Chapter :1: Introduction and Literature Review

1.1.Introduction

The fresh water is essential for life on Earth, as safe environments and pure water sources are vital for human health and survival. Yet, the rapid expansion of industries globally has

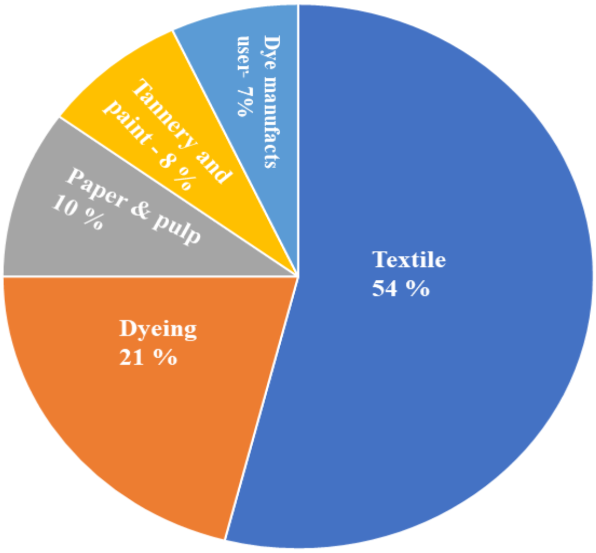

Figure 1.1: Source of dye wastewater [6].

Figure 1.2: Source of textile dye effluents [5].

worsened industrial waste problems. Industrial wastewater is steadily polluting natural water bodies, and the substantial water needs of these industries are compounding the pollution of water resources worldwide [1]. Nowadays, fresh water is very challenging for humans. According to the report of the World Health Organization (WHO), 700 million people from all over the world suffer from the problem of safe drinking water [2]. Industry plays a crucial role in economic growth for developing countries; however, rapid industrialisation negatively impacts the environment. Mainly, the industry directly affects water sources such as rivers, ponds, and groundwater. Water became poisonous because there were a lot of heavy metals, dyes and acids, such as effluents of dischargeable industries' water [3].A hygienic environment and fresh drinking water are essential requirements for healthy living. Water is most important for living cells, and no one can live without water. On the earth's surface, 70 % of the water is mainly covered by water; among these, only 3 % of water is consumed by humans, and the other 97 % is salty [4].Four billion people worldwide face water scarcity annually for at least one month [5]. Textile and other industries, such as paint, paper, cosmetics, pharmaceuticals, food, etc, produce colour wastewater. Among these industries, the textile industry produces 54 % of the total wastewater (Figure 1.1); the other amount comes from the dyeing, paper & pulp, tannery & paint, and dye manufacturing users [6]. People cannot use wastewater for irrigation because it disrupts soil fertility and plant growth or may enter our food chain. The colourful wastewater (Figure 1.2) disbalances the aquatic system because it opposes light penetration into the surface water due to the high concentration of pollutants. It also looks very dark, which results in a decrease in photosynthetic activity and diffusion of oxygen in the water. Therefore, the aquatic system's equilibrium is destroyed by the effluent, which changes the water's pH and reduces the chemical (COD) and biological oxygen demands (BOD) [7]. Dyes are devided based on the structure, source, and purpose. They are generally divided into three main types: (a) anionic dyes, which include direct, acid, and reactive types; (b) cationic dyes, consisting of all basic dyes; and (c) non-ionic dyes, such as dispersed dye [8]. Figure 1.3 illustrates the wide use of synthetic dyes in the textile industry, including azo, direct, reactive, mordant, acid, basic, disperse, and sulfide dyes. The industry also uses natural and synthetic fibres like wool, cotton, silk, polyester, polyamide, and acrylic [9]. Wastewater containing dye is an efficient polluter that affects the environment, and textile industries produce bulky amounts of colourful wastewater containing various pollutants [10]. Annually, in the world, 7×10^7 tons of dye are produced by this industry, with over 10,000 tons of dye used by textiles [11].

Most dyes have wide applications in various industries, such as paper, print, paint, tannery, and textiles, and they require large amounts of water for washing and cleaning purposes. To do this, textile industries release wastewater without proper treatment, damaging the quality of water sources, such as ponds, rivers, and groundwater. In this industry, most dyes are synthetic dyes; these are very useful as colour agents in the textile industry. Among these synthetic dyes, azo dye is very useful due to its high affinity towards the cellulose fibre and easily dissolves in water [12,13]. However, the dye does not tightly bind with cellulose fibre, which is discharged by washing into aquatic systems such as lakes, ponds, and rivers without proper treatment and poses serious toxicological threats with toxic effects on environmental organisms [10]. Dye decolourisation is becoming necessary due to its sullen nature. Therefore, wastewater needs to be properly treated before being discharged due to the high effluent.

1.2. Toxicity and the impact of textile dye

Untreated wastewater from textile industries contains a high level of organic pollutants. A large class of the dyes utilised in these industries are azo dyes, with one or two azo groups in their molecular composition. The ineffective dyeing processes in textile

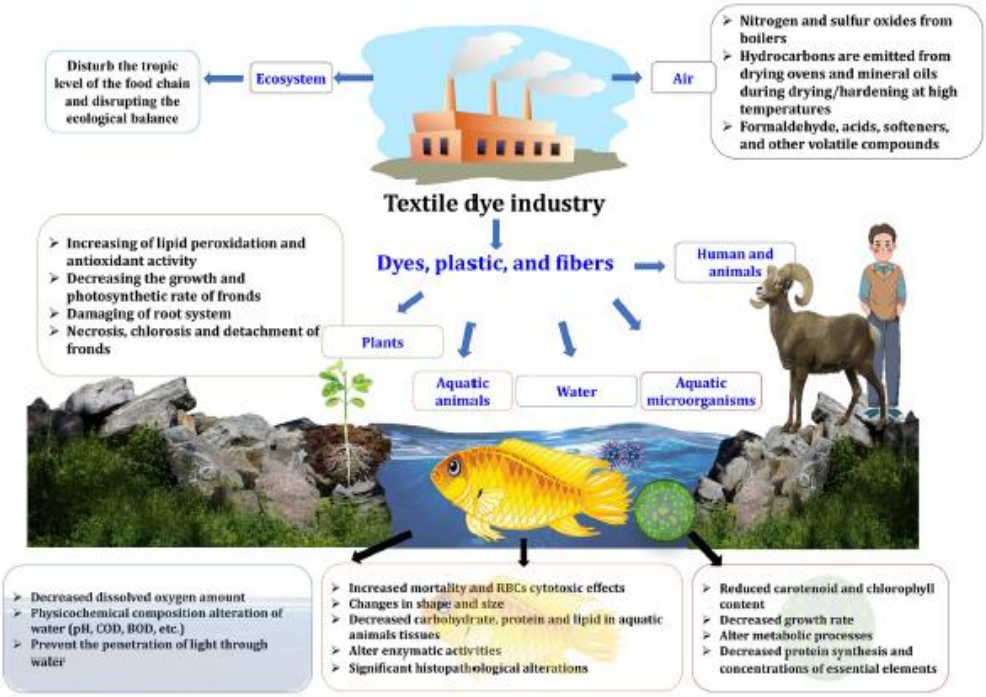

Figure 1.3: Ecotoxicological impacts of dye-containing textile wastewater on the environment and living microorganisms [9].

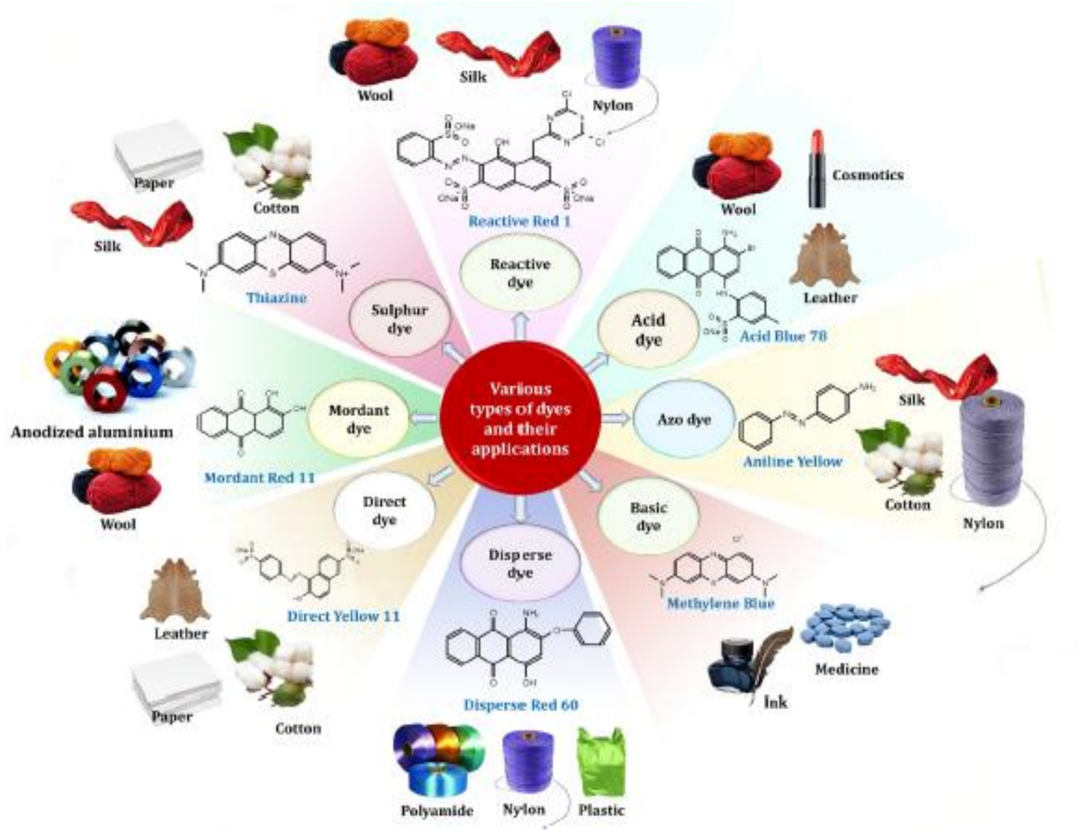

Figure 1.4 : various types of dye present in textile industries wastewater [9].

industries cause 15-50% of azo dyes to remain unbound to the cellulose fibres, resulting in a large quantity of dye being released in untreated wastewater. Specific textile industries properly treat their wastewater before discharging it into water sources, ensuring no dyes are present. In contrast, other industries release untreated wastewater into rivers and ponds, creating toxic conditions that threaten the environment and living organisms (Figure 1.4). Azo dyes are emitted into aquatic environments decrease light penetration, impairing the growth of algae and aquatic plants. Aquatic organisms can metabolise these dyes into toxic intermediates, adversely affecting their health and higher trophic levels. Humans may also be exposed to these toxins through ingestion or dermal contact, where intestinal microbiota can convert azo dyes into harmful metabolites that impact various tissues. Furthermore, skin bacteria can degrade azo dyes, leading to the formation of carcinogenic amines. Given the substantial volumes of dye-contaminated wastewater produced by textile industries, effective wastewater management is critical to mitigate environmental contamination and support sustainability. The selection of appropriate treatment methods must consider the presence of other toxic constituents and comply with environmental discharge regulations [9,14,15].

Several techniques can be used, such as chemical, biological, and physical. Adsorption, sedimentation, filtration, coagulation, photocatalysis, oxidation, and ozonation are all methods used to decolour wastewater. Among these methods, adsorption is very effective due to its low operation cost, simple operating system, eco-friendly nature, and energy-saving method. The main drawbacks of other methods are high operating costs and chemical or energy-intensive processes, which produce secondary waste. Additional operation costs may be needed to extract the secondary waste. So, the adsorption method is being sought for attention today [16]. So, this thesis focuses on preparing Ternary Layered Double Hydroxide (LDH) to treat the wastewater emerging from the textile industries. The dye extraction from the wastewater can be achieved using various types of adsorbents such as activated carbon, metal oxide, biochar-based material, layered double hydroxide, and various kinds of magnetic material. The disadvantages of this material are the cost of preparation and regeneration.

Layered double hydroxide (LDH), a family of inorganic layered materials, is easily available in nature and can be synthesised. The general formula of the ternary layered double hydroxide is $[M'^{2+}_{1-(x+y)}M''^{2+}_{y}M^{3+}_{x}(OH)_2][(A^{n-})_{\frac{x}{n}}.mH_2O]$, where M'^{2+}, M''^{2+} are divalent cations and M^{3+} trivalent cations, A^{n-} is the intercalated anion of charge n and x, y (0.2 to 0.4 for better stability for LDH) are molar ratios, $x = {M^{3+}}/{(M^{3+} + M'^{2+} + M''^{2+})}$, $y = {M''^{2+}}/{(M^{3+} + M'^{2+} + M''^{2+})}$. A^{n-} is the intercalated anion such as CO_3^{2-}, NO^-, Cl^- and SO_4^{2-} etc. [17]. Due to the unique structure of the LDH, it is used as an efficient material in various fields. It has attractive properties such as a layered structure, high surface area, and high anion exchange property. This property is utilised in multiple fields, like drug delivery, energy storage, wastewater treatment, etc [18–20]. Herein, we have introduced this material as an adsorbent to eliminate the contaminants from the wastewater. Although numerous individual researchers have already developed LDH as an adsorbent, there remain challenges in creating a novel material that is both highly efficient and possesses excellent recyclability while also being cost-effective. Some materials are widely used in this field, such as activated carbon, binary LDH, biochar composite LDH, various metal oxides, etc. M. K. Purkait et al. synthesised activated carbon to extract the CR from the aqueous medium [15]. Ran-ran-Shan et al. synthesised binary Mg-Al-CO_3 using the coprecipitation method to adsorb three red dyes, congo red, reactive red and acid red, from the aqueous solution [14]. The current thesis focuses on developing ternary layered double hydroxides to remove the pollutants from the wastewater.

As previously discussed, LDH is widely applicable across several fields; however, we have introduced this material as an effective adsorbent. The adsorption process occurs efficiently through specific methods: (a) anion absorption via ion exchange and (b) anion adsorption through structural reformation or the memory effect.

1.2.1. Adsorption of anions by the Ion exchange

LDHs exhibit excellent anion exchange capabilities due to their large interlayer spacing, making them highly effective for removing pollutants from wastewater. This effectiveness is further enhanced when the material is thermally activated. Selecting the appropriate anion is crucial, as carbonate has a higher affinity than other anions such as CO_3^{2-}, Cl^-, and NO_3^-. Consequently, LDHs with carbonate exhibit a reduced anion exchange capacity due to this strong affinity. For LDHs that do not contain carbonate, it is important to minimise carbonate adsorption from the environment or dissolved sources [21].

In 1999, Miyata investigated a notable study on the ion exchange behaviour of LDHs. He synthesised three distinct Mg/Al LDH samples, each containing a different interlayer anion—nitrate, chloride, or sulfate. These samples were then treated with varying solutions of anion, such as F^-, Br^-, I^-, OH^-, CO_3^{2-}, SO_4^{2-}, and the anionic dye Napthanol Yellow S (BYS_2^-) with the formula $C_{10}H_4N_2Na_2O_8S \cdot 3H_2O$. The mixtures were kept at a stable temperature of 25 °C with continuous mixing overnight and then filtered to separate the contents. Various wet chemical and instrumental analysis techniques measured anion concentrations in the resulting filtrate [22].

Miyata designed ion exchange isotherms for every sample to calculate the selectivity coefficient ($KANO_3$) compared to the nitrate-containing LDH. The discrimination sequence for monovalent anions was observed as $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$, while for divalent anions, the sequence was $CO_3^{2-} > NYS^{2-} > SO_4^{2-}$. It was noted that all samples, apart from the iodide-containing LDH, exhibited a Langmuir-type adsorption isotherm [23,24].

1.2.2. Adsorption of Anions by the Reconstruction Effect

Thermal activation (TA) involves heating LDH at 300–500 °C temperatures, eliminating interlayer water and intercalated anions, and producing mixed metal oxides. A distinctive property of thermally activated layered double hydroxides (TA-LDH) is their ability to restore their initial structure when exposed to water and anions. This reformation occurs through water and anion adsorption, known as the memory effect. Removing as many anions as possible during heat treatment enhances the reformation effect. Therefore, selecting anions easily eliminated at high temperatures is crucial for creating stable and non-toxic decomposition products. Carbonate is an ideal intercalated anion for this purpose. As a carbonate-containing LDH decomposes, it releases both stable and non-toxic carbon dioxide and water vapour. LDHs also show a greater attraction for carbonate than other anions, reducing the likelihood of non-removable anion exchange during continuing storage. This characteristic also eliminates the need for measures to prevent non-carbonate LDHs from adsorbing carbonate from the air or dissolved sources in water [25].

As previously noted, the heat treatment method removes surface water and interlayer intercalated anions. This treatment boosts the material's surface area and porosity, improving adsorbent performance. High-temperature treatment of the LDH structure changes it into stable crystalline oxides that cannot revert, which reduces anion adsorption capacity as part of the adsorbent becomes inactive. Therefore, thermal activation is an essential part of the heat treatment process, and achieving optimal anion adsorption efficiency requires balancing these elements [26]. Hassina Zaghouane-Boudiaf et al. synthesised MgNiAl ternary layered double hydroxide using the well-known coprecipitation method to adsorb Methyl Orange from an aqueous solution. They calcined the material at 500 °C to improve the adsorption capacity of the dye from the aqueous medium. The adsorption capacity of the uncalcined and calcined LDH was 118.5 and 375.4 mg/g, respectively [27]. Chunsheng Lei et al. synthesised hierarchical calcined NiMgAl LDH to extract CR and Cr ions from the aqueous medium. The adsorption capacity of the material was 1250 and 103.4 mg/g [28]. Rodrigo Morais Menezes dos Santos and his team prepared MgAl-CO_3 layered double hydroxide (LDH) to remove Acid Yellow 42 from aqueous solutions. To enhance its removal capacity, the material underwent calcination. The adsorption capacities were 330 mg/g for uncalcined LDH and 1266 mg/g for calcined LDH [29].

This study examines the degradation of azo dyes using LDH. The LDH effectively adsorbed usable dyes from the textile industry, including Methyl Orange (MO) and Congo Red (CR), which are commonly utilised due to their chemical properties. These dyes exhibit a strong affinity for the cellulose fibres used in textile production. The research aims to develop a highly efficient and long-range recyclable material for dye degradation, which can be effectively reused to eliminate dyes from wastewater.

1.3. Azo Dye

In the last hundred years, colour has been a crucial visual element for people, especially in the textile industry, where it is an indispensable component. Two methods are involved in the colouring, such as dyeing and printing. Several are available, but azo dyes are particularly significant for colouring [30,31]. Azo dye is a prominent and commercially significant group of synthetic dyes. Azo dyes hold the top position in dye chemistry by production volume, and their importance is projected to grow. They are essential in regulating the dye and printing market [32]. Azo dyes are the most frequently utilised dyes, making up more than 60% of the total dye market [33,34]. Approximately 70 % of the dyes employed in industrial applications are azo dyes [35,36]. Due to their various chromophore structures, Azo dyes are grouped in the twenty-five group [37]. Azo dyes are widely used due to their simple synthesis, broad range of structures, high molar destruction coefficient, cost-

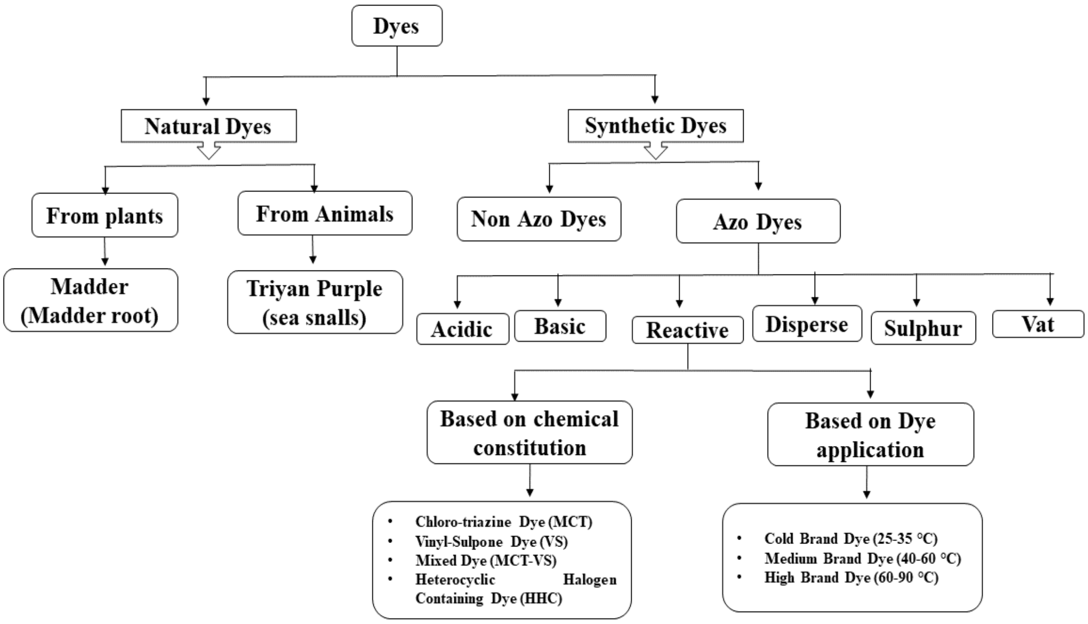

Figure 1.5: Flow chart of dye classification based on the chemical constitution and its application.

effectiveness, and moderate to high durability against light and moisture [38]. Therefore, dyes are applied in numerous areas, including the colouring of natural and synthetic materials and inks, cosmetics, food, leather, and paint [39–41].

Azo compounds are signified as $R - N = N - R'$, where R or R′ can be either aryl or alkyl compounds and $-N = N-$ is the azo group [40]. Dyes are usually classified into various groups and categories according to their source, chemical structure, and types of fibres they best match, as depicted in Figure 1.5 [42]. Azo dyes are characterised by a nitrogen double bond (–N=N–), with at least one nitrogen atom bonded to an aromatic group such as naphthalene or benzene rings. Figure 1.6 represents congo red (CR) and methyl orange (MO) chemical structures. They also display amphoteric properties due to additional functional groups like carboxyl, hydroxyl, amino, or sulfoxyl. Depending

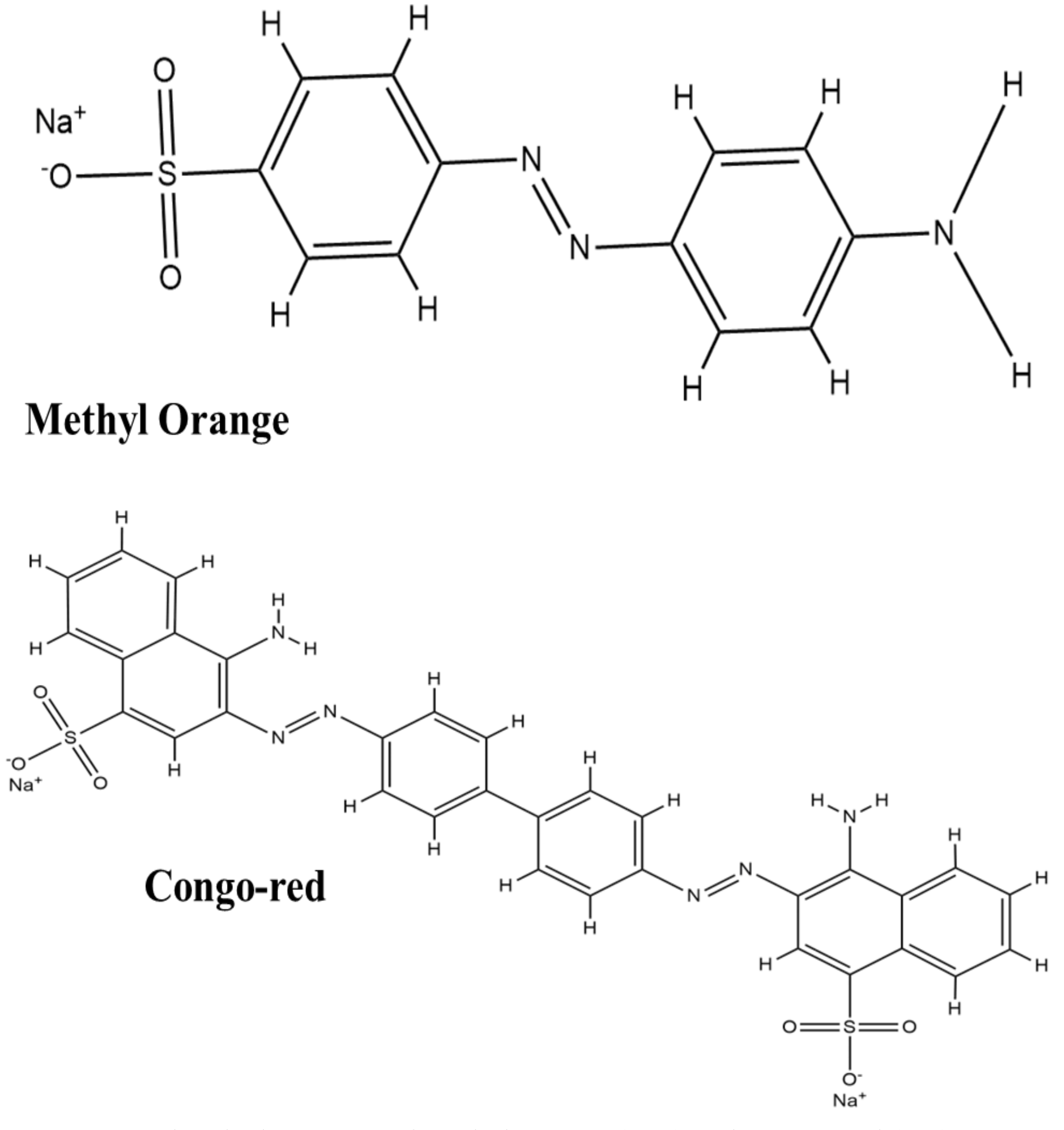

Figure 1.6: Chemical structure of Methyl Orange (MO) and Congo Red (CR) [42].

on the pH of the medium, azo dyes can function as anionic (when deprotonated at an acidic group), cationic (when protonated at an amino group), or non-ionic. Key types of azo dyes include acid dyes, basic dyes (cationic dyes), direct dyes (substantive dyes), disperse dyes (non-ionic dyes), reactive dyes, vat dyes, and sulphur dyes. Dyes can be further classified based on their general structure into anionic, non-ionic, or cationic categories. Anionic dyes include direct, acidic, and reactive dyes; non-ionic dyes primarily consist of disperse dyes that do not ionise in water, and cationic dyes include basic dyes, and some disperse dyes [43,44]. This study examines MO and CR as the main compounds, with their chemical structures shown in Figure 1.6. Both dyes are pH indicators, changing colour in response to the solution's pH shifts. MO appears red in acidic conditions and yellow in basic ones. As the acidity decreases, MO transitions from red to orange and finally to yellow; the reverse occurs when the pH shifts towards acidity. MO's pH range is 3.1 to 4.4, primarily used for acidic solutions [45]. CR changes colour from dark blue at pH levels between 2.0 and 4.0 to red from pH 4 to 12, with the intensity of the red colour varying across this pH range. Therefore, CR is used as a pH indicator [46].

The textile industry produces substantial wastewater containing high levels of dye pollutants, most of which are synthetic. These dyes often include amine groups or benzene rings, making them carcinogenic and mutagenic. In aquatic environments, they damage ecosystems and disrupt processes like photosynthesis and oxygenation. Because most dyes are water-soluble, living cells can easily absorb them, harming organs such as the liver, skin, and nasal passages. Their mutagenic and carcinogenic properties lead to long-lasting environmental impacts [47].

Azo dyes possess a strong affinity for cellulose, making them extensively used in dyeing and colouring processes. However, releasing synthetic dyes containing azo groups into river and groundwater systems results in significant pollution. Contaminated water is characterised by elevated levels of Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD), along with distinct colouration, toxicity, surfactants, fibres, and turbidity. High BOD depletes dissolved oxygen (DO) rapidly, while elevated COD levels are toxic to aquatic organisms. These dye pollutants also limit light penetration, inhibiting photosynthesis and adversely impacting aquatic ecosystems. When organisms such as fish, insects, and algae are exposed to such contaminated water, ecological and human health are indirectly affected. Therefore, it is essential to degrade dyes in textile wastewater. Dye degradation involves the adsorption of dye molecules onto specific materials or their breakdown into non-toxic byproducts like H_2O, CO_2, and other mineral compounds [48,49].

During the past two decades, various methods have been used to degrade the dye from the wastewater. This is briefly discussed below.

1.4. Wastewater Treatment Techniques and Methods

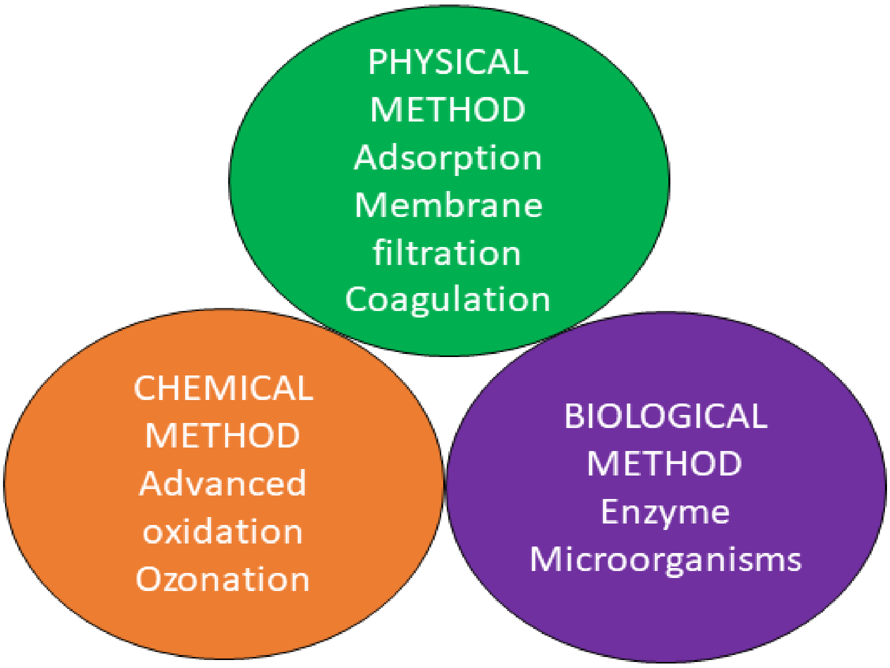

Figure 1.7: Possible wastewater treatment techniques.

Many people are engaged in this field, and continuous progress is being made in developing new wastewater treatment strategies to meet clean water needs. However, treating wastewater from textile industries is particularly challenging. Several techniques have already been mentioned in the introduction and are depicted in Figure 1.7. The selection of a method depends on various factors such as dye concentration, sewage composition, process costs, and additional impurities present in the water [50–52].

The chemical process is effective but demands additional chemicals and energy for dye breakdown. Moreover, it produces secondary waste that requires further treatment, increasing the total cost [53]. The addition of extra chemicals to facilitate the recycling process raises operating costs. Biological and physical methods, especially adsorption techniques, provide several advantages over chemical methods. They are more cost-effective, environmentally friendly, and do not produce secondary effluents during operation. However, biological methods have limitations that need to be addressed by the scientific community before they can be widely implemented for dye remediation.

- Biological methods involve live organisms that have a maximum tolerance for dye. As a result, eliminating very high concentrations of dye with these methods can be difficult.
- Biological processes are less dependable than physical and chemical methods because they rely on living organisms.
- The sluggish speed of biological processes for dye remediation also challenges researchers.

1.4.1. Physical method

1.4.1.1. Adsorption

It is a physical method for extracting the effluents from the wastewater. This method is highly popular because it is visible, environmentally friendly, easy to operate, and uses very inexpensive adsorbents. The man-made adsorbent and natural adsorbent are available for this process. Among these adsorbents, activated carbon is a very popular and commonly used adsorbent for wastewater treatment. The main problem with the adsorbent is its ineffective regeneration process and limited efficiency in dye removal [54].

Nurul Umairah M. Nizam et al. reported the extraction of anionic and cationic dyes from an aqueous solution using biomass-based activated carbon. As per the Langmuir isotherm, the maximum adsorption capacity for methylene blue (MB) was 769.23 mg/g, whereas for Congo Red (CR), it was 458.43 mg/g [55]. Syieluing Wong et al. synthesised coffee waste modified with polyethyleneimine for Reactive Black 5 and Congo-red adsorption. The adsorbent exhibits a higher maximum adsorption capacity for Reactive Black 5 (77.52 mg/g) compared to Congo Red (34.36 mg/g), owing to the more significant number of functional groups in Reactive Black 5 that interact with the adsorbent [56]. Abdul Ahad Khan et al. synthesised Algal biochar to remove for the removal of Congo-red dye from textile wastewater. The optimal conditions, with a dye concentration of 1 mg/L, resulted in the highest Congo Red removal efficiency (96.14%) and the maximum adsorption capacity of algal biochar (186.94 mg/g) [57].

Anyu Li et al. reported that they had made the Zn-Al and modified Zn-Al with zeolitic imidazolate framework (ZIF) LDH for degradation of the CR from the aqueous medium. They observed the effects of temperature and pH on the adsorption, finding that the maximum adsorption capacities of ZIF-Zn-Al and Zn-Al LDH were 909.09 and 625.00 mg/g, respectively. Recycle experiments verified that even after four adsorption cycles, CR removal rates stayed at 57.78% for Zn-Al LDH and 67.11% for ZIF-Zn-Al LDH [58]. Jie Yang et al. reported that they prepared the three-dimensional hierarchical Ag/Mg (Ni)Al LDH to remove organic pollutants like CR. The adsorption capacity of the composite material was 350.16 mg/g, 1.3 times greater than the Mg-Al LDH. They investigated the factors affecting the adsorption process, such as solution pH, temperature, and the recyclability of the composite material up to 4th cycle [59]. Yuxiang Chen et al. reported synthesising acid salt-treated Co-Al LDH to remove the MO from the aqueous medium. The influence of initial adsorbent concentration, pH, competing anions, and temperature was also examined. The adsorption capacity of Co_4Al_1-Cl was 827.50 mg/g [60]. Ariel Guzman-Vargas et al. synthesised the Cu-Al LDH to extract the methyl-violate 2B dye from the aqueous solution. Physicochemical characterisation was conducted using XRD, FTIR, UV-vis, TGA/DSC, and SEM techniques. The adsorption capacity of the material was 360.01 mg/g [61]. Ran-ran Shan et al. synthesised the magnetic Fe_3O_4/Mg-Al LDH composite to remove three red dyes such as reactive red (RR), Congo-red (CR) and acid red (AR1), from the aqueous solution. The adsorption process is directly affected by factors such as the adsorbent dosage, contact time, initial dye concentration, and the temperature of the solution. The adsorption capacities were 97 mg/g for RR, 253 mg/g for CR, and 92 mg/g for AR1 by the composite material [62]. Santos et al. synthesised calcined and uncalcined Mg-Al LDH to remove Acid Yellow 42. They investigated the adsorption dose, contact time, solution pH, dye concentration and solution temperature for dye adsorption from aqueous solution. In studying azo dye adsorption, several factors were considered, including kinetics, adsorption capacity, the effect of temperature, initial pH, and adsorbent recyclability. The calcined LDH (CLDH) showed an adsorption capacity nearly four times higher than its precursor, with 1266 $mg \cdot g^{-1}$ and 330.0 $mg \cdot g^{-1}$, respectively, at a pH of 7.0 and 25 °C. The ability of AY to adsorb onto CLDH was assessed across five regeneration cycles. After the initial use, the adsorption capacity retained 100%, 98.9%, 90.1%, and 62.5% of its initial level, respectively [63]. Anyu Li et al. synthesised Zn-Al LDH and zeolite imidazolate framework-based Zn-Al LDH for the adsorption of organic pollutants from wastewater. Moreover, ZnAl-LDH and ZIF-ZnAl-LDH were analysed through Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) analysis, and X-ray photoelectron spectroscopy (XPS). The maximum adsorption capacity of congo red obtained from the Langmuir isotherm was equal to 625.00 and 909.09 mg/g for these two compounds, respectively. The recyclability of both materials was demonstrated up to the 4th cycle [64]. Lunhong Ai et al. synthesised Mg-Al LDH using the hydrothermal method to remove the MO aqueous solution. The material was characterised by x-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy. Parameters such as initial dye concentration, contact time, and solution pH were studied. Equilibrium adsorption data were evaluated using the Langmuir isotherm model, indicating a maximum adsorption capacity of 0.453 mol/kg. No recyclability of the material was observed [65]. Benedicte Prelot et al. synthesised Mg-Al LDH to remove the methyl orange from the aqueous solution. In this study, the exchange-adsorption of three azo dyes, Methyl Orange (MO), Orange II (OII), and Orange G (OG), from aqueous solutions onto Mg-Al-LDH-NO_3 layered double hydroxides was examined. The dye adsorption isotherms displayed differences in the maximum adsorption capacities: 5.5 mmol g^{-1} for MO, 2.7 mmol g^{-1} for OII, and 1.7 mmol g^{-1} for OG. The materials did not demonstrate recyclability for pollutant removal from aqueous solutions [66]. Chuan Jing et al. prepared NiAl-CO_3 LDH via the hydrothermal method and then used acid salt treatment to produce Mg-Al-Cl LDH for methyl orange adsorption from aqueous solutions. The LDH exhibited a maximum adsorption capacity of 853.19 mg/g, but recyclability was not observed [67]. Manling Zhang et al. synthesised carbon dot-based Mg-Al LDH to remove the MB from the aqueous solutions. The obtained LDH-carbon dot composites were analysed using XRD, FTIR spectroscopy, high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), and the N_2 adsorption-desorption method. The maximum adsorption capacity of methyl blue from aqueous solution was 185 mg/g, but the material exhibited no recyclability [68]. Ridha Lafi et al. synthesised Mg-Al LDH through coprecipitation with a molar ratio 2 at a constant pH of 9 to remove Congo red from aqueous solutions. The material was characterised using XRD, FTIR, SEM, and TEM. The study investigated the effects of parameters like solution pH, contact time, and dye concentration on adsorption. While the material reached a maximum adsorption capacity of 111.11 mg/g, it was not recyclable [69]. N. Ayawei et al. synthesised Ni-Fe LDH via the coprecipitation method and characterised it using XRD, FTIR, and EDX. This material was applied to remove Congo red. Batch adsorption experiments were carried out to evaluate the effects of various parameters on the adsorption behaviour of Congo red onto the LDH, including initial dye concentration, contact time, and temperature. The material was not tested for recyclability [70]. Weike Zhang et al. synthesised Mg-Al LDH using a hydrothermal method with ultrasound assistance for congo red removal. The maximum adsorption capacity of 934.43 mg/g was achieved at an optimal ultrasonic power of 180W. After three cycles, the adsorption rate remained above 60% [71]. Narges Safar Beyranvand and her team synthesised Mg-Al LDH via the coprecipitation method to remove Congo red from aqueous solutions. XRD, FTIR, and SEM characterised the material. The maximum adsorption capacities of Mg-Al-LDH for Congo red were 100, 105, and 86.8 mg/g at temperatures of 308, 318, and 328 K, respectively [72]. M.A. Ahmed et al. synthesised mesoporous Mg/Fe LDH nanoparticles using a sol-gel route for the adsorption of indigo carmine. The material was characterised by XRD, FTIR, SEM and TEM analysis. IC was effectively adsorbed onto LDH nanoparticles, which had a surface area of 85.6 m^2/g, across different pH levels. The highest adsorption capacity was 62.8 mg/g at pH 9.5. The material recyclability was not reported [73]. Noha Almoisheer and her team developed a copper-aluminum-layered double hydroxide/single-walled carbon nanotubes (CuAl-LDH/SWCNTs) composite for the removal of the organic dye indigo carmine (IC) from aqueous solutions. The adsorption of IC followed the Langmuir isotherm model, exhibiting a maximum monolayer adsorption capacity of 294.117 mg/g at 20°C, but the material showed no recyclability [74]. Wen Yao et al. synthesised uncalcined glycerol-modified nanocrystalline Mg/Al layered double hydroxides (called G-LDH) and calcined G-LDH (referred to as G-LDO) with a Mg molar ratio of 3:1 through a straightforward and green hydrothermal process to remove methyl orange from aqueous solution. The synthesised material was analysed using SEM, TEM, N_2 Brunauer–Emmett–Teller surface area measurement, FT-IR spectroscopy, and XRD. MO adsorption on G-LDH and G-LDO fit well with the Langmuir model, with G-LDO demonstrating a much higher maximum adsorption capacity (q_{max} = 1062.3 mg/g) than G-LDH (q_{max} = 443.5 mg/g) at a pH of 4.5. Recyclability was observed for both materials until the 6th cycle [75]. Zhuojun Wei et al. synthesised a magnetically double-shelled layered double oxide (LDO)/LDO/γ-Fe_2O_3 composite for the highly efficient removal of CR. $MgFe_xAl$-LDO/LDO/γ-Fe_2O_3

magnetic composites (where x = 0, 0.1, and 0.5) were prepared using an economical two-step coprecipitation method and suitable calcination. The MgAl-LDO/LDO/γ-Fe_2O_3 and $MgFe_{0.1}Al$-LDO/LDO/γ-Fe_2O_3 composites demonstrate outstanding adsorption efficiency for Congo red, with closely matching q_{max} values of 3980 and 3832 mg/g, respectively. The efficiency of up to 84% in the fourth cycle suggests a promising potential for application [26]. Jie Yang et al. synthesised a three-dimensional hierarchical Ag/Mg(Ni)Al LDH Janus micromotor derived from lotus pollen to remove organic pollutants actively. The Ag/MgAl-LDH micromotor also reached a maximum congo red (CR) adsorption capacity of 350.16 mg/g, 1.33 times greater than the MgAl-LDHs without the micromotor design. The adsorption capacity of congo red by Ag/Mg(Ni)Al- LDH was 261.61 mg/g. The material's recyclability was observed up to 4th cycle [76]. Garima Rathee et al. synthesised NiFeTi LDH using a hydrothermal route for the removal of anionic dye MO, CR, MB, and OG, and the adsorption capacity was 32.61, 29.97, 29.94 and 39.95 mg/g. The material exhibited up to 3rd cycle for removal of methyl orange [77]. E.E. Abdel-Hady et al. developed a hierarchical ternary ZnCoFe layered double hydroxide as an effective adsorbent. They had synthesised ZnCoFe/LDH with a 2:2:1 molar ratio through co-precipitation. This material successfully demonstrated an adsorption capacity of 58.26 mg/g for MB from wastewater [78]. Tayyaba Waheed et al. developed Ni/Mg/Al LDH and modified it with montmorillonite (NMA-MMT-LDH). The physicochemical properties of the resulting materials were evaluated using a range of characterisation methods, including XRD, SEM, FTIR and BET analysis. The highest monolayer adsorption capacities for CR and MB were 344 and 200 mg/g, respectively. The material demonstrated recyclability up to the 3rd cycle [79]. Snehprave Das et al. developed ternary Mg/(Al+Fe) to remove malachite green (MG) from the aqueous solution. The experimental results showed that the Mg/(Al + Fe) adsorbent, with a molar ratio of 10:2 + 3, achieved an impressive 99.94% removal of MG, with an initial concentration of 1000 mg/L, at around pH 9, room temperature, and within 5 minutes. The material's recyclability was observed up to 3rd cycle [80]. Taye Saheed Kazeem et al. developed MgCoAl (MCA) LDH, and its graphene-based nanocomposite (GMCA) was fabricated via a simple coprecipitation method. The composites and their calcined forms (MCA-C) and (G/MCA-C) were used as adsorbents to remove the MO from the aqueous phase. Characterisation techniques, such as scanning electron microscopy and transmission electron microscopy, revealed a consistent distribution of graphene on the MCA. The material showed the recycle for MO removal up to the 3rd cycle [81]. Garima Rathee et al. developed NiAlTi ternary LDH using hydrothermal to remove anionic dyes from aqueous solutions. The NiAlTi LDH demonstrated excellent performance in removing anionic dyes (orange II and methyl orange) across a broad pH range of 4 to 10, with tetracycline removal being most effective at pH = 9. The maximum adsorption capacities for the organic dyes were impressive, reaching 1250 mg/g for MO and 2000 mg/g for Orange II. The material demonstrated recyclability up to the 5th cycle [82]. Nazir et al. synthesised ternary NiZnAl LDH using the hydrothermal method to remove rhodamine B (Rh-B) and methyl orange (MO). The adsorption process is affected by several factors, such as solution pH, contact time, adsorbent dose, and dye concentration, which were investigated. Using the Langmuir model, the maximum adsorption capacities (q_{max}) were 97.09 mg/g for Rh-B and 105.26 mg/g for MO. The material's recyclability was observed up to 4th cycle [83].

The literature review report concludes that we must develop cheap, highly efficient, and highly recyclable materials for dye degradation. In this thesis, we have focused on synthesising the ternary layered double hydroxide for degradation of the most popular usable dye in the textile industries due to its high affinity with cellulose fibres such as CR and MO.

1.4.1.2. Filtration

Many researchers are focused on developing a semi-permeable membrane enhanced with an adsorbent to better separate dyes from wastewater, and this approach has proven effective for dye filtration. To treat this dye, wastewater must be pre-treated to remove suspended particles. Standard methods for this treatment include ultrafiltration, nanofiltration, and reverse osmosis. This method is costly due to the high pressure needed for filtration and the high expense of preparing the membrane.

1.4.2. Chemical methods

1.4.2.1. Advanced oxidation process

This conventional dye removal approach uses oxidising solid agents like H_2O_2, Fenton's reagent ($H_2O_2 + Fe^{2+}$), and Cl_2 to produce hydroxyl radicals. These radicals oxidise dyes into CO_2, H_2O, and inorganic salts by targeting the dye's chromophore group. They can be generated with oxidising agents in the presence of a catalyst or UV radiation, leading to either non-photochemical (e.g., H_2O_2, O_3, Cl_2) or photochemical (e.g., UV/H_2O_2, O_3/UV, $UV/O_3/H_2O_2$, $Fe^{3+}/UV/H_2O_2$) processes. Although this method is more cost-effective than others, it has limitations, such as sludge formation and high electricity consumption for ozone production. Additionally, incomplete oxidation can produce toxic by-products. According to numerous studies, ozone, a more potent oxidising agent than H_2O_2 and Cl_2, has demonstrated effective dye removal [84–86].

1.4.2.2. Coagulation

This method is widely favoured due to its low operating cost and reduced likelihood of producing harmful secondary intermediates. In this method, chemicals are used to succeed in the degradation process. This technique utilises salts based on Al^{3+} or Fe^{3+}, such as aluminium sulphate, aluminium chloride, ferric chloride, ferric sulphate, calcium oxide, and magnesium oxide are used. These salts are inexpensive chemicals readily available in the market, and flocs are formed by neutralising the cation (Al^{3+} or Fe^{3+}) with the anionic dye. The main limitation of these methods is their lack of effectiveness in treating low molecular weight, highly soluble, and cationic dyes. Furthermore, they produce a considerable amount of sludge due to floc formation [87,88].

1.4.2.3. Solvent extraction

This new method for dye degradation from textile industries requires an exceptionally high purity level to be effective. It can include solid-liquid or liquid-liquid extraction, employing a solvent that does not mix with the wastewater. The principle of this method is that the dye's distribution coefficient should be more significant in the solvent than in water. Different types of solvents used for this method, such as benzene, xylene, toluene, chloroform, and hexane, have been reported by many researchers. Sonawane et al. efficiently removed crystal violet from textile wastewater using Tributyl Phosphate (TBP) as the extractant and 1-Dodecanol as the diluent. Likewise, Muthuraman et al. reported the removal of Methylene Blue using Benzoic acid as the solvent. Unlike dye degradation, this method focuses on recovering dye from wastewater. It provides benefits like high-purity dye and operational simplicity. However, a significant drawback is that separating the dyes from the solvent demands extra energy, rendering the process energy-intensive [89,90].

1.4.3. Biological methods

The biological method is beneficial due to its environmental friendliness, cost efficiency, and low sludge production. In this technique, the main microbial species are used for dye degradation. These methods stand out from others due to the genetic diversity of microbial species, which allows for the development of biological techniques capable of treating a wide range of dyes. They partially decompose the dye into stable, non-toxic substances. The final products of this process are water, CO_2, and harmless inorganic salts. The benefit of the microbial-based technique is that microbial species can adapt and evolve in reaction to various pollutants, which may lead to the development of new, more efficient strains capable of converting toxic dyes into non-toxic compounds. Dye degradation can be accomplished through various methods, including microbial degradation, bio-absorption, and bioaccumulation, utilising living and dead biomass and microorganisms such as fungi, algae, yeast, and bacteria [91,92].

1.4.3.1. Biosorption and Bioaccumulation

When a pollutant (dye) adheres to the surface of dead biomass, it is known as biosorption (adsorption). Conversely, when a pollutant attaches to and accumulates inside the cells of a living microorganism, it is referred to as bioaccumulation (adsorption). Examples of biomass include bacteria, fungi, yeast, algae, seaweeds, and industrial and agricultural waste. This technology is primarily for non-degradable dyes. Biosorption is more commonly used and favoured over bioaccumulation because the dead biomass in biosorption does not require nutrients for growth or maintenance and has a higher removal rate. In contrast, living organisms involved in bioaccumulation need nutrients and time to grow, making it a slower process. The toxicity of dyes to living microorganisms is another factor influencing bioaccumulation, which makes biosorption a preferred method for removing non-biodegradable dyes. In biosorption, only the surface of the biomass cells is accessible for binding, whereas in bioaccumulation, the pollutant is initially adsorbed and then transported into the cell structure. As a result, bioaccumulation offers more binding sites for pollutants than biosorption. The adsorption capacity is affected by several factors, such as pH, temperature, biomass adsorbent type, and other competing pollutants. Mona et al. successfully removed 94% of Reactive Red 198 (100 ppm) dyes using the cyanobacterium Nostoclinckia HA 46, which has a dye uptake capacity of 93.5 mg/g [93]. Daneshvar et al. reported that the biosorption of Acid Blue 25 (AB25), Acid Orange 7 (AO7), and Acid Black 1 with the brown macroalgae Stoechospermummarginatum, which exhibited adsorption capacities of 22.2, 6.73, and 6.57 mg/g, respectively [94].

1.4.3.2. Microbial degradation (bioremediation)

In current research, bioremediation is essential as it allows for the breakdown of dyes in microbial fuel cells through bioremediation. Bioremediation is a process that utilises the inherent ability of living microorganisms to convert waste into less harmful or non-toxic substances. They are mainly of two types: aerobic and anaerobic. Azo dye degradation occurs when the Azo bond is broken, transforming the dye into a less toxic compound than the parent dye. Azo dyes are electron-deficient because of the (−N=N−) chromophore and several electron-withdrawing groups, which can obstruct or reduce degradation efficiency by other methods. According to the metabolic pathways, a single bacteria species can produce different enzymes, making the process very efficient for the degradation of azo dye. Due to the complex structures of azo dyes, their degradation process involves two steps. The first step is the anaerobic breakdown of the Azo bond, resulting in colourless aromatic amines. In the second step, these aromatic amines are aerobically catabolised into non-toxic compounds. So, combining aerobic and anaerobic biological treatments has shown to be promising for dye degradation. Microbial degradation involves various microorganisms, from bacterial cultures, yeast, and fungal cultures to consortia.

Bacteria are capable of degrading dyes efficiently in both aerobic and anaerobic conditions. However, anaerobic, or facultative microbes are more effective and faster at breaking down Azo dyes. This degradation process involves reducing Azo dyes into colourless aromatic amines, which are then metabolised into electrophilic species. These species form irreversible covalent bonds with DNA [95,96].