicals, Vasic et al. (2021). Minor components like waxes can be extracted using organic solvents and are used in biodegradable coatings, cosmetics, and pharmaceuticals, Pashova (2023). The comprehensive utilization of SCB not only adds value to this agricultural by-product but also supports sustainable industrial practices by providing eco-friendly alternatives to fossil-fuel-based products, Bhardwaj et al. (2020). Combining synthetic and natural adsorbents in hybrid systems is also gaining attention for enhanced wastewater treatment efficacy, Queffelec et al. (2024). Hybrid materials can leverage the strengths of both types of adsorbents to achieve synergistic effects, such as improved selectivity, increased adsorption capacity, and enhanced stability under varying environmental conditions, Davoodbeygi et al. (2023). For example, incorporating natural materials like biochar into synthetic matrices or modifying natural adsorbents with synthetic polymers can optimize their performance for specific contaminant removal tasks, Badran et al. (2023). This approach not only enhances treatment efficiency but also line up with sustainability goals by dropping dependence on purely synthetic materials and promoting resource efficiency in wastewater management strategies, Silva (2023).

Overall, the choice between synthetic and natural adsorbents in wastewater treatment depends on factors like the nature of pollutants, treatment objectives, cost considerations, and environmental impacts. Both kinds of adsorbents provide significant benefits to sustainable water management techniques, tackling issues with water quality and bolstering initiatives for resource conservation and environmental stewardship, Selvakarthi and Ragupathy (2024).

## 1.13 Adsorption

Physical adsorption and chemical adsorption are the two types of adsorptions. Physical adsorption, also known as physisorption, occurs when adsorbates fail to establish robust chemical interactions with substrate atoms. It results from the action of forces, similar to the Van der Waals forces that exist between molecules, between the adsorbate molecules and the solid surface. Low temperatures and an adsorption heat of around 42 KJ/mol are ideal for this kind of adsorption, Agarwala & Mulky (2023). When the adsorbed molecules are bonded to the surface molecules via chemical bonds, the process is known as chemisorption. The ideal adsorbate-substrate bonding determines the adsorbate locations or sites in chemisorption since the adsorbate-substrate forces are often weaker than the adsorbate-substrate binding forces. Over 83 kJ/mol is the heat of adsorption, Kecili & Hussain (2018). A reduction in free energy is a common feature of all adsorption processes, whether they are physical or chemical in nature. Conventional and non-conventional adsorbent has been successfully used for technological application, Gupta et al. (2021).

## 1.14 Adsorption kinetics

The study of adsorption kinetics examines how quickly adsorbate molecules build up on an adsorbent's surface. Designing and improving adsorption systems for a variety of uses, including wastewater treatment, air purification, and catalysis, requires an understanding of the kinetics of adsorption, Musah et al. (2022). The adsorption process is described and predicted by a number of kinetic models, such as the pseudo-first-order and pseudo-second-order models, Aljeboree et al. (2017).

### Pseudo-First-Order Kinetic Model

The Lagergren equation, another name for the pseudo-first-order kinetic model, postulates that the quantity of vacant sites and the rate at which adsorption sites are occupied are proportionate. The model is expressed as, Fatima et al. (2023).

$$dq_t/dt=K_1\ (q_e-q_t) \qquad 1.1$$

where:

- $q_t$ is the amount of adsorbate adsorbed at time t (mol/g).
- $q_e$ is the amount of adsorbate adsorbed at equilibrium (mg/g or mol/g).
- $K_1$ is the rate constant of the pseudo-first-order adsorption (1/min).

### Pseudo-Second-Order Kinetic Model

According to the pseudo-second-order kinetic model, the square of the number of vacant sites determines the rate of adsorption. The model is expressed as, Vareda (2023).

$$dq_t/dt=K_2\ (q_e-q_t)^2 \qquad 1.2$$

where:

- $K_2$ is the rate constant of the pseudo-second-order adsorption (g/mol·min).

In summary, adsorption isotherms are vital tools in adsorption science and technology, providing fundamental intuitions into the adsorption process and enabling the development of efficient adsorption-based procedures for various applications, Raji et al. (2023).

### Factors influencing adsorption:

The effectiveness and capacity of adsorbents are impacted by a number of parameters that impact the adsorption process. These variables include temperature, solution conditions, the kind of adsorbent and adsorbate, and the existence of competing compounds. Optimising adsorption systems in a variety of applications requires an understanding of these parameters, Karimi et al. (2019).

### 1. Nature of the Adsorbent

- **Surface Area**: Adsorbents with larger surface areas provide more adsorption sites, enhancing adsorption capacity.
- **Pore Size and Volume**: The size and volume of pores in the adsorbent influence the accessibility of adsorbate molecules. Micropores (<2 nm) are effective for small molecules, while mesopores (2-50 nm) and macropores (>50 nm) are better for larger molecules.
- **Surface Chemistry**: Functional groups on the adsorbent surface (e.g., hydroxyl, carboxyl) can interact with adsorbate molecules through hydrogen bonding, van der Waals forces, or covalent bonds.

## 2. Nature of the Adsorbate

- **Molecular Size**: Small molecules can extra easily penetrate in the pores of the adsorbent, leading to higher adsorption.
- **Polarity**: Polar adsorbates tend to adsorb more readily on polar adsorbents, while non-polar adsorbates are more compatible with non-polar adsorbents.
- **Solubility**: Adsorbates with lower solubility in the solvent tend to adsorb more readily onto the adsorbent surface.

## 3. Solution Conditions

- **pH**: The pH of the solution affects the ionization state of the adsorbent and adsorbate, influencing the adsorption capacity. For example, an adsorbent with acidic functional groups will adsorb basic adsorbates more effectively at lower pH values.
- **Ionic Strength**: The presence of salts can affect the adsorption process by competing with the adsorbate for adsorption sites or by screening electrostatic interactions.
- **Concentration of Adsorbate**: Higher initial concentrations of adsorbate in the solution generally lead to higher adsorption until the adsorbent reaches saturation.

## 4. Temperature

- **Effect on Adsorption Capacity**: Adsorption can be either endothermic or exothermic. Adsorption capacity rises with temperature in endothermic reactions. Adsorption capacity for exothermic processes falls as temperature rises.\.
- **Effect on Kinetics**: Higher temperatures generally rise the rate of adsorption by providing the adsorbate molecules with more kinetic energy, leading to faster diffusion to the adsorption sites.

### 5. Contact Time

- **Equilibrium Time**: The amount of time needed for the adsorption procedure to reach equilibrium varies depending on the system. Longer contact times classically lead to higher adsorption until equilibrium is achieved.
- **Kinetic Models**: Different kinetic models (e.g., pseudo-first-order, pseudo-second-order) can be used to describe the rate of adsorption and predict the equilibrium time, Revellame et al. (2020).

### 6. Presence of Competing Substances

- **Multi-Component Systems**: In solutions with multiple adsorbates, competition for adsorption sites can reduce the adsorption capacity for each individual adsorbate.
- **Synergistic Effects**: Through cooperative interactions, the presence of one adsorbate can occasionally improve the adsorption of another.

## 1.15 Objectives

- The objective of the present investigation is to explore and evaluate low-cost adsorbents for the effective treatment of textile and pharmaceutical wastewater.
- The study focuses on both single and multi-component systems (sugarcane bagasse and Polyaniline/Ganga Sand composite) to determine their efficiency in eliminating pollutants such as dyes and antibiotic.
- The objective to identify that adsorbents are affordable, readily available, and environmentally friendly, offering sustainable alternatives to conventional methods.
- In addition, the investigation seeks to optimize the adsorption process by studying various parameters such as effect of grain size distribution, maximum removal of dyes

and antibiotics, initial dyes concentration, contact time, adsorbent dosage, pH, temperature, adsorption kinetics and isotherms.

- The performance of different adsorbents is compared to establish their suitability for large-scale application in wastewater treatment, with a focus on improving water quality while minimizing costs and environmental impacts.

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