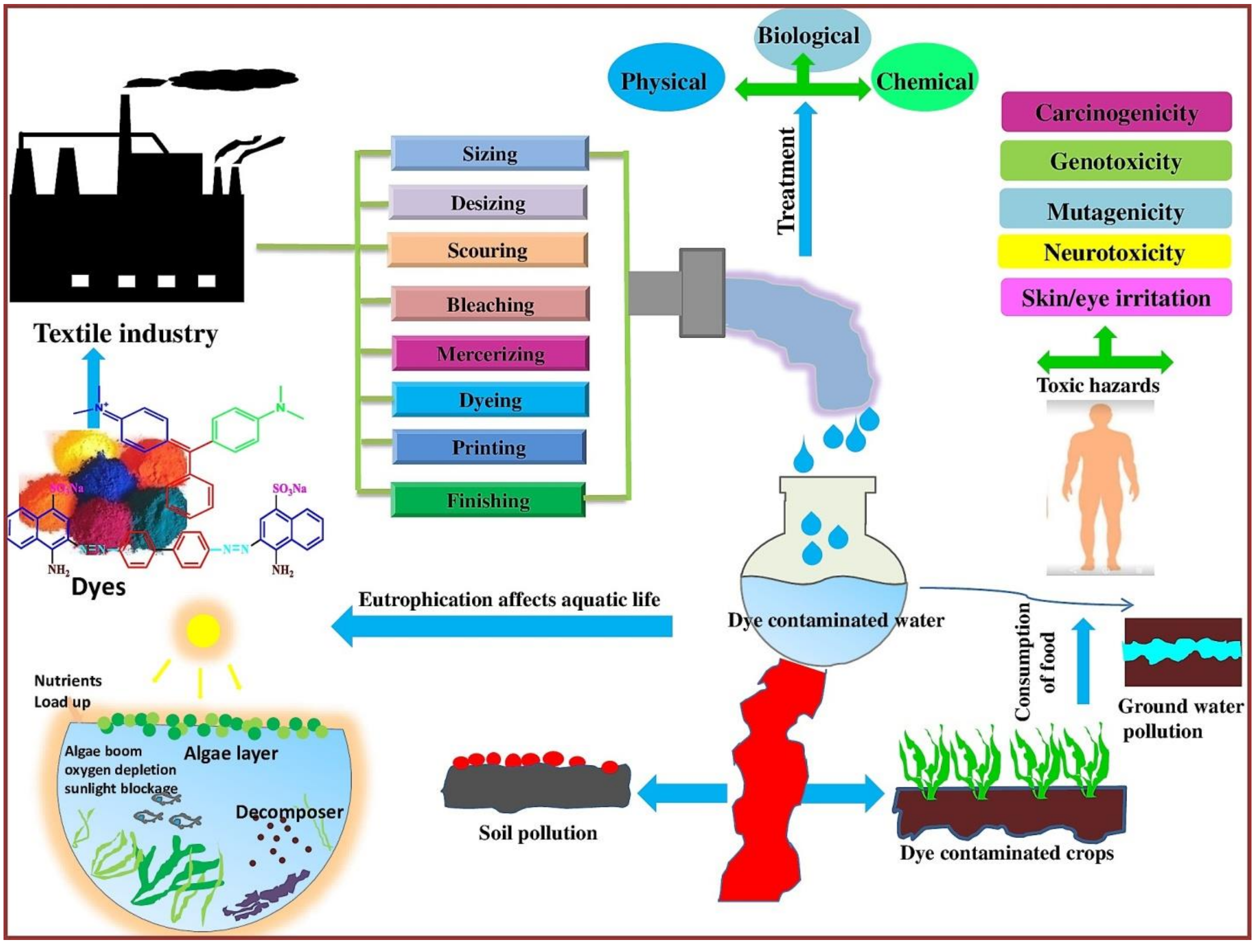
Chapter-I

Introduction and Literature Review



I.1.1 Introduction

With the advent of science and technology in the modern age, the rapid growth of industrialization has had a huge detrimental impact on modifying the world-wide environment. In general, industrial pollution has persisted as a significant contributor to the deterioration of the ecosystem around us, affecting soil, water and air.[1] Among this water contamination is one of the most serious environmental challenges confronting the entire world. This pollution can be caused by both natural and anthropogenic activities. For instance, the textile manufacturer and dyeing industry use million of gallons of water every day and are the major industrial sectors responsible for discharging large quantity of polluted water containing refractory compounds like dyes.[2] However, these industrial discharged mainly comprises of organic and inorganic pollutants. The most common organic contaminants consist of textile dyes, pesticides, pharmaceuticals, surfactants, phenolics, and personal care products, etc., which are dissipated through industrial activities.[3,4] In contrast, the inorganic contaminants include heavy metals, halides, oxyanions, cations, radioactive materials, etc. The coexistence of heavy metals like Cr, Hg, Pb, Cd in synthetic dyes is exceedingly noxious to living organisms. Nevertheless, textile dyes reduce the esthetic qualities of water bodies by increasing BOD and COD, impairing photosynthesis, inhibiting plant growth, entering the food chain, causing recalcitrance and bioaccumulation, and potentially promoting toxicity, mutagenicity, and carcinogenicity.[5,6] Thus, the removal of hazardous toxins from waste water generated by industrial processes is crucial from an environmental perspective. To reduce the environmental impact of textile dyes, sustainable methods must be used across the textile supply chain. This includes employing safer and more environmentally friendly dyeing strategies, introducing new efficient water treatment methods, encouraging the use of non-toxic dyes, and advocating reusable and suitable disposal method. [7, 8]

Layered double hydroxide (LDH), also known as hydrotalcite like compounds, is one of the most promising and versatile classes of materials that are gaining popularity due to their numerous applications in adsorption, catalysis, flame retardant, medicine delivery, carbon dioxide sequestration, sensors, anti-microbial materials, cosmetics, and environmental remediation.[9-17]

The attractive qualities of this two-dimensional material include low toxicity, anion exchangeability, porosity, chemical stability, and customizable structure through metal change. However, in order to design an effective sorbent material, it is critical to fully grasp the structural property-function relationship of materials. Consequently, many studies have been conducted to change the fundamental properties of LDH through surface modification and compositing, which can further enhance its capacity to adsorb ionic species.[18]

In recent years, extensive research efforts have been devoted to developing composite materials between LDH and biomass ash. In general, biomass ash is the solid product obtained from the thermochemical treatment of organic matter from various biomass feed stocks. It is a complex heterogeneous mixture comprising organic and inorganic matter with a polycomponent and variable composition. Specific properties of biomass ash include hygroscopicity, long term stability, highly porous, and having a large surface area.[19] Consequently, biomass ash finds significance as an adsorption of environmental pollutants, fertilizer in agriculture, catalyst for zeolite and biodiesel synthesis, recovery of rare earth elements, and supplementary cementious material in concrete production.[20-23] Besides, it is also considered a suitable candidate for supporting nanometric particles by improving surface area and reducing the agglomeration of supported particles. Biomass ash can act as an effective matrix for the modification of LDH to form composite materials, which can be applied as a sustainable low-cost adsorbent in waste water treatment. The dispersion of LDH on biomass ash appears to be an intriguing and alternative solution that allows for the simultaneous and synergistic utilization of the adsorption capabilities of both materials. Furthermore, LDH/Biomass ash composite can be synthesized via a hydrothermal process, co-precipitation of LDH metal salts over biomass ash, or co-precipitation followed by the thermal decomposition method.[24,25]

Researchers are constantly investigating the performance of Zr-based adsorbents in pursuit of more viable and effective adsorbents. The Zr-based adsorbents are extremely efficient and easily adaptable to the contaminants of interest. As a result, these adsorbents have emerged as excellent potential materials preferred by researchers.[26] A variety of Zr-containing sorbents have been notably utilized in the remediation of different contaminants from water, so considering the unique capabilities of versatile Zr and its application as an adsorbent, it becomes necessary to gather its behavioural and functional features for further study. The fabrication of adsorbent surface by incorporating Zr has shown remarkable outcomes with great selectivity in the immobilization of pollutants such as fluoride, phosphate, carbonate, arsenate, chromate, molybdenate, and dyes, etc. In addition, zirconium also finds significance in photocatalysts, ion exchangers and coagulation, etc.[27,28]

Another unique approach for modifying the physico-chemical properties of LDH involves the use of anionic surfactants. Surfactants serve critical roles in the spontaneous self-assembly synthetic method of LDHs. Much study has been conducted to investigate the alignment of surfactants in the interlayers of LDHs as well as the effect of surfactant concentration on the physical characteristics of LDH particles. However, the role of surfactants in the synthesis of LDH, especially the lamellar development of LDH nanosheets and their stacking in to LDH particles, is not well understood. By intercalation LDH with surfactants, the hydrophobic nature of the LDH can be improved, which further increase the adsorption affinity for organic pollutants. Several instances revealed the feasibility of surfactant- modified LDH as an adsorbent in the removal of various dye compounds. Therefore, surfactant-modified three-dimensional LDH can be advocated as a potential broad-spectrum adsorbent for the treatment of anionic, non- ionic, and cationic dyes from aqueous medium.[29]

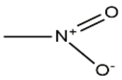
In this thesis, we have demonstrated the synthesis of surfactant-modified LDH (CuAl/SDS-LDH), biomass ash/LDH composite (CHA/CoAl-LDH), Zr-modified LDH (ZrO_2/MgAl-LDH), and ternary LDH (CaNiAl-LDH), which are further implemented for the adsorption of dyes from aqueous solutions. The synthesis of these adsorbent was conducted via co-precipitation, urea hydrolysis, calcination-co-precipitation, and the hydrothermal method. We have discussed the removal of targeted dye pollutants by employing methyl red, congo red, malachite green, methylene blue, and methyl orange dye in an aqueous medium. The effects of various adsorption parameters on the uptake of organic molecules have been studied.

I.1.2 Dyes chemical structure and properties

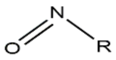
Dyes are complex organic compounds with wide applications in different industries, including textiles, cosmetics, plastics, the food industry, and the photographic and paper industries.[30] From ancient times throughout the history, people have learned to dye their textiles and materials by using locally available natural dyes such as tyrien purple, and crimson kermes. Later on, with rapid industrialisation in 1856, the first synthetic mauve was prepared by William Henry Perkin. The discovery of mauve dye led to increased interest and started a surge in synthetic dyes and organic chemistry.[31,32] Till now, more than a thousand varieties of synthetic dyes have been globally manufactured and turned into a multibillion-dollar industry. Both natural and synthetic dyes are of great interest in modern days and play a key role in our daily life. Despite their wide application, dyes are also harmful and can cause several diseases, such as skin and eye irritation, cancer, etc., when not properly disposed in the environment. The efforts to replace the harmful toxic dyes with natural dyes are currently under investigation.[33]

Chemists have been very intrigued with varieties of colour exhibited by dye molecules and its relationship with the structure. Subsequently, the origin of colour has been fascinated by researchers and considered special subject for study. Organic dye molecules are generally composed of three main components, namely chromogen, chromophore, and auxochrome. The chromogen is a chemical compound containing aromatic structures such as benzene, naphthalene and anthracene rings, which can be coloured by the addition of certain substituent groups. These substituent groups that impart coloured in chromogen are known as chromophores. The commonly known chromophore groups responsible for the appearance of colour in organic dyes are azo (-N=N-), carbonyl (-C=O), double bond (C=C), (C-C) triple bond, CN, nitro ($-NO_2$), nitroso (-NO, -N-OH), carboxylic (-COOH), ester (-COOR), (=C=S), etc. The conjugated or alternating double bond and single bond structure of chromophore facilitates the absorption of radiation in the visible region of the spectrum (400-700 nm).[34] In general, most of the coloured dye molecules contain chains of methine (-CH=) groups where electron donor (N) and electron acceptor (O) atoms are present at the end of the chain, whereas in some dyes, indamines (-N=) groups are present in place of methine (-CH=) group.[35] Moreover, auxochrome is a substituent group such as $–NH_2$, -OH, -SH, X_2, SO_3^{2-} etc., when attached to the chromogen influences the intensity of the colour. For instance, in the case of benzene, the λ_{max} = 256 nm and ε_{max} = 200 nm, when the auxochrome –OH is attached on the benzene ring, the resulting λ_{max} and ε_{max} values increase to 270 nm and 1450 nm, respectively, and it can be attributed to the conjugation with the help of OH group containing a lone pair on the O atom. It also provides adherences of the chromophore-chromogen structure to fiber and enhances the solubility of dye in water.[36]

The chromophore containing only π electrons may give rise to π-π^* electronic transition, whereas those chromophores (C=O, CN, N=N) containing both π and non-bonding electrons may undergo π-π^*, n-π^*, and n-σ^* transitions. The conjugated chromophore results in the shifting of absorption maxima to the higher wavelength with an increase in intensity as compared to the unconjugated chromophore. For instance, the observed λ_{max} and ε_{max} value of ethylene (171 nm, 15530) and 1,3-butadiene (217 nm, 21000), respectively. Due to conjugation in 1,3-butadiene, the π-molecular orbital of alkene group results in the formation of two bonding molecular orbitals π_1 and π_2 and two antibonding molecular orbital π_3^* and π_4^*. The energy gap between the HOMO (π_2) and LUMO (π_3^*) is low, as a result the electronic transition occurs at lower energy, and a higher λ_{max} value will be observed compared to the higher energy transition (π-π^*) in the unconjugated ethylene molecule (λ_{max}=171 nm).[34,37,38] In general, the values of λ_{max} and ε_{max} increase with increasing conjugated system, and adequate conjugation in the molecule results in absorption in the visible region of the electromagnetic spectrum, therefore causing colour to the molecules. For example, the orange pigment (carotene) present in carrot contains eleven conjugated bond and imparts colour by absorbing at λ_{max} 450 nm and ε_{max} 14 x 10^4. **Fig.I.1** illustrates a list of the few chromophore groups present in the organic dye molecules shown below: [34,39]

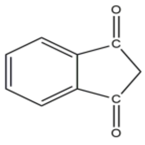


Nitro

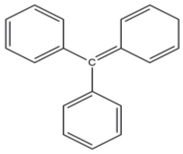


Nitroso

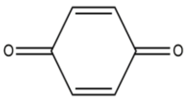
Azo



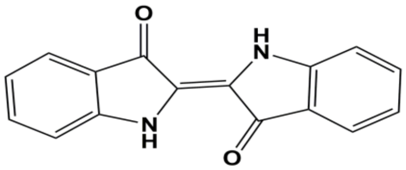
Phthalein



Triarylmethane



Quinoid



Indigo

Fig I.1: Chemical structure of various chromophoric groups.

I.1.2.1 Classification of dyes

Dyes can be classified in numerous ways, depending on several factors. It can be categorized by fabric type, like nylon dyes, cotton dyes, polyester dyes, etc. Dyes can also be classified according to how they are applied to the substrate. And this classification would be more appropriate and essential to a literature about the technology of applying dyes to a substrate rather than classification based on synthesis and chemistry.[40] Based on their application in industries, dyes are classified and briefly described as follows:

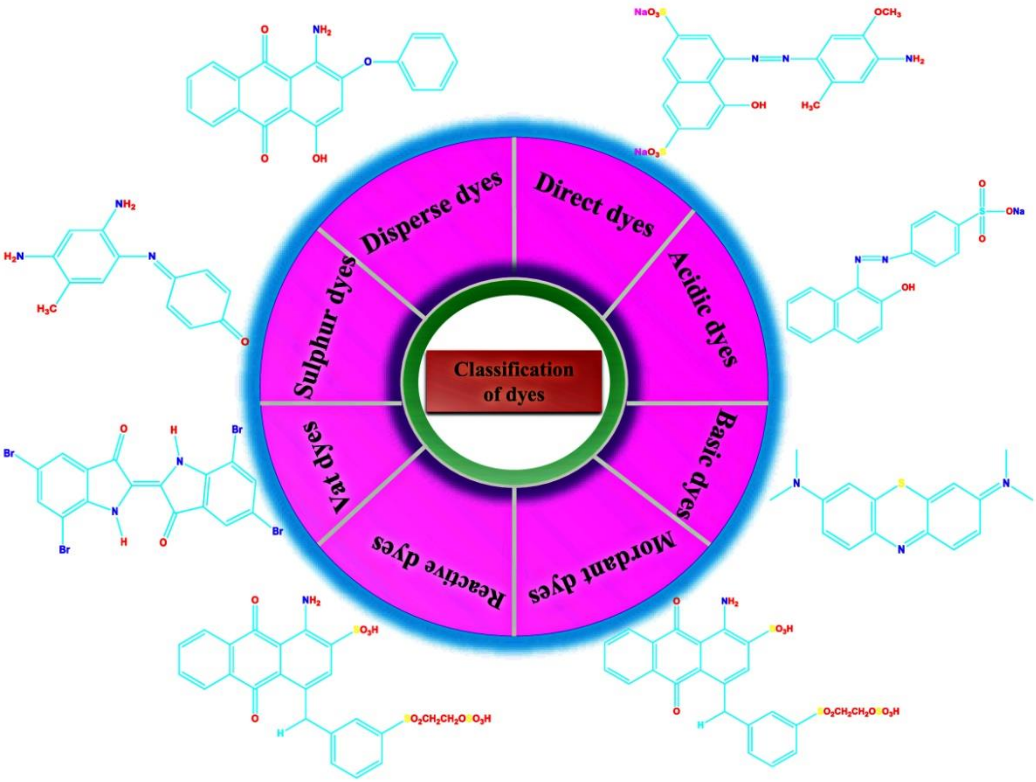


Fig I.2: Classification of dyes.

I.1.2.2 Direct dyes

It is a water-soluble anionic dye containing a sodium salt of sulphonic acid in its chemical structure. It has a strong affinity for cellulosic materials such as cotton, wool etc. It produces vibrant colour and binds to the substrate material without the application of any additional chemicals. Direct dyes are applied by dissolving in an aqueous solution containing NaCl and Na_2SO_4, thereby producing ions such as DSO_3^- and Na^+. These coloured ions are then diffused in to the fibre, which is held by physical forces.[41] Examples: Congo red, Martius yellow, Direct black, Direct violet, Direct red, and Direct blue.

I.1.2.3 Acid dyes

Acid dyes, from the name itself, suggest the presence of acidic groups like –COOH and -SO_3H, along with colour producing chromophore group such as azo, nitro, etc. Acid dyes are water soluble and applied to textiles at a low pH. It shows better lightfastness than basic dyes, although its washfastness is poor. Mainly, it is used for colouring nylon, silk, wool etc.[42] Since the dye and fibre contain oppositely charged groups, the dye uptake on the fibre is very fast, and to retard the process, an electrolyte is added. Although the acidic dyes produce cations on the fibre, the negative part of the dye can be substituted by controlling the dyeing temperature. Examples: Acid yellow 36, Acid orange 7, Acid blue 83, acid blue 7 etc. [42,43]

I.1.2.4 Basic or Cationic dyes

Basic or cationic dyes are the salts of organic bases and contain a cationic group that is responsible for the strong ionic bonding with the negative part of the acrylic fibre. As a result, the use of suitable retarding agents and controlling temperature are required for the levelling dyeing process. Most of the basic dyes are slightly soluble in aqueous solutions. Basic dyes are well known because of their brilliant bright colour and very high intensity. Examples: Methylene blue, Crystal violet, Toluidine Blue, Thionine, etc.[44]

I.1.2.5 Mordant dyes

Mordant dyes are those dyes which require a mordant such as Cr, Al, etc. for the formation of a stable coordination complex that deposits as an insoluble colour on the substrate. Common mordants include tannic acids, oleic acids, steric acid, Al, Cu, Fe Sn, etc. Mordant generally improves the lightfastness of dye. Most of the mordant dyes have –COOH and hydroxyl groups as negatively charged groups. When mordant dyes form lakes with metal, colour change can be observed.[45] Upon incorporation of low energy atoms in the delocalised dye system, bathochromic shifts occur, and the delocalised electron in the system is responsible for the colour. It is used for wool and polyamide fibres dyeing. They have good wetfastness and lightfastness. Mordant dyes can create lakes with metal hydroxides or oxides, when textile fibres create lakes, they exhibit excellent fastness in future wet treatments. The excellent washing fastness of textile material dyed with mordant dyes is because of the large size of the dye molecules or lakes that are formed within the polymer system of the fibre.[46]

I.1.2.6 Sulphur dyes

Sulphur dyes are water-insoluble dyes whose structure contains complex heterocyclic ring molecules, which are obtained by treating organic compounds containing amino or nitro groups with sulphur and Na polysulphide. These dyes have S-linkage such as di(S-S) and poly($-S_n-$) within the structure. The subunits present are thiazoles, thiazones, thianthrenes, etc. Sulphur dyes are highly coloured and have good lightfastness and excellent washfastness. Since it is insoluble in water, sulphur dyes have to be transformed into their leucoform by reducing with dilute Na_2S. The leucoform of sulphur dyes has good substantivity towards the substrate molecule and is easily applicable to various articles like cotton. Example: Sulphur black, Indophenol, etc.[47]

I.1.2.7 Vat dyes

Vat dyes are named from the process where dyeing is carried out in a vat or bucket. The initial vat dyes, also known as indigo dyes, are water-insoluble and feature best fastness properties, including washing, light, and chlorine fastness. The vatting process is necessary for making the insoluble vat dyes into soluble form in order to apply them to cellulosic material. The basic molecular structures of these dyes are quinoid. Since, in oxidised form, it is insoluble, therefore conversion into reduced formed is important and is carried out under alkaline condition. They are classified as (a) Indigoid (b) Anthraquinoid. The dyeing process includes three steps such as vatting, drying and oxidation.[48]

I.1.2.8 Reactive dyes

Reactive dyes are water-soluble anionic dyes that contain reactive groups capable of forming strong covalent bonds with the substrate molecule and becoming an integral part of it that cannot be removed even after repeated treatment. In general, this covalent bond is formed between the reactive group and OH group of the cellulosic fibre and the NH_2 of the polyamide polymer. It covers a wide range of colour spectrum, has good washing and light fastness, and is an inexpensive, easy dyeing method process. Other advantages include high levelling quality, lower cost, and low-temperature dyeing.[49] Reactive dyes can be classified based on (a) reactive group (X_2 halogen, activated vinyl compound) and (b) Reactivity. For lower reactive dyes, pH is maintained at 12-12.5 with NaOH in the bath, while for medium reactive groups, pH (11-12) is adjusted with Na_2CO_3, and for higher reactive dyes, pH (10-11) is maintained with $NaHCO_3$. The colour of reactive dye is not due to reactive group; rather, the chromogen is responsible for it. As the number of reactive group increases, their capability to bind also increases. The reactive group X_2 has lesser reactivity than vinyl sulphone group.[50]

I.1.2.9 Disperse dyes

Based on the chemical constitution, the different categories of disperse dyes are: (1) Nitro Dyes (2) Diazo dyes (3) Amino ketone dyes (4) Anthraquinoid dyes (5) Monoazodyes. Disperse dyes are non-ionic, unsaturated organic dyes used for colouring hydrophobic fibres. Among all dyestuffs, these dyes have the smallest molecular size.[51] Disperse dyes are insoluble in water, and their aqueous dispersion is applied to the surface of the substrate. Since it is non-ionic, it does not affect the negative charge present on the fibres, like polyester. Consequently, disperse dyes have good light fastness value (4-5) and moderate to good wash fastness (3-4). Based on the energy requirement Disperse dyes can be grouped in to three categories: [52]

(a) Low energy: The dyeing temperature is maintained at 77 ℃ with the aid of a carrier and has poor resistance to sublimation.

(b) Medium energy: The dyeing temperature lies between 109 and110 ℃ and exhibits better sublimation fastness compared to low-energy dyes.

(c) High energy dye: The dyeing temperature is carried out above 129 °C. These dyes have superior fastness properties than both low energy and medium energy dyes.

I.1.3 Dye as pollutants

Colour is typically referred to as the first contaminant of waste water that can be easily observed and provides clear remarks of pollution in discharge effluents from various industries such as pharmaceuticals, textile, paints, varnishing, food, leather, household, water treatment plants, etc. However, the numerous utilizations of dye in daily life necessitates their discharge together with other hazardous organic and inorganic chemicals from industrial effluents, thus, having negative impact on the environment. In general, dyes are mainly produced from two major sources viz; natural and anthropogenic. Natural dyes are obtained from sources including minerals, plants, animals, and insects, whereas artificial or synthetic dyes are manmade and prepared via complicated and multiple steps involving the reactions of organic and inorganic molecules.[53]

Annually, 7×10^5 tons of 10000 varieties of dyes are manufactured globally. Approximately, 1-2 % of these dyes are lost during production, and 10-15 % escaped from the fibre is released from different industries as pollutant due to in efficient dyeing process.[54] Among top nations, India is the worlds second-largest producer of textiles, accounting for more than 2% of total GDP. It is one of the most important industries, employing around 4.5 crore people. Moreover, due to considerable global demand for fabrics like cotton and polyester, there have been an increasing number of textile industries in India. As a result, the Indian textile industry consumes large quantity of water, approximately 435000000 gallons of water every day, based on World Resources Institute reports. Nevertheless, this sector also utilizes 80% of the entire manufacturing of 6000 tons of dyes.[55] Since the manufacturing of textiles is a complex process, it requires a large amount of chemicals and involves several phases such as sizing, desizing, scouring, bleaching, mercerization, dyeing, printing, and finishing. Thus, all these stages involve generation of waste water, and based on World Bank Report, the dyeing and finishing phases solely produces 17-20% of industrial effluent. The textile industry effluents are the major sources of water pollution and contain a high concentration of dyes, salts and hosts of other organic and inorganic compound [56]. Nevertheless, textile waste water is characterized by colour, high value of pH, BOD, COD, high concentration of suspended solids, salts, and temperature. If such untreated effluent is released directly into the environment, it contaminates soil and water bodies in the vicinity, causing immense harm to both terrestrial and aquatic life. Subsequently, the determination of various chemical parameters such as dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD), pH, hardness, etc. is necessary for monitoring the quality of water. The low value of dissolved oxygen (DO) indicates highly polluted water due to more consumption of dissolved oxygen while decomposing organic matter in water. Since dyes are organic compounds, their level of contamination can be estimated from such parameters.[57] Several instances on the physicochemical assessment of textile effluents are reported, Sivakumar et al. demonstrated that the waste water from the final clarifier of textile industrial effluent treatment plant in India contains excess levels of BOD (2895 mg/L), COD (3458 mg/L), TDS (3108 mg/L), Cl^-(942 mg/L), SO_4^{2-}(758 mg/L), phenol (155 mg/L), and dye (45 mg/L).[56,58] Patricia A. Carneiro et al. reported the detection of disperse dyes from textile effluents by using HPLC coupled diode array detector method. Their findings indicate quantification of disperse dye such as disperse orange 37, disperse violet 93 and disperse blue 37 over the range of 0.50-35 ng with detection limit of 0.09 ng, 0.84 ng, and 0.08 ng, respectively.[59] Deepika Bhatia et al. investigated the physicochemical parameters of textile effluent discharged in Buddha Nallah water in Punjab. The quantification of BOD and COD at two different sites ranged from 12-580 mg/L and 240-990 mg/L, respectively which is relatively higher than the WHO water quality standard of 30 mg/L for BOD and 250 mg/L for COD.[60] In another study, Thoker Farook Ahmed et al. reported the physicochemical characterisation of Kshipra river of Ujjain that receives polluted water from Bhairavgarh dye industries. The determine parameters indicate high level of pH (7.6-9), TS (2100-6050 mg/L), TDS (1990-5820 mg/L), DO (0-8mg/L), COD (73-345 mg/L), and hardness (321-880 mg/L) that exceeds the standard permissible limit.[61]

I.1.3.1 Harmful impacts on human health

Humans are also highly vulnerable to the toxic effects of dyes discharged from textile effluents. The utilization of dye containing waste water in arid region for irrigating soil was also prevalent in developing nations. Thus, a large quantity of dye gets concentrated near the ground surface of textile power plants. Besides, dyes are capable of remaining in soil for a long period of time and get solidify quickly. Humans may be exposed to these dyes in one of two possible ways: either by ingestion of contaminated food like fish or by consuming crops grown in soil that has accumulated hazardous dyes or their degraded forms. Therefore, these toxins can affect human organs by entering the food chain and leading to a number of diseases.[62]

For instance, azo dyes are the most common type of industrial dye, accounting for 65-75 % of all textile dye products. These water-soluble dyes are widely utilized in a variety of industries, including textile, paper, printing, and food, and are typically discharged into industrial waste water. They are synthetic compounds containing -N=N- group and contact the human body through multiple exposure routes, thereby triggering toxic effects. Many azo dyes and their reductively cleaved derivatives, as well as chemically related aromatic amines, have been linked to allergies and other human illness. In particular, azo dyes can be carcinogenic because of their cleavage product, benzidine, which induces human and animal tumours. P-phenylenediamine, another component of azo dyes, is responsible for causing allergies.[63] The basic dye malachite green (MG) has been identified as a persistent colouring pollution that has a negative impact on human health by reducing food intake, growth, and reproductive rates and causing harm to the kidney, spleen, heart, and liver. It also leads to an increase in WBCs, anaemia, a fall in RBCs, and lesions on the eyes, skin, lungs, and bones. Due to its hazardous effects, MG dye is currently prohibited in many countries and is not permitted by the US Food and Drug administration, yet it continues to be utilized in a number of countries.[64]

Ito et al. illustrate the negative effects of long-term exposure to complex metal dyes on human health, demonstrating the harm caused by industrial effluents. Nickel, cobalt, copper, and chromium are the heavy metal cations that are primarily found in dyes used in the textile industry and are reported to accumulate in fish tissues after being released into water bodies and eventually affect humans. These dyes may also come into contact with human via inhalation of dust containing dye contaminants. Nevertheless, prolonged exposure to these dyes for long duration can caused various diseases related to skin, central nervous system, liver, kidney, enzymatic, and reproductive system.[65] The replacement of enzymatic cofactors by dye components can also lead to the inactivation of enzymatic activity. In particular, industrial workers handling dyes such as reactive dyes are at a greater risk of developing diseases, which include dermatitis, allergic conjunctivitis, rhinitis, and asthma. The reactive dyes are known for acting as antigens, and after interaction with human serum albumin, they produce the antibody immunoglobulin E(IgE), which gets attached to histamine, causing allergy. For diseases like asthma, the chromogen part of this dye induces an immune response by acting as a haptans. Moreover, textile dyes such as malachite green, congo red, methylene blue, methy orange, and methyl red are widely utilized for industrial applications Despite the prohibited agreement, still more than 100 dyes out 4000 dyes have been found toxic and available on the market.[66]

I.1.3.2 Impacts on aquatic life

Microalgae is a vital species for toxicological investigation in aquatic ecosystems. It can act as a pollution indicator, and due to contact with organic dye pollutants from textile manufacturers, the growth of protein, pigment, and nutrients in microalgae is extremely inhibited. For instance, Sudarshan et al. tested the toxicity of rhodhamine B dye on the microalgal species chlorella vulgaris. The experiment was carried out for a time period of 24-96 hours. The SEM analysis revealed shrinkage in the cell surface, inhibition in growth, pigment synthesis, and protein content. The investigated results also confirmed a disruption in metabolic activities in microalgae due to the acute toxicity of rhodhamine B dye. However, high concentrations of dye in water deplete O_2 level as well as block sunlight from entering the photic zone of the aquatic environment. Consequently, the rate of photosynthesis decreases due to changes in the ecological environment. Fish are also susceptible towards the change in aquatic environment resulting from the effluent discharge of textile industries, which can be manifested from the alteration in various parameters such as histological, biochemical, and physiological.[67] Ayebidun et al. have reported the toxic effect of indigo dye on Oreochromis niloticus juvenile. However, the studies suggested degeneration of cells, space formation, slight cellular changes, and vacuolation of the fish after treatment with a high dose of indigo dye ranging from 1.5-2.5 mg/L.[68] Sinha et al. conducted behavioural, hispatological, ultra-structural, and biochemical studies on fingerlings of Cyprinus curpio fish by injecting a sublethal dose (0.087 mg/L) of malachite green dye. However, the results obtained from scanning emission microscopy studies confirmed various abnormalities like clubbing, budding in peripheral erythrocytes, damage to pavement cells, and change in cells shaped, increased intramicroplicae, etc. Furthermore, the bioaccumulation studies indicate 3.06-fold dye deposition. Thus, malachite green dye can be considered a highly toxic dye, even at sublethal dosages.[69] In other studies conducted on Labeo rohita fish by exposing them to methyl orange dye for 7 days. The results indicate that the treated methyl orange dye solution did not causes abnormal behavioural changes compared to untreated methyl orange dye. However, upon histological examination, various disorders such as nerosis, haemorrhage in the gills, shrunken glomeruli, and congestion was evident, which clearly confirms the toxicity of exposed dye.[70]

Table I.1. Summary of industrial application and toxic effects of organic dyes.[71-73]

Organic Dyes	Industrial uses	Health/Environmental effect
Direct dyes	Leather, nylon, wool, silk, as pH indicator, biological staining, applied in curtain fabric, finishing.	Irritation of eye, skin, respiratory tract, cytotoxic, mutagenic and carcinogenic.
Acid dyes	Food colorants, staining organelles, dyeing natural proteins such as silk, wool.	Toxic when inhaled and ingested, hispathological changes observed in fish on liver, stomach, intestine, hemorrhage and necrosis in liver, acute depletion of epithelium.
Basic dyes	Dyeing acrylics and modified acrylics, paper, dyeing textiles, production of ink, leather.	When contact causes vomiting, heart beat increase, jaundice, tissue necrosis, cyanosis, carcinogenicity.
Mordant dyes	Dyeing wool, gram staining in microbiology and tanning leather.	Mordant dye containing metal is toxic and safe use and disposal is required. Alizarin caused mutagenic and carcinogenic, induce oxidative damages in organism.
Azoic dyes	Used in textile, leather articles and food industries, printing, paper manufacturing, fibre, cosmetics.	Mutagenic, carcinogenic, allergic reactions, bioaccumulation.
Sulphur dyes	Dyeing cellulosic material such as polyester/cotton yarn, leather.	Creating dye bath effluent, DNA damage (genotoxicity) in tadpoles.
Vat dyes	Use in cellulosic fibre, leather, viscose rayon and other fibres.	Redness, swelling, rashes, dry and brittle hair, skin sensitizers, allergic skin, toxic to soil organism like earthworm.
Reactive dyes	Dyeing wool, polyamide and cellulosic fibres such as cotton, viscose and proteins. Discharge printing and inkjet printing.	Recalcitrant to biodegradation, aesthetic, acute and chronic toxicity problems in receiving water
Disperse dyes	Cellulose ester, acetate, polyester fibres, nylon and acrylic fibres etc.	Causes sensitization elicitation of skin, allergens, carcinogenic, induced contact dermatitis.

I.1.3.3 Guidelines and legislation on textile effluents

Over the years, more attention has been paid to environmental issues associated with industrial activity. As a result, environmental laws and standards are being enforced in order to apply restrictive legislation. In the United States, the Clean Water Act (CWA) is one of the most prominent environmental laws for regulating water pollution. Its goal is to restore and sustain the physical, chemical, and biological integrity of country's water. The CWA criteria are mostly based on United State Environmental Protection Agency (USEPA) water quality standards. These guidelines describe a water body's purpose by identifying its uses and establishing provisions to protect water quality from pollution. Furthermore, the rules apply to textile dyeing by restricting the discharge of organic species and metals such as Cu, Cr, Ag, and Zn.[74] The REACH regulation, which is the principal EU legislation in terms of chemical substances control, prohibits the utilization of compounds such as azo dyes, dimethyl fumarate, and phthalates in textiles and footwear. It also establishes limits for compounds such as polyaromatic hydrocarbons and metals like Cd, Cr, As, Pb, and others that are utilized in various stages of the textile production cycle, including dyeing, manufacturing, and integration, to provide particular qualities to items. Furthermore, the prohibition of these substances is required to maintain textile safety for human health and environmental protection.[75] The Bureau of Indian Standards (BIS) additionally promulgated drinking water regulations in which the acceptable limit of color in water is 5 hazen and the permissible limit is 25 hazen. Accordingly, numerous attempts should be made to remove as much color and unpleasantness as possible. The central ground water authority of India has also released guidelines stating that ground water abstraction using powered pumping may only be permitted for drinking water needs, and the water-intensive sectors like textiles must obtained a No Objection Certificate from the competent authorities in locations where the ground water status is categorized as critical and semi critical.[76] In addition, China has the world's greatest textile manufacturing, and according to annual ecological environment statistics, an excessive amount of textile waste water in China totals approximately 1.84 billion tons per year. However, in order to safeguard the environment and manage pollution, various laws and regulations, such as the Environmental Protection Law of the People's Republic of China, were enacted in 1992. This regulation encourages the improvement of textile dyeing and finishing production processes and pollution remediation technology. It has also developed the standard discharge limit of water pollutants, in addition to monitoring and controlling the textile manufacturing process.[77]

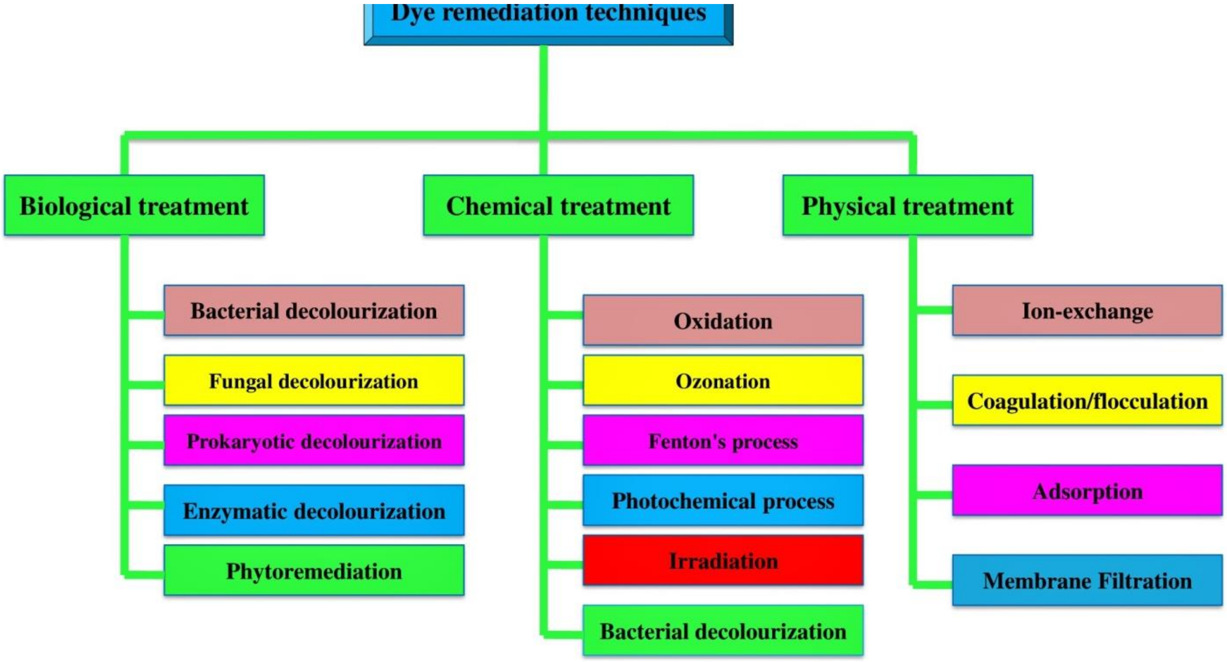
The international dye industry waste water has applied the zero discharge of hazardous chemicals programme (ZDHC) to prevent textile industries from effluent discharge that are beyond the restricted limit. The various parameters, such as pH, BOD, COD, TDS, TSS, temperature, and colour level are accounted for determining the toxicity level in waste water and should be below the permissible limit mentioned according to international standards.[78] In India the discharge limits of industrial effluents in to inland surface water, marine or coastal area and permissible limits from dye and textile industries according to environmental protection rules 1986, is summarized in **Table I.2**.

Table.I.2: Discharge limits based on environmental protection rules 1986.[79]

Parameters	Dye and textile industry	Marine/Coastal area	Inland water surface
pH	6-8.5	5.5-8.5	5.5-9
Temperature	Less than 5 ℃	-	40 ℃
TSS	100 ppm	100 ppm	100 ppm
TDS	-	-	2100 ppm
BOD	100 ppm	100 ppm	30 ppm
COD	-	250 ppm	250 ppm
Colour	400 Hazen	Absence of colour	Absence of colour
Oil and Grease	10 ppm	20 ppm	10 ppm
Toxicity (e.g fish eggs)	90 % survival of fish after 96 hr.	90 % survival of fish after 96 hr	90 % survival of fish after 96 hr

TSS = Total suspended solid, TDS = Total dissolved solid, BOD = Biological oxygen demand, COD = Chemical oxygen demand, ppm= Parts per million

Fig.I.3 Various dye remediation techniques.



I.1.4 Different techniques for dye remediation

Considering an increasing concern for health, primarily on aesthetic grounds, researchers started to draw attention to dye pollution in the early 1980s. Since then, information on the detrimental effects of consuming-coloured substances has been public, and dye producers, consumers and concerned authorities have come ahead and implemented significant steps to deal with the dye- containing waste water sources. Dyes containing effluents are highly challenging for treatment using traditional approaches because they contain recalcitrant organic molecules that are resistant to aerobic digestion as well as light, heat, and oxidizing agents. Because of dyes chemical stability and poor biodegradable properties, traditional biological water treatment approaches, as well as conventional primary and secondary systems, remain ineffective and unsuitable for treating dye waste water. As a result, the elimination of dyes from industrial waste water in an environmentally benign manner remained a major challenged for current research. To reduce the harmful effects of synthetic dyes, a variety of dye treatment approaches have been explored. Essentially, three dye removal techniques are discussed and included in three categories: chemical, physical, and biological.[80]

I.1.4.1.1 Biological treatment method

In biological treatment method, the degradation of dye is carried out with the aid of microorganisms such as algae, fungi, bacteria, and yeasts. The method involves treatment under aerobic, anaerobic or a combination of both aerobic and anaerobic process. This technology offers numerous benefits, such as being very cheap, providing a low operational cost, and ensuring that the end products are completely mineralized and non-hazardous. However, the main disadvantages of this method include: (1) Incomplete degradation of dye. (2) The xenobiotic dyes containing complex chemical structures cannot be removed. (3) It takes longer time and large land area for the process to occur. (4) Less flexibility in the treatment method.

In the case of the bacterial degradation of azo dye, both aerobic and anaerobic conditions are required for the complete decolourisation of the dye. It offers a high degree of biodegradation and produces minimal sludge. For instance, the first azo dye degradation with bacterial species Bascillus subtilis was reported by Horitsu et al.[81] The degradation of phenolic and non-phenolic dyes with the aid of fungi acting as an oxidising agent was also studied. In general, decolourization of dye with fungi is more preferred when there are fewer nutrients (C, N, O) in the surrounding environment. Furthermore, the decolourization process is also affected by a variety of factors, such as contaminant concentration, dye concentration, starting pH, temperature, etc. Although this method of treatment is appropriate for some dyes, the majority of them are resistant to biological degradation or are not adaptable under aerobic conditions.[82]

Since algae act as pollution indicator in aquatic marine environments, it can also be proposed as a solution to the global environment problems related to waste water remediation. Several species of algae, viz., chlorella, spirogyra, and oscillateria show excellent performances in the detoxification of dye from wastewater. In addition, yeast species like candida zeylanoides and ascomycete have also been reported in dye remediation process. However, it was suggested that both algae and yeast degrade dye through adsorption and enzymatic action.[83]

Several attempts were made to use the enzyme in the dye removal process. The Microbial enzymes azoreductase found in cytoplasm of general microbes has been investigated and found to be responsible for reducing chromophoric azo –N=N- group into amine group by cleaving and causing them to transfer four electrons. The reduced amine group can be further decomposed via an aerobic process.[84] Another Cu-bearing enzyme known as laccase is also a potential candidate for decolourizing azo and phenolic compounds. Dye decolouring peroxidises (DyP) also show degradative dominance and high enzymatic activity for a wide range of organic dyes, primarily anthraquinone dyes. It can oxidize polycyclic dyes and phenolic compounds due to its distinct sequence and protein composition compare to other peroxidise enzymes.[85]

I.1.4.1.2 Phytoremediation method

In this method, plant derived microbes, or microbiota, are utilized to clean contaminants from waste water and soil. The decontamination takes place naturally via decomposition, elimination, and retention during the process. This method involves several advantages, such as low-cost, environment friendly, and a sustainable procedure for the treatment of dye-polluted ecosystems. However, the rate of dye remediation is very slow and may last for many years. In addition, the process may be delayed due to several factors, like seasonal vegetation damage, pests, and plant diseases. Several plant species have been reported in the decolourisation of textile effluents. For instance, macrophytes such as phragmites australis and rheum rhabarbarum have been used for the removal of acid orange 7.[86] In another study, it was shown that the roots of the water hyacinth may remove methylene blue and methyl orange dye. Furthermore, the degradation of direct blue 129 using the aquatic plant spirodela polyrrhiza was also reported based on artificial neural networks. Therefore, the phytoremediation prospective has been widely explored by researcher for treatment of textile dyes.[87]

I.1.4.2.1 Chemical treatment method

In this method, dye degradation is performed under the assistance of chemical agents such as $KMnO_4$, H_2O_2, and NaOCl, etc. The method offers a highly efficient removal percentage of textile dyes. Besides, the process also showed many limitations, which are as follows: (a) It is an expensive process that involves a large consumption of chemicals and electrical energy. (b) Most of the processes are influenced by the pH of the solution, except electrochemical destruction technology. (c) A secondary pollutant may be produced. However, the commonly used chemical methods for dye treatment are as follows: [88]

I.1.4.2.2 Oxidation

Various chemical oxidants, such as Cl_2, $KMnO_4$, NaOCl, K_2FeO_4, etc., are used for the degradation of dye. These chemical agents have strong oxidation potential to destroy the chemical bonds responsible for exhibiting colour in dye. This process requires less time to complete the reaction, as well as low quantities of oxidising agents are used. Moreover, the cost of this method depends on the dosages of oxidant used. Larger doses lead to better effluent quality, but the cost of treatment increases.[89]

I.1.4.2.3 Ozonation

Despite its wide application as a disinfectant agent, O_3 is also used for the treatment of organic dyes in waste water. It is one of the most powerful oxidants with a high oxidative potential (2.07 V) and is considered as an eco-friendly method where various pollutants, microorganism, odour, etc. are treated without the generation of harmful chlorinated products. However, the half life period of O_3 is very short, around 20 min, consequently, continuous supply is necessary, which may increase the cost of operation. The method is influenced by both the pH and temperature of the medium. Under acidic conditions, it leads to the formation of radicals such as ·OH, which further aids in the breakdown of organic pollutant structure. The typical reaction involved during the ozonation process in water is represented as follows: [90]

$$3O_3 + OH^- + H^+ \longrightarrow 2\cdot OH + 4O_2 \qquad (1)$$

I.1.4.2.4 Fenton process

In this process, Fentons reagent ($H_2O_2.Fe^{2+}$) is used for the oxidation of dye contaminants in waste water. This method is part of an advanced oxidation process where various toxic organic compounds can be degraded. The reagent is pH-sensitive, as both low and high pH is not favoured. At low pH, Fe^{2+} undergoes complexation and is not available for the generation of oxidative species (·OH), whereas at high pH, hydrogen peroxide becomes unstable, leading to self-decomposition as well as a decrease in the reduction potential of generated ·OH radical. However, in an acidic medium, the Fenton reagent is relatively stable. The typical mechanism for dye degradation by Fenton process is shown below:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {\cdot}OH \tag{1}$$

$$RH + {\cdot}OH \longrightarrow {\cdot}R + H_2O \tag{2}$$

$${\cdot}R + Fe^{3+} \longrightarrow R^+ + Fe^{2+} \tag{3}$$

$$Fe^{2+} + {\cdot}OH \longrightarrow Fe^{3+} + OH^- \tag{4}$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + H^+ + HO^{\cdot}_2 \tag{5}$$

$$Fe^{3+} + HO^{\cdot}_2 \longrightarrow Fe^{2+} + O_2 + H^+ \tag{6}$$

Ferrous ions are produced in theFenton process by the reaction between ferric ion and H_2O_2 in reaction (5) and (6) in an acidic medium. These reactions increase the advantages of Fenton processes because the regenerated Fe^{2+} will undergo further Fenton reactions.[91]

I.1.4.2.5 Photochemical process

Photocatalysis has evolved as a green method for the complete mineralization of potentially hazardous organic compounds into water, carbon dioxide, and mineral acids at ambient temperature. It is a light-induced reaction that is aided by the presence of a catalyst. In this method, light radiation of suitable wavelength under UV and visible regions acts as a source of photons that fall upon the surface of the photocatalyst like TiO_2, ZnO, CdS, ZrO_2, WO_3, etc. As a result, the transfer of electron takes place from the valence band to the conduction band of the semiconductors. The excited electrons in the conduction band react with O_2 to produce superoxide O_2^- species, and the holes created in the valence band react with water to generate ·OH radicals. These species have a high oxidation potential to destroy various organic pollutants including dye. The essential steps involved have been pictorically represented below.

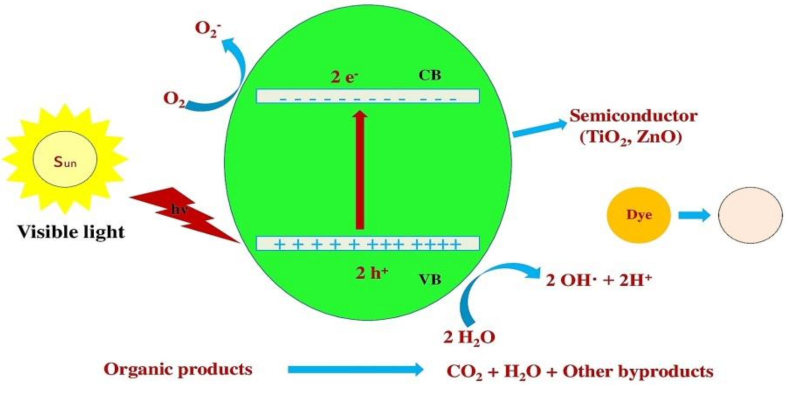


Fig. I.4 Mechanism of photocatalytic degradation of dye.

However, the photocatalytic process is affected by various parameters like the type of semiconductor used, light source and intensity, pH, catalyst dosages, doping of the photocatalyst, temperature, etc. The main advantages of this method are low energy consumption, broad applicability, long-lasting, residual-free, and sustainable, relying on natural processes like sunlight. On the contrary, the method is not highly selective and can degrade both pollutants as well as important compounds, which may lead to undesirable consequences. In addition, the degradation process can be slow, and the deactivation of photocatalyst may take place over time due to poisoning. Other drawbacks include light dependency and a high initial cost that needs to be considered when choosing it as a treatment option.[92]

I.1.4.2.6 Electrochemical process

Electrochemical treatment is a unique method for organic pollutant remediation and superior to the existing process. The main advantage of this method is that it is free from limitations such as sludge creation, requirement of large chemical agents, high electrical energy consumption, and complicated operations. The process required the use of a suitable electrode, which is kept in contact with waste water and ultimately oxidises the pollutant. The chemical reaction involved depends on the nature of the dye and electrochemical properties of the electrode used. The method is clean compared to various existing methods and is found effective for the degradation of harmful dyes into less harmful products.[93] In general, a chemical reaction involved in the electrochemical degradation of organic compounds by using metal oxides as anode material was introduced by Comninellis and Pulgarine. Considering this in the first step, water molecules accumulate on the surface of the anode to create adsorbed hydroxyl radicals, and the next step involves the formation of metal oxide layer, as given in reaction (1) and (2). In the third step, the oxidizable organic compounds (R) undergo oxidation:[93, 94]

$$MO_x + H_2O \longrightarrow MO_x({}^{\cdot}OH) + H^+ + e^- \quad (1)$$

$$MO_x({}^{\cdot}OH) \longrightarrow MO_{x+1} + H^+ + e^- \quad (2)$$

$$MO_x({}^{\cdot}OH)_n + R \longrightarrow MO_x + n\,CO_2 + nH^+ + n\,e^- \quad (3)$$

$$MO_{x+1} + R \longrightarrow MO_x + RO \quad (4)$$

I.1.4.3 Physical treatment method

Traditional physical dye removal methods include ion-exchange, coagulation-flocculation, adsorption, and membrane filtration. The physical technique for water treatment is most commonly utilized due to its ease operation, simple set-up, and highly efficient dye removal.

I.1.4.3.1 Ion exchange method

The ion exchange method of dye removal is a process that utilizes the principle of ion exchange to remove dyes from waste water. It employs ion exchange resins, which are generally functionalized polymeric beads with ability to bind ions of opposite charge. Depending on the nature of the resins, such as anionic or cationic exchange resin, the selectivity and removal of dyes are decided. Some of the commercially available anion exchange resins reported in dye removal are Amberlite IRC-71, Zeolite based macrosorb, Purolite, Dower Dow. Non commercial anion exchange resinS such as microcrystalline cellulose gel, chitosan-polyaniline/ZnO hybrid composite, starch/polyaniline nanocomposite, α-cellulose/polypyrrole, etc. have been investigated for the removal of reactive dyes. However, the resin used in the method requires regeneration once it gets saturated with dyes. The need of flushing and backwashing to repair the ion exchange media limits its application in water treatment, and it also adds to the overall cost and makes the process more complicated. Besides, it also revealed several important features like being less expensive, simple operation, and reusability, etc.[95]

I.1.4.3.2 Coagulation/Flocculation

It is a cheap and robust method that uses chemical agents known as coagulants and flocculants to separate dyes from wastewater. A coagulant such as ferric chloride, aluminium sulphate, polyaluminium chloride (PAC) destabilize the suspended particles having opposite charge and attracts them to form larger aggregates, which can be further enhanced by the addition of flocculants, leading to bigger flocs. These flocs can be easily removed by various techniques, such as filtration and sedimentation. Moreover, such inorganic chemical agents cannot remove highly soluble dyes. The demerits of this process involve the creation of secondary pollutants.[96]

I.1.4.3.3 Adsorption

Adsorption is a surface phenomenon that results in the transfer of a molecule from the bulk fluid to the solid surface. It is the adherence of an adsorbate molecule to the surface of solid material known as an adsorbent. This can occur because of physical forces or by chemical bonds. In physical adsorption, weak forces such as hydrogen bonding, vander Waals force, and dipole-dipole interactions participate, and the process is usually reversible in nature, but in chemical adsorption, strong covalent or coordinate bond exist in the adsorbate-adsorbent system, which makes it difficult to remove the adsorbed species. Among several techniques of dye remediation, this method is widely used and accepted as the best method owing to its special advantages like simple process, low cost, highly efficient, etc. For this technique, varieties of adsorbents like natural and synthetic clay, commercial activated carbon, metal organic framework, agriculture waste, polymer-based composite, etc. are employed for the treatment of dye contaminated water.[97] Therefore, the application of such a technique with a properly designed system is highly recommendable for decolorizing organic contaminated water and also for detoxifying metals.

I.1.4.3.4 Membrane filtration

Membrane possesses interesting properties for the physical separation of dyes and dyes auxiliaries from water. It is based on the principle of size exclusion, and the ability to separate contaminant is determined by the pore size of the membrane and the molecular size of the contaminant molecules. In this method, dye-contaminated waste water is allowed to pass through the membrane, where the large dye molecules having a greater size than the membrane pore are retained on the surface of the membrane. The smaller molecules and pure water leave the membrane after filtration. The main advantages of this process are speed of operation, reusability, covering a wide range of dyes, and less space required. On the other hand, the limitations include regular maintenance and cleaning of membranes, short life time, etc. In addition, depending on the membrane pore size, the different types of filtration methods are categorized as ultrafiltration, nanofiltration, microfiltration, and reverse osmosis. Among these methods, the membrane used in reverse osmosis is of the smallest pore size and also reveals high dye removal efficiency.[98]

I.1.5 Development of adsorption technology

The properties of various solids to decolourize liquids are well known throughout the ages. Similarly, the unpleasant odour of the polluted air can also be treated by flowing air through the vessel fixed with charcoal adsorbents. Despite the fact that such phenomena were not clearly comprehensible in the early 20th century, it delineates the origin of adsorption technology, which has served as a means of decontaminating both liquid and gaseous medium in the current scenario. However, the subject of adsorption is extremely interesting and has attracted wide attention among researchers, thereby resulting in a new emerging technology compared to other well-established techniques such as membrane filtration, photocatalytic degradation, coagulation, and flocculation.[99] Several efforts were made to gain deeper insight into the decolourization of waste water and the removal of unpleasant odour from the air stream. This led to the quantitative determination of adsorbate concentrations present in both liquids and gases. The classical experiment conducted by several scientists, such as Langmuir, Brunauer, Emmett, Teller, and Bakr, etc., further elucidates the properties of solid adsorbents in abstracting objectionable components from gases and solutions. Consequently, their original research had significantly contributed to the development of quantitative theories that worked well over a long period of time. For instance, the adsorption phenomena were also well described as the accumulation of sorbate components on the surface of solid materials due to the association of physical and chemical forces on the adsorbate-adsorbent system. In addition, from their experimental studies, it became more obvious that the porous material has a greater ability to retain component molecules from the bulk phase.[100,101]

The adsorption process played an indispensable role in water remediation for several years, and due to continuous discovery of new pollutant in water cycle, it is becoming increasingly important. Its attractive features include low cost, simple design, ease of implementation, high efficiency, and low maintenance. Another advantage of this method is that it does not generate harmful secondary products, and the applied adsorbents can be easily recycled for repeated use. Alternatively, it is reported as a more effective method for the removal of various inorganic and organic contaminants from wastewater. However, the process is largely dependent on the nature of contaminants and adsorbent employed. Several adsorbent materials for decontamination of effluents were investigated, which include agro-waste derived activated carbon, metal organic framework, zeolite, polymer-based gel, grapheme oxide nanomaterial, and clay minerals. Most of the studies reported are limited only to laboratory scales because commercial production of adsorbents and their utilization on an industrial scale encounter major challenges such as disposal problem, high energy consumption, and the requirement of large chemical precursors, which are not adequately mentioned. Moreover, in search of outstanding adsorption performance and to make sustainable adsorbents, the need for developing adsorption technology should be continuously explored by researchers.[102]

I.1.5.1 Adsorption technology

The residual forces on the solid surface have the ability to attract atoms, ions, and molecules from the liquid and gases when they come close to it. This residual force is generated due to the disruption of bonds between atoms present on the solid surface. In other words, mass transfer takes place towards the solid surface during interaction with liquid and gas molecules. This phenomenon, where the solute molecules accumulate over the solid surface, is known as adsorption. The solid substance where adsorption takes place is called adsorbent, and the adsorbed substance is referred to as adsorbate. Moreover, the surface that separates adsorbent and adsorbate is known as the interface.[103] Depending on the nature of the force that exists in an adsorbate-adsorbent system, adsorption process can be classified in to following types:

I.1.5.2 Physical adsorption

In this process the adsorbate molecules are held by the adsorbent surfaces due to the presence of weak vander Waals forces. It is a reversible process where the adsorbed molecules can be desorbed by altering the experimental conditions. No chemical bond occurs between the adsorbate and the adsorbent. The heat of adsorption or enthalpy change involved during adsorption is the amount of energy released when 1 gram mole of an adsorbate molecule is adsorbed over the surface of an adsorbent. Since the forces existing between adsorbate-adsorbent interactions is weak. Therefore, it is associated with the low enthalpy change during the process, which lies in the range of (20-40) KJ/mol. It is a non-specific process where the adsorbent does not have preference for the sorption of any particular gas molecules. In this type, adsorption also depends on physical parameters such as temperature and pressure. At high temperature, the weak force cannot sustain itself, which results in the destruction of the physisorption process and converts it to chemisorptions. In addition, at low pressure, monolayer adsorption is preferred, while with increasing pressure, the process of adsorption is enhanced and further forms multilayer adsorption of molecules.[104]

I.1.5.3 Chemical adsorption

In chemical adsorption, the sorbate molecules are accumulated on the adsorbent surface due to the association of strong chemical forces such as ionic bond, covalent bond, etc. It is a highly selective process since only certain types of adsorbate molecules can be retained by specific adsorbent molecules. It does takes place whenever a chemical reaction occurs between solute molecules and the surface molecules of solid substances. Unlike physisorption, it involves a larger value of enthalpy change, around 200 KJ/mol, due to the strong force of attraction. In general, formation of monolayer adsorption is expected when the adsorbate molecules do not bind each other, rather, a chemical bond is formed between the active sites of the solid surface and the adsorbed molecules. The interaction between adsorbate and adsorbent is characterized by having all the properties of a true chemical bond. It is an irreversible process due to the requirement of large amount of energy to break the strong chemical bond.[105]

I.1.6 Description of LDH structure and its features

The naturally occurring anionic clay or mineral known as hydrotalcite was discovered around1842 in Sweden. It is the hydroxycarbonate of Mg and Al, and its correct molecular formula was first suggested by Manasse, which is presented as [$Mg_6Al_2(OH)_{16}CO_3.4H_2O$]. Similarly, the termed layered double hydroxide (LDH) is used to designate synthetic anionic clay or hydrotalcite-like compounds.[106] Layered double hydroxides are generally constructed by brucite-type layers, which comprises of divalent M^{2+} and trivalent M^{3+}cations along with intergallery anions such as A^{2-} and A^- (NO_3^-, Cl^-, CO_3^{2-}, etc.,) between the brucite sheets. In the layer structure of LDH, the high-density positive charges due to metals are balanced by the intergallery anions, and the metal cations are coordinated octahedrally by the hydroxyl group. Consequently, each hydroxyl group are directed towards the vertices of octahedron which results in the formation of layer having infinite sheets. Moreover, the arrangement of metal cation is regular throughout the layer. The interaction of the positively charge cation with the inter layer anions is electrostatic in nature, and the lamellar hydroxyl group also generates hydrogen bonding with the electronegative atom of intergallery ions. Basically, the molecular formula of LDH is represented by $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}(A^{m-})_{x/m}.nH_2O$, where M^{2+} and M^{3+} are divalent and trivalent cation, and A is a counter anion with a negative charge m.[107] The structure of LDH has been depicted in **Fig I.5**.

With an emphasis on the synthesis of LDH, the optimum ionic radius for divalent and trivalent cations should lie in the ranges of 0.65-0.80 Å and 0.62-0.69 Å, respectively. Beyond these ranges, the formation of LDH is not feasible, and the inappropriate larger ionic radii of the metal cation can alter the actual brucite structure of LDH by reducing the octahedral symmetry of D_{3d} to C_{3V}, which can occur due to the replacement of one hydroxyl group of the octahedron with a water molecule present in the inter lamellar domain. In general, metal cations with extremely low or high ionic radii than Mg^{2+} are not suitable for LDH synthesis, besides, it may form other compounds. And the most favourable compositional range corresponding to LDH formation lies approximately at $(0.2 \leq x \leq 0.4)$.[108] However, the existence of several LDHs with different compositions outside these ranges is also possible and found in impure state. The relative number of intergallery ions can also be correlated by changing the M^{2+}/M^{3+} metal ratio, which can further influence the charge density of host sheets. Therefore, the arrangement of inter layer anions is dependent on the size of anion, temperature and charge density of the lamellar.[109]

An exceptional feature of LDH materials is their ability to exchange interlayer anions, which makes them distinct from other inorganic materials. A wide range of anionic species, including small to big anions such as sulphate, nitrate, chloride, carbonate, surfactants, amino acids, polyoxometalates, organic biomolecules, etc., can be intercalated within the inter layer space of LDH via simple co-precipitation, ion exchange, and reconstruction method. Another attractive feature associated with LDH is their properties to regain initial layered structure, which is known as called memory effects. In particular, LDH loses its interlayer anions (NO_3^-, CO_3^{2-}, Cl^-, etc.,) when it is subjected to conventional heating, and interestingly, it generates homogeneous mixed metal oxide of the starting materials. The resulting homogeneous mixed oxide, when immersed in an aqueous solution or solution of desired anions, therefore transforms in to a brucite-type layered material with OH^- or targeted anions inside the layer space. Moreover, the control over appropriate temperature (400-550 ℃) is essential because, at higher temperatures, a stable spinel is formed, which can inhibit subsequent rehydration and prevent the formation of actual layered structure.[110] The memory effect can play a vital role in tailoring LDH materials, which can extend the application of the material in diverse fields.

LDH based material holds great advantages, including non-toxicity, chemical stability, flexible structure, low cost, facile synthesis, memory effect, colloidal and thermal behaviour, etc., compared to other layered materials. Such properties make LDH versatile and attractive in the coming year for researchers in catalysis, functional materials, nano-composite material, sensors, anti-microbial materials, and separation science. Besides, LDH materials are also not completely free from limitations; it faces many disadvantages such as an average surface area, agglomeration of particles, exfoliation, low mechanical resistance, lesser functional groups, limited quantity of production, and fewer applications in real waste water. Other challenges include lack of knowledge on the exact structure, postulation of interlayer arrangements.

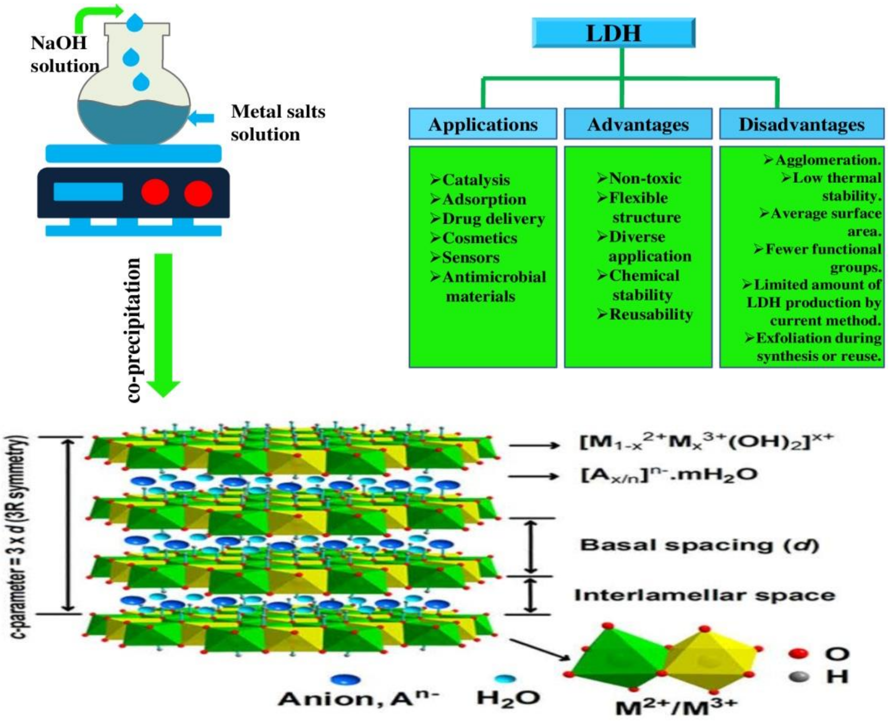
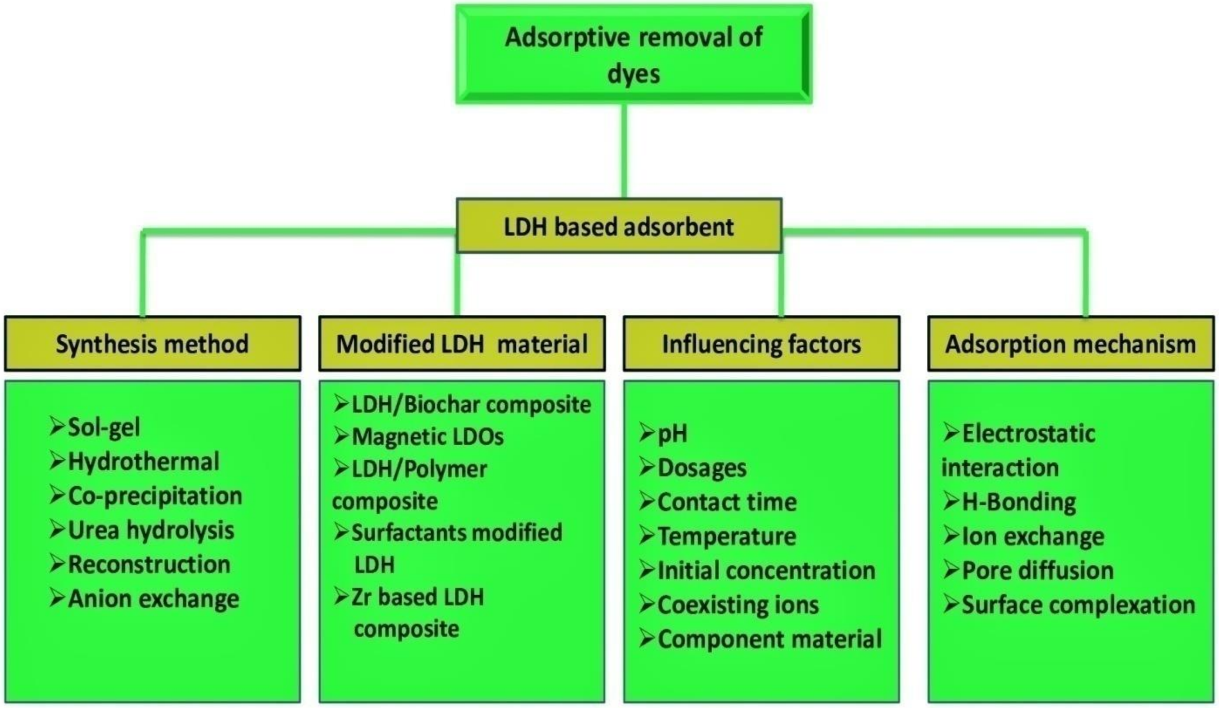


Fig. I.5. The basic structure of layered double hydroxide (LDH) and its application.[111]
(Reproduced with permission from reference number 111)

I.1.6.1 Utilization of LDH based adsorbents in water remediation



Many different low-cost and innovative adsorbents were investigated with moderate success throughout the year; however, the LDH-based adsorbent offers an intriguing low-cost material to be employed for environmental restoration, especially for the removal of dye chemicals. The significant anion exchange capability, moderate surface area, porous characteristics of LDHs, and flexibility of the interlayer region accessible to a variety of ionic and non-ionic chemicals are essential properties that promise to improve pollutant removal efficacy in aqueous systems.

I.1.6.2 Overview of LDH synthesis

In order to overcome different challenges, tailoring the LDH structure with a new design possessing desirable properties is crucial. However, it is well known that the synthesis technique may influence the final properties of LDH and hence their specific applications. As a result, various kinds of synthetic approaches have been employed in the production of LDH, which include co-precipitation, ion-exchange, reconstruction, urea hydrolysis, hydrothermal, and sol-gel.[112] The most commonly used synthetic technique is the co-precipitation method, which involves dissolving the divalent and trivalent metal salts at the proper molar ratio in an aqueous solution with further drop wise slow addition of alkali solution under continuous stirring. In this method, the pH of the solution plays a crucial role in influencing the chemical and structural properties of LDH and should be maintained constantly in the range of 8-10 to obtain precipitation. The precipitate obtained is then aged, washed with deionized water, and dried in a vacuum to get the desired product.[113]

The introduction of various anions in the interlayer region of LDH has provided a new way of synthesizing LDH material. In the ion-exchange method, the interlayer ion of the initially synthesized LDHs is replaced with the desired incoming guest ions to obtain the required LDH. The tendency of the ion exchange generally depends on the coulombic attraction between brucite sheets and exchanging anions. If this attraction is strong, then ion exchange becomes difficult. However, strong attraction exists if the molar ratio of M^{2+}/M^{3+} decreases, which could be possible by substituting divalent metal with more trivalent metal cations. The drawback of this method is that the intercalation of ions is not always successful and may reduce the efficiency of the material.[114]

Although both methods can be applied for synthesizing LDH of variable composition by changing divalent and trivalent metal cations, the obtained product shows poor crystallinity, which could be further improved by subjecting it to thermal aging step.

Another unique method for preparing LDH is known as the reconstruction method, which is based on the phenomenon called ‘the memory effect’ as already mentioned in the earlier discussion. In this method, the Layered Double Oxide (LDO), which is obtained after calcinations of LDH, is subjected to rehydration by immersing in the aqueous solution of the desired ions to be intercalated, and the original brucite structure of LDH is regenerated, which depends on the experimental conditions such as calcinations temperature, duration, and rate of heating. In addition, this method finds more significance in synthesizing LDH intercalated with large organic anions.[115]

The most important method, called urea hydrolysis, has been proposed to improve crystallinity along with controlled and uniform morphology in LDH synthesis. In this method, urea, which is a weak Bronsted base, is used as a favourable precipitating agent for metal ions in its aqueous solution. During the process, urea decomposes slowly at a temperature of around 90 ℃ and increases pH up to 10, resulting in a lower degree of supersaturation. And the hydrolysis process involves the formation of ammonium carbonate, which is essential for providing optimum pH in building LDH. In addition, due to thermal treatment and slow hydrolysis of urea, urea-based co-precipitation offers superior crystallinity and particle size compare to other synthesis method.[116]

Another widely used method known as the hydrothermal process can be used to increase the particle size and crystallinity of LDH. It is comparable to the co-precipitation method, in which the basic solution is added drop wise to a homogeneous mixture of bivalent and trivalent metal salt solutions, and the suspension is transferred to a teflon-lined autoclave and heated at 150 ℃ for several days. With this process, it enables the synthesis of micrometer-scale LDH particles, and the morphology and size of the LDH particles may be altered by varying the heating temperature and metal ratio. Although it promotes crystallinity, it is a more energy-intensive and time-consuming procedure.[117]

LDHs may also be produced via a sol-gel method that involves the hydrolysis and condensation of alkoxide precursors in alcohol or the hydrolysis of acetate precursors in polyol medium. There are various advantages to using this technology over other synthetic processes. It is a straightforward method for obtaining nano-scaled particles with a high specific surface area and narrow pore size distribution, and it provides for precise control over the structural and textural aspects of high-purity products.

I.1.6.3 Critical factors influencing dye adsorption by LDH based adsorbent

(a) **pH**: The pH level of a solution is considered to be a crucial parameter affecting the adsorption process, influencing the structure and surface characteristics of adsorbents. The variation of solution pH not only affects the surface charge of LDHs but additionally the extent of ionization of the material, the dissociation of functional groups on the active sites of LDHs, and the solubility of certain dyes. Furthermore, the pH influence on dye intake by LDHs varies depending on the type of dye and LDH used.[24]

(b) **Dosages**: The analysis of the optimum amount of adsorbent used in the dye solution is very important for maintaining a cost-effective system. Usually, with the increasing quantity of adsorbent dosages, the removal capacity also increases due to the increase number of active adsorption sites on the surface of the adsorbent.[29]

(c) **Initial dye concentration**: In general, increasing the initial dye concentration leads to an increase in the ability to adsorbed until all the unsaturated active sites of the adsorbent get saturated during the adsorption process.[108,109]

(d) **Contact time**: Increased contact duration improves adsorption until equilibrium between the active sites of the adsorbent and dye molecules is attained. In general, dye adsorption rises with contact duration, while adsorbate species elimination is quick initially and then decreases to near equilibrium. Due to the suitable free adsorptive sites and a large dye concentration gradient during the initial time. Later, the remaining unoccupied sites become less accessible to adsorption due to the repulsive interactions that develop between both adsorbed and free molecules over time.[17]

(e) **Temperature**: Temperature has the ability to affect dye mobility, solubility, and equilibrium capacity. Depending on the favourability of the temperature, the adsorption process can be either endothermic or exothermic.[24] The majority of the reactions are endothermic, indicating that adsorption tends to occur at higher temperatures. This could be attributed to increased dye molecule mobility and a surge in the total number of readily accessible sites for adsorption as the temperature rises. Moreover, adsorption process is also not desirable at very high temperature.[24,118]

(f) **Coexisting ions**: The coexistence of ions can compete with LDH and suppress the sorption of dyes. However, some studies revealed that the influences of competing anions are in the order PO_4^{3-}> CO_3^{2-}> SO_4^{2-}>NO_3^->Cl^-. In methyl orange dye adsorption by LDH, the study indicates that the anions of higher valence have a more significant interfering effect than the monovalent anions.[18,118]

(g) **Material components**: In various research studies, the nature of the LDH precursors metals, especially diverse combination of metals and atomic ratios of metals, was investigated and found to display distinct LDH features. Nevertheless, the finest crystalline LDH phase was frequently achieved by using a M^{2+}/M^{3+} ratio of 3:1 for a given choice of metal cation and interlayer anions.[108,109] As a result of their effect on the crystallinity of the sample, the nature and content of precursors had an essential effect on adsorption. For example, the influence of Zn and Au content on the Au/Zn-Al LDO composite was tested, and it become apparent that the sample with a higher Zn (87%) content demonstrated superior MO dye adsorption compared to an increasing Au amount in the composite.[118]

I.1.6.4 Mechanism of sorption by LDH based adsorbents

Mechanistic investigations regarding dye removal by LDHs have already been conducted using either the analysis of the structures of the LDHs before and after adsorption using techniques such as FTIR, XRD, HRTEM, and FE-SEM or speculation based on the extensive experimental observations on adsorption kinetics and isotherms. However, the plausible mechanism or interactions involved in dye removal by LDH are (1) Ion exchange (2) Electrostatic (3) Reconstruction (4) H-bonding (5) Surface Complexation and (6) non-covalent interaction (π-π, n-π,)

The ion-exchange mechanism plays a vital role and occurs between the initial intergallery ions of LDH and the incoming anions or ligands to be intercalated. It contributes to the expansion of the interlayer space of the original LDH structure. Ion-exchange successfully removes the dye molecules from solution and immobilizes them within the LDH structure. Besides, anion exchange can also take place even on the external LDH surfaces. Surface carbonates or hydrogen carbonates can be easily substituted by anionic dyes, and anion exchange can still occur even if the interlayer ion is carbonate ion, which is particularly difficult to replace from the interlayer space.[119]

Electrostatic attraction is the most predominant mechanism involved in dye adsorption, which contributes to almost all types of adsorbents compared to various interactions. It is a strong force that holds the adsorbate molecules tightly, making it difficult to regenerate from the surface of the adsorbent. This attraction can exist between the negatively charged anionic dyes and the positively charged surface of LDH clay or between the cationic dyes and negatively charged intercalated ligands.[120]

Another important mechanism is the reconstruction mechanism, in which the original structure of LDH is retained after immersion in the aqueous solution of the targeted pollutants. This type of mechanism is mostly prevalent in calcined LDH. For instance, in the adsorption studies of methyl orange by calcined LDH, the layered structure of LDH regenerates back by intercalating methyl orange ions, OH^- and few CO_3^{2-} ions. Moreover, OH^- ions are liberated in the aqueous medium, raising the pH of the solution. This mechanism is also primarily accountable for the higher sorption capability of calcined LDH in comparison to pristine LDH because of its increased surface area and basic sites. A further benefit associated with this mechanism is that it requires less time to attain equilibrium.[121]

In addition, the intermolecular H-bonding interaction can occur between the OH-groups of brucite sheets and the functional groups of incoming dye molecules. As a result, the creation of H-bonds promotes dye adsorption. Besides, other weak non-covalent interaction such as vander Waals force, π-π, and n-π may also be prevalent in the adsorption process of LDH/Biochar composites or charcoal-activated LDH.[24,25]

The metal-containing dyes may undergo surface complexation with the surface functional group of LDH. Although this type of interaction is rarely observed in the adsorptive removal of dyes, but it is mainly reported in metal adsorption. Surface complexation can be formed by either of the two possible mechanisms, namely, via outer sphere and inner sphere complexation. When a water molecule exists between LDH surface functional group and the adsorbate ions or molecule, then the complexation is referred to as an outer sphere. In contrast, inner sphere complexation does not contain bonded water molecules between incoming dye molecules and adsorbent surface. In inner-sphere complexes, metal may be bonded to one O atom (monodentate) or two O atom (bidentate). Furthermore, outer-sphere complexes form on surfaces that have opposite charge on the adsorbent. It is also known as cation exchange, and it is frequently a fast reversible process. Inner sphere complexation, on the other hand, can be slower than outer sphere complexation and is often irreversible.[122]

I.1.7 Review on LDH based adsorbents

I.1.7.1 Pristine LDH in dye remediation

Pristine layered double hydroxides (LDH), also referred as anionic clay, are a versatile material and possess interesting properties, therefore, receiving significant attention in the field of waste water remediation. By taking into account LDHs important physicochemical characteristics like textural, structural, morphological, chemical composition, and synthesis technique, consequently, the use of LDH as an adsorbent has been widely investigated and found to be highly promising, sustainable, and efficient for the purification of water. For instance, Haziri et al. synthesized a quadrimetal LDH (MgAlCuFe-LDH) and applied it to the adsorption isotherm studies of acid-red AR dye under an initial dye concentration of 200-800 mg/L.[123] Their results on isotherm modelling showed the highest coefficient of determination (R^2) value for Sip and Toth models. In addition, the maximum monolayer q_{max}(mg/g) reaches up to 125.22 mg/g. However, it was suggested that the dye removal % was found to be more in an acidic medium or with the addition of salts that can enhance the acidic environment of the solution. Shamim et al. employed ZnAl-CO_3 LDH in the adsorption of Evan blue dye from an aqueous solution.[124] A series of ZnAl-CO_3 LDH with different layer charge densities ranging from 0.2-0.33 was prepared and investigated. The highest monolayer adsorption capacity up to 113.64 mg/g was obtained, corresponding to LDH having greater charge densities (0.33). Under the experimental conditions of 313 K and 60 min contact time, the 99 % removal of Evan blue was accomplished. The synergistic effect of high anion exchange capacity and surface area contributed on the observed greater q_{max} value. The temperature dependent studies also suggest spontaneous and exothermic processes that take place via chemisorption reactions. According to Abdellaoni et al. textile dye acid yellow 42 was effectively adsorbed on uncalcined MgAl-CO_3 LDH with an adsorption capacity of 330 mg/g under a neutral pH and an operating temperature of 25 °C.[125] In similar work, MgAl-NO_3 and MgAl-CO_3 were utilized in the adsorption of amaranth azo dye, exhibiting q_{max} values of 0.8 and 0.2 mmol/g, respectively. The studies also observed that the effect of coexisting ions on dye adsorption increases in the order $Cl^- < SO_4^{2-} < CO_3^{2-} < HPO_4^{2-}$. The adsorption equilibrium was achieved within a time period of 3 hours. The kinetics and isotherm data fitted well according to Langmuir and pseudo-second-order model. In another work Setti et al. demonstrated the sorption of anionic dye benzopurpurine 4B over MgAl-LDH adsorbent with a sorption capacity of 153.88 mg/g.[126]

Recently, hexagonal-shaped mesoporous MgAl-LDH nanoplatelets were prepared via the facile hydrothermal method and successfully employed to remove brilliant yellow dye, exhibiting q_{max} value of 115 mg/g and reaches equilibrium after 15 min. However, the adsorption process is also pH-dependent and thermodynamically favoured, thereby indicating a spontaneous and exothermic process. Lei et al. used hierarchically porous NiFe-LDH for removing congo red dye, and the obtained monolayer adsorption capacity was 205 mg/g in 15 hr at 30 ℃. The mechanistic study showed that anion exchangeability is the sole factor responsible for the sorption process.[127]

Bharali et al. prepared a series of CuMgAl-LDH by varying the Cu/Mg molar ratio and applied it for the preferential adsorption of various organic dyes, including methyl orange, methylene blue, rhodamine B, congo red, bromothymol blue, and eriochrome black T.[128] The studies advocate that the presences of Cu components in ternary LDH greatly improved the sorption capacity. However, the increasing order of dye removal % under the experimental conditions (pH 7, 25 ℃, and 5 mg dose) is as follows: Rh B< MB<CR <EBT<BTB<MO. The adsorption affinity for anionic dyes is found to be higher than that of cationic dyes over CuMgAl-LDH.

I.1.7.2 Surfactants modified LDH for dye remediation

Surfactants are widely used as structure-directing agents for the synthesis of adsorbent materials. It enhances important structural properties by imparting porous structure, a high surface area, and a hydrophobic surface. Several studies have reported that the surfactants fabricated LDH have great capacity for the sorption of cationic and non-ionic organic pollutants from waste water. Owing to its flexible structure, LDH can be easily intercalated with anionic surfactants, which can act as adsolubilization medium in the interlamellar space, thereby improving the affinity for several toxic organic compounds. The modification of LDH with surfactants of varying length, such as sodium hexane sulfonate (SHS), sodium nonane sulfonate (SNS), and sodium dodecane sulfonate (SDS) is also reported. The surface properties of LDH were inverted from hydrophilic to hydrophobic by modifying with surfactants. The longer chain SDS modified LDH revealed good adsorptive characteristics for cationic and non-ionic dyes, while the intermediate chain SNS-LDH is found to be favourable for a broad spectrum, including anionic, cationic, and non ionic. In addition, the relatively shorter chain SHS-LDH showed only considerable adsorption capacity for anionic dyes.[129]

Lei et al. reported a one-step hydrothermal synthesis of SDS intercalated MgAl-SDS-LDH and surface-modified LDH.[130] The adsorbents were implemented for the treatment of methyl orange dye from its aqueous solution and exhibited high adsorption capacity of 846.6 mg/g and 327.4 mg/g, respectively for intercalated and surface modified LDH. The unique properties of intercalated structure and easily accessible surface-modified LDH are mainly responsible for its excellent high dye sorption performances.

Synthesis of dodecyl benzene sulfonate intercalated LDH via the rehydration method and its application for basic dye (Safrazine) removal was tested by Bouraada et al.[131] Similar work was illustrated for the removal of the acidic dye green bezanyl-F2B on to hydrotalcite (HT-SDS) adsorbent, which was also found to be more effective than pristine hydrotalcite (HT).[132] Zhang et al. reported the use of composite material Fe_3O_4@SDB@LDH for the adsorptive removal of brilliant green (BG) dye.[133] In previous work, Starukh et al. conducted synthesis of organo/ZnAl-LDH via the reconstructed method and examined the sorption capacity of methylene blue in an aqueous solution.[134] A recent work investigated by Kheradmand et al. demonstrated the biosurfactant rhamnolipid-Co/Al-LDH and tested for the uptake of reactive orange 16 and methylene blue dye from an aqueous solution. The proposed adsorbent showed good adsorption characteristics for both anionic and cationic dyes and revealed the maximum monolayer adsorption capacity for methylene blue (54.01 mg/g) and reactive orange RO16 (53.04 mg/g), respectively.[135]

I.1.7.3 Biomass ash/LDH composite

In the past two decades, agricultural waste-derived biochar produced by the straight-forward pyrolysis of biomass has shown incredible promise as an adsorbent for the elimination of dyes from waste water. The adsorption efficacy of biochar is significantly less than that of other adsorbents, despite its many benefits, including low cost, eco-friendliness, high surface area, and porosity. Its surface may have lesser active functional groups, resulting in a lower capacity for ion exchange. Consequently, surface modification is an appealing method for fine-tuning the surface properties of biochar and enhancing its adsorption performance. Recently, numerous research has revealed that biochar supported with clay like LDH showed increased removal capacity compare to pristine LDH.[136] In previous studies, varieties of waste material such as rice husk, date palm ash, etc. have been implemented as an important source for obtaining precursors carbon, which can be utilized for synthesizing composite materials. For instance, Zubair et al. demonstrated a date palm biochar-LDH composite for the remediation of methylene blue dye.[137] Their study revealed an improvement in the adsorption capacity of the composite material due to hybridisation and exhibited q_{max} value up to 302.75 mg/g compared to biochar (206.61 mg/g). However, the main adsorption mechanism involved can be attributed to ion exchange, surface adsorption, pore diffusion, etc. In addition, the adsorption of methylene blue was favoured at lower temperatures, which indicates exothermic process. In similar work, biochar-supported CuFe-LDH was used for the removal of eriochrome black tea and achieved a maximum adsorption capacity of 565.31 mg/g.[138] Meili et al. reported the synthesis of MgAl-LDH/biochar obtained from bovine bone and conducted the methylene blue adsorption experiment.[139] The studied isotherm and kinetics data were best fitted to Redlich-Peterson and pseudo-second order kinetic models, respectively. The observed equilibrium time was approximately 20 min, and a maximum adsorption capacity of 406.47 mg/g was achieved. Moreover, the studies also showed that at optimum pH 12, the removal percentage for all the composites was greater than 95 %. According to Palapa et al. biochar produced from rice husk is also suitable for synthesizing composite material with CuAl-LDH, which exhibited large surface area (200.9 m^2/g) and found to be very effective adsorbent for the elimination of malachite green dye.[140] These studies showed that the removal percentage exceeds up to 99% with increasing solution pH. Moreover, the optimum pH at 9 was observed, and due to the negative surface of the adsorbent, typically it favours high uptake of malachite green dye. In another work, Juliano Missau et al. developed phosphoric acid activated CaAl-LDH/biochar composite for effective sorption of crystal violet dye from aqueous solution.[141] The maximum adsorption of 101 mg/g was observed while with increasing temperature at 50 ℃, it surpasses to 496.55 mg/g. Additionally, the outcome demonstrates that even after four cycles of reuse, 71 % of the initial dye adsorption capacity was retained.

Walnut shell-based biochar/NiCr-LDH composite showed a maximum adsorption capacity of 108.2 mg/g for the remediation of methyl orange.[142] The results indicated 100 % removal of methyl orange dye within 1 hour was attained when the biochar content of the adsorbent was 22.3 wt% and the optimum dose was 1 mg/mL. Wang et al. developed corn cob biochar/NiAl-LDO exhibiting a high surface area 552.62 m^2/g and tested the adsorption ability of acridine orange dye.[143] The adsorption capacity of corn cob biochar was found to be relatively 90% less than that of the modified adsorbent, corn cob biochar/NiAl-LDO. The experimental studies suggest that the proposed material is a low-cost, economical adsorbent that is reusable up to 9th cycle.

I.1.7.4 Magnetic LDH composite for dye removal

A functionally efficient and magnetically separable Fe_3O_4-PEG-MgAl-LDH adsorbent with varying molecular weight of PEG components was developed via simple precipitation and utilized for the adsorption of methyl orange dye. A detailed analysis of the adsorption mechanism suggests the presences of anion exchange, hydrogen bonding and electrostatic attraction between dye and adsorbent. The excellent reusability performance of the adsorbent up to 100 % efficiency was observed even after 31st cycle. The results confirmed that with increasing molecular weight of PEG, the maximum adsorptive capacity of the adsorbents denoted as 2FPL, 4FPL and 6FPL also increases and showed 775.19 mg/g, 826.44 mg/g and 833.33 mg/g, respectively.[144]

A cross linked bionanocomposite (BNC-CL) was prepared by chemical modification of guar gum with Fe_3O_4/NiAl-LDH and tested for the adsorption of methylene blue dye.[145] The studies indicate 84 % removal of dye at optimum pH 9 within 120 min of equilibrium time. Moreover, an enhancement in thermal properties up to (35-47 %) was obtained compared to pristine polymer and non-cross-linked bionanocomposites. Yan et al. developed a magnetic hierarchical Fe_3O_4-MgAl-CO_3 LDH adsorbent via in situ growth of LDH platelets over the surface of Fe_3O_4 nanospheres.[146] The studies indicate that the successful preparation of the desired material is influenced by several factors, like the methanol/water ratio, aging time, and temperature. During the multiple reusability test of acid yellow 219, an adsorption capacity of 1024 mg/g was observed even after the third cycle. The exceptional high adsorptive performance can be attributed to the core shell architecture of the adsorbents.

Taher et al. demonstrated the synthesis of magnetic nanoparticles incorporated NiFe-LDH via the hydrothermal method.[147] Their result illustrates the uniform distribution of nanoparticles over the LDH surface. Nevertheless, the isotherm and kinetics studies executed in the adsorption of congo red dye provide that the results are consistent with the Langmuir and pseudo-second order model, respectively, and exhibited a q_{max} value of 79.6 mg/g. The electrostatic interaction presents between the dye and the LDH positive surface is mainly responsible for dye uptake.

Sun et al. synthesized hierarchically porous magnetic $ZnFe_2O_4$/MgAl-LDH adsorbent via the biotemplate method, where the LDH nanosheets are combined on the surface of $ZnFe_2O_4$ sphere.[148] The SEM analysis confirmed that the outer surface of the composite material revealed the attachment of LDH nanosheets over the vertically align pollen-shaped $ZnFe_2O_4$ sphere. However, in the adsorption of congo red dye, the as-synthesized sample adheres to pseudo-second-order kinetics, and the temperature dependence studies indicate a spontaneous and exothermic process. As evident from the q_{max} value 294.12 mg/g, the fabricated adsorbent has a high adsorption capacity and can be easily recovered magnetically.

In another work, Adlnasab et al. fabricated mesoporous MCM-41 with CuFe-LDH and magnetic nanoparticles Fe_3O_4 by using cationic surfactant for the elimination of alizarin yellow dye.[149] Their finding showed that adsorption isotherm data was fitted according to the Langmuir model, exhibiting a q_{max} value of 121.95 mg/g. The limits of detection of the contaminants concentration and precision was determined to be 0.5 μg/L and 6.5%, respectively.

I.1.7.5 Polymer-based LDH composite

Polymer/LDH-based adsorbents are commonly used in dye treatment due to their high surface area, porous surface texture, chemical and thermal stability, flexibility, ease of fabrication, and biocompatibility. Various polymers, such as chitosan, polyethyleneimine, polyvinylidene fluoride, polypyrrole, poly (levodopa) and polymeric resins etc., are reported and typically used in synthesizing composite adsorbents for water remediation. For instance, Ghanbari et al. studied the selective adsorption of methylene blue dye by using a polyethyleneimine (PEI) functionalized LDH nanocomposites. They suggested that the proposed adsorbent showed excellent affinity, with a maximum adsorption capacity of 1428.57 mg/g at 35 °C. The effect of temperature studies indicates a decrease in removal capacity with increasing temperature from 35-65 °C, which further implies the exothermic nature of adsorption. The mechanistic investigation also revealed the revealed the presence of electrostatic and H-bonding interactions due to surface hydroxyl and NH_2 groups on the polymer/LDH composite.[150]

According to Abbasi et al., the CuAl-LDH/PVDF composite achieved a maximum adsorption capacity of 17.36 mg/g for the removal of Erythrosin B from an aqueous solution.[151] The composite material displayed an improvement in hydrophilic nature compared to pristine polyvinylidene fluoride (PVDF). The isotherm and kinetic studies agreed well according to the Langmuir and pseudo-second order models, with a maximum q_{max} value of 17.36 mg/g. In addition, they inferred that the better adsorption performance of CuAl-LDH/PVDF could be due to the growth of well-crystalline CuAl-LDH over the PVDF surface.

In another work, Mohamed et al. used a hydrothermal technique to create polypyrrole nanofibre/LDH and evaluated it for safranin dye removal.[152] The morphological features of the composite material displayed plate-like ZnFe-LDH covered by a layer of fibrous polypyrrole with a smooth surface and uniform diameters. The equilibrium isotherm studies manifested a maximum q_{max} of 63.4 mg/g and were best fitted to the Freundlich model, which further implies a multilayer adsorption process. Besides adsorption, the synthesized adsorbent also possesses photocatalytic properties and can completely degrade a concentration of 5 mg/g of safranin dye in 120 minutes at 0.05 g dosages.

Zhao et al. designed a poly(levodopa) functionalized MgAl-LDH that was used to remove methylene blue dye from an aqueous solution.[153] According to their findings, the maximum adsorption capacity of 102 mg/g was obtained at 25 ℃. Furthermore, it was obvious that methylene blue adsorption on PDOPA-LDH is a spontaneous and exothermic process. The synthesized adsorbents demonstrate a high potential for cationic dye adsorption in an aqueous medium.

Further, Khalili et al. described the hydrothermal synthesis of MnFe-LDH coated chitosan fiber and investigated its adsorption behaviour.[154] The effective adsorption capacities of indigo carmine and sunset yellow dyes were 1785 and 1137 mg/g, respectively. Nevertheless, the thermodynamic study showed an endothermic adsorption process, and the isotherm and kinetics experimental data are satisfactorily described by the Langmuir and pseudo-second-order models.

Table I.3: Summary of LDH based adsorbents reported in decontamination of organic dyes.

Adsorbents	Dyes	q_{max} (mg/g)	Isotherm	Kinetics	Thermodynamics	Ref.
Mg-Al-Cu-Fe-LDH	Acid red 66	125.22	Sips and Toth	Pseudo-second-order	Endo	123
ZnAl-NO_3 LDH	Evans blue	113.64	Langmuir	-	Exo	124
MgAl-CO_3	Acid yellow 42	330	Langmuir	Pseudo-second-order	Endo	125
MgAl-NO_3	Amaranth azo dye	0.8 mmol.g^{-1}	Langmuir	Pseudo-second-order	-	125
MgAl-CO_3	Benzopurpurine	153.88	Langmuir	-	Endo	126
MgAl-LDH	Brilliant yellow (BY)	115	Langmuir	Pseudo-second-order	Endo	127
DI-LDH Ns DM-LDH Ns	Methyl orange	846.6, 327.4	Langmuir	-	-	130
SHS-LDH SNS-LDH SDS-LDH	Acid red GR	619.45, 462.49, 424.54	Langmuir	Pseudo-second-order	Exo	129
HT-SDS HT-SDBS	Safranine	83.3, 40.5	Langmuir	Pseudo-second-order	Exo	131
HT-SDS HT	Green Benzanyl-F2B	188.68, 52.08	Langmuir	Pseudo-second-order	-	132
Fe_3O_4@SDBS@LDH	Brilliant green	329.1	Langmuir	Pseudo-second-order	Endo	133
ZnAl-LDH/DS	Methylene blue	113	Langmuir	-	-	134
Fe_3O_4@RL-LDH	Reactive orange 16 Methylene blue	53.04, 54.01	Langmuir	Pseudo-second-order	Endo	135
Date palm biochar-MgAl-LDH	Methylene blue	302.75	Langmuir	Pseudo-second-order	Exo	137

Table I.3 (Continued)

Date palm biochar-CuFe-LDH	Eriochrome black T	565.32	Langmuir Redlich-Peterson	Pseudo-second-order	-	138
Bone biochar/MgAl-LDH	Methylene blue	406.47	Redlich-Peterson	Pseudo-second-order	-	139
CuAl/Biochar	Malachite green	470.96	Langmuir	Pseudo-second-order	Endo	140
CaAl-LDH/biochar	Crystal violet	496.55	Langmuir	Pseudo-second-order	Endo	141
Walnut shell biochar/NiCr-LDH	Methyl orange	108.2	Freundlich	Pseudo-second-order	-	142
Corncob biochar/NiAl-LDO	Acridine orange	108.6	Langmuir	Pseudo-second-order	-	143
Fe_3O_4-PEG-MgAl-LDH	Methyl orange	833	Langmuir	Pseudo-second-order	Endo	144
GG-LDH-Fe_3O_4	Methylene blue	64.5	Langmuir	Pseudo-second-order	-	145
Fe_3O_4@Mg_3 Al-CO_3 LDH	Acid yellow 219	1392	Langmuir	-	-	146
NNPs@NiFe-LDH	Congo red	79.6	Langmuir	Pseudo-second-order	Endo	147
$ZnFe_2O_4$/MgAl-LDH	Congo red	294.12	Langmuir	Pseudo-second-order	Endo	148
Fe_3O_4@MCM-41@CuFe-LDH	Alizarin yellow	121.95	Langmuir	-	Endo	149
PEI-functionalized LDH	Methylene blue	1428.57	Langmuir	Pseudo-second-order	Exo	150
CuAl-LDH/PVDF	Erythrosin B	17.36	Langmuir	Pseudo-second-order	-	151
Polypyrrole nanofibre/LDH	Safranin	63.4	Freundlich	Pseudo-second-order	-	152
Polylevodopa/MgAl-LDH	Methylene blue	102	Langmuir	-	Exo	153
MnFe-LDH Chitosan fibre	Indigo carmine, sunset yellow	1785, 1137	Langmuir	Pseudo-second-order	Endo	154

Although significant advancements have been made in the study of dye adsorption by LDHs, research in waste water removal has to be expanded. It is still extremely desirable to create innovative approaches for the production of new LDH-based materials that have excellent adsorption efficiency.

I.1.8 Aims and objectives of the present study

The aim of this work is to synthesize LDH-based adsorbents like zirconium metal oxide modified LDH, sodium dodecyl sulfate modified LDH, coconut husk ash fabricated LDH and ternary LDH. The prepared new adsorbents were applied for the removal of textile dyes such as congo red, methylene blue, methyl red, malachite green, and methyl orange, which is the major part of this research work. Considering the critical and severe hazards posed by textiles dyes to human and aquatic organisms, the following objectives of the present study have been set:

1. To synthesize efficient adsorbents, including pristine and modified Layered double hydroxide and their application as sorbent for cationic and anionic dye removal from aqueous solutions.
2. To characterize the adsorbents with PXRD, FT-IR, XPS, HRTEM, FESEM-EDX, BET, and TGA techniques.
3. To study the isotherm, thermodynamics, and kinetic aspects during the dye adsorption process.
4. To investigate the adsorption efficiency of the synthesized adsorbent by employing dyes such as congo red, methylene blue, methyl orange, malachite green, and methyl red.

I.1.9 Summary

As discussed in the previous discussion, the discharge of coloured waste water into the ecosystem has decreased the availability of fresh water, which compels scientists to reconsider the accessibility of clean and safe water. Further, it has been reported that the existence of poisonous and colourful chemicals in dye containing waste water causes mutagenic, carcinogenic, allergic, and dermatitis effects in living creatures. Thus, it indicates the urgent demand for finding highly efficient adsorbents for the remediation of textiles dyes. Since then, LDH-based adsorbents have shown great potential in addressing the environmental challenges associated with dye pollution, providing a sustainable and efficient means of treating coloured effluents. Therefore, the combination of LDH with other materials such as agrowaste ash, metal oxide, and surfactants for removing dyes has been investigated in the present study. However, finding low-cost, high-performance adsorbents with significantly improved activity and long-term stability remains a difficulty and should be continuously under research.

I.2. References

1. R.K. Ibrahim, M. Hayyan, M.A. Alsaadi, A.H. Shaliza, *Environ. Sci. Pollut. Res*., 223, **2016**, 13754-13788.
2. T. Hussain, A. Wahab, *J. Clean. Prod*., 198, **2018**, 806-819.
3. S. Mandal, A. Kuhikrishnan, N.S. Bolan, H. Wijesekara, R. Naidu, *Environmental Materials and Waste*, ed. M.N.V. Prasad, K. Shih, Elsevier, **2016**, vol., ch. 4, pp.73-89.
4. A.L. Srivastav, M. Ranjan, *Inorganic Pollutants in Water*, ed. P. Devi, P. Singh, S.K. Kansal, Elsevier, **2020**, ch. 1, pp. 1-15.
5. S. Velusamy, A. Roy, S. Sundaram, T.K. Mallick, *Chem Rec*., 21, **2021**, 1570-1610.
6. B. Leillis, C.Z. Favaro-Polonia, J.A. Pamphile, J.C. Polonio, *Biotechnol. Res. Innov*., 3, **2019**, 275-290.
7. A. Azanaw, B. Birlie, B. Teshome, M. Jemberie, *Case Stud. Chem. Environ*., 6, **2022**, 100230.
8. B. Pizzicato, S. Pacifico, D. Cayuela, G. Mijas, M. Riba-Moliner, *Molecules*., 28, **2023**, 5954.
9. T. Sudare, S. Tamura, H. Tanaka, F. Hayashi, K. Teshima, *Inorg. Chem*., 58, **2019**, 15710-15719.
10. G. Rathee, S. Kohli, S. Panchal, N. Singh, A. Awasthi, S. Singh, A. Singh, S. Hooda, R. Chandra, *ACS Omega*., 5, **2020**, 23967-23974.
11. T. Jiang, C. Liu, L. Liu, J. Hong, M. Dong, X. Deng, *RSC Adv*., 6, **2016**, 91720-91727.
12. S. Yu, G. Choi, J.H. Choy, *Nanomaterials*., 13, **2023**, 1102.
13. N. Dewangan, W.M. Hui, S. Jayaprakash, A.R. Bawah, A.J. Poerjoto, T. Jie, A. Jangam, K. Hidajat, S. Kawi, *Catal. Today*., 356, **2020**, 490-513.
14. L. Vigna, A. Nigro, A. Verna, I.V. Ferrari, S.L. Marasso, S. Bocchini, M. Fontana, A. Chiodoni, C.F. Pirri, M. Cocuzza, *ACS Omega*., 6, **2021**, 20205-20217.
15. A. Mohammad, H. Abdolvand, S.A.A. Najafabadi, F. Najaddehbashi, S. Beigi-Boroujeni, P. Makvandi, H. Daemi, *Appl. Bio Mater*., 5, **2022**, 5800-5815.
16. S.K. Pillai, P. Kleyi, M.D. Beer, P. Mudaly, *Appl Clay Sci*., 199, **2020**, 105868.
17. P. Lyu, L. Li, X. Huang, G. Wang, C. Zhu, *Sci. Total Environ*., 823, **2022**, 153743.
18. U.A. Mohanty, D.P. Sahoo, L. Paramanik, K. Parida, *Sustainable Energy & Fuels*, 7, **2023**, 1145-1186.
19. S.V. Vassiley, D. Baxter, L.K. Andersen, C.G. Vassileva, *Fuel*., 105, **2013**, 40-76.
20. F.C. Silva, N.C. Cruz, L.A.C. Tarelho, S.M. Rodrigues, *J. Clean. Prod*., 214, **2019**, 112-124.
21. N.S. Samanta, P.P. Das, P. Mondal, M. Changmai, M.K. Purkait, J. Indian Chem. Soc., 99, **2022**, 100761.
22. G. Yadav, N. Yadav, M. Ahmaruzzaman, *RSC Adv*., 13, **2023**, 23197-23210.
23. O.J. Olatoyan, M.A. Kareem, A.U. Adebanjo, S.O.A. Olawale, K.T. Alao, *Hybrid Advances*., 4, **2023,** 100076.
24. M. Zubair, H.A. Aziz, I. Ihsanullah, M.A. Ahmad, M.A. Al-Harthi, *Chemosphere*, 307, **2022**, 136054.
25. H. Bian, M. Wang, J. Han, X. Hu, H. Xia, L. Wang, C. Fang, C. Shen, Y.B. Man, M.H. Wong, S. Shan, J. Zhang, *Chemosphere*, 324, **2023**, 138333.
26. S. Sonal, B.K. Mishra, *Chem. Eng. J.*, 424, **2021**, 130509.

27. Z. Milavanovic, S. Lazarevic, I. Jankovic-Castvan, Z. Radovanovic, S. Cvetkovic, D. Janackovic, R. Petrovic, *Water*, 15, **2023**, 2376.
28. M.A. Khan, *Groundw. Sustain. Dev*., 11, **2020**, 100427.
29. A. Grover, R. Kaur, I. Mohiuddin, A.K. Malik, J.S. Aulakh, Y.F. Tsang, K.H. Kim, *Environ Res*., 177, **2019**, 108605.
30. A. Kumar, U. Dixit, K. Singh, S.P. Gupta, M.S.J. Beg, Dyes and Pigments-Novel Applications and Waste Treatment, ed. R. Papadakis, Intech open, **2021**, ch. 1, pp. 1-3.
31. J.A. Rippon, D.J. Evans, Handbook of Natural Fibres-Processing and Applications, ed. R.M. Kozlowski, Elsevier, **2012**, vol. 2, ch. 3, pp. 63-140.
32. E. Hagan, J. Poulin, *Herit. Sci*., 9, **2021**, 33.
33. S.S. Affat, *University of Thi-Qar Journal of Science*, 8, **2021**, 130-135.
34. A. Gurses, M. Acikyildiz, K. Gunes, M.S. Gurses, Dyes and Pigments, Springer briefs in Molecular Science, Springer Cham, **2016**, ch. 2, 13-29.
35. H. Mustroph, Dyes and Pigments., 208, **2023**, 110783.
36. R. Khanum, R.A.S. Ali, H.R. Rangaswamy, S.R.S. Kumar, A.G. Prashantha, A.S. Jagadisha, *Results Chem.*, 5, **2023**, 100890.
37. L.D.S. Yadav, Organic Spectroscopy, Springer Dordrecht, **2005**, ch. 2, pp. 7-51.
38. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, **2010**, Vol. 99.
39. M. Hagos, M. Redi-Abshiro, B.S. Chandravanshi, E.E. Yaya, *Int J Anal Chem*., 2022, **2022**, 9363692.
40. S. Benkhaya, S. M′ rabbet, A. E. Harfi, *Inorg. Chem. Commun*., 115, **2020**, 107891.
41. A. Gurses, M. Acikyildiz, K. Gunes, M.S. Gurses, Dyes and Pigments, Springer briefs in Molecular Science, Springer Cham, **2016**, ch. 3, 31-45.
42. N. Sekar, Handbook of Textile and Industrial Dyeing-Principles Processes and Types of Dyes, ed. M. Clark, Elsevier, **2011**, vol. 1, ch. 15, pp. 486-514.
43. W.R. Remington, E.K. Gladding, *J. Am. Chem. Soc.*, 72, **1950**, 2553-2559.
44. R. Al-Tohamy, S.S. Ali, F. Li, K.M. Okasha, Y.A.G. Mahmoud, T. Elsamahy, H. Jiao, Y. Fu, J. Sun, *Ecotoxicol. Environ. Saf.*, 231, **2022**, 113160.
45. A. Zannat, M.N. Uddin, S.T. Mahmud, R. Mia, T. Ahmed, Renewable Dyes and Pigments, ed. S.U. Islam, Elsevier, **2023**, ch. 13, 271-287.
46. K.H. Prabhu, A.S. Bhute, *J. Nat. Prod. Plant Resour*., 2, **2012**, 649-664.
47. J. Robinson, *J. Soc. Dye*., 111, **1995**, 172-175.
48. J.J. Lee, W.S. Shim, I.S. Kim, J.P. Kim, *Fibres and Polym*., 6, **2005**, 244-249.
49. U.H. Siddiqua, S. Ali, M. Iqbal, T. Hussain, *J. Mol. Liq*., 241, **2017**, 839-844.
50. D.M. Lewis, Handbook of Textile and Industrial Dyeing-Principles Processes and Types of Dyes, ed. M. Clark, Elsevier, **2011**, vol.1, ch. 9, 303-364.
51. J. Koh, Textile Dyeing, ed. P. Hauser, Intechopen, **2011**, ch.10, 195-220.
52. A.K. Roy Choudhury, Handbook of Textile and Industrial Dyeing-Applications of Dyes, ed. M. Clark, Elsevier, **2011**, vol. 2, ch. 2, 40-128.
53. V.K. Garg, M. Amita, R. Kumar, R. Gupta, *Dyes and Pigm*., 63, **2004**, 243-250.
54. M.M.H. Elzahar, M. Bassyouni, *Sci. Rep*., 13, **2023**, 15750.
55. T. Hussain, A. Wahab, *J. Clean Prod*., 198, **2018**, 806-819.
56. D.A. Yaseen, M. Scholz, *International Journal of Environmental Science and Technology*., 16, **2019**, 1193-1226.

57. S. Khan, A. Malik, Environmental Deterioration and Human Health, ed. A. Malik, E. Grohmann, R. Akhtar, Springer, Dordrecht, **2014**, ch. 4, 55-71.
58. D. Sivakumar, D. Shankar, A.J.R.V. Prathima, M. Valarmathi, *Int. J. Environ. Sci*., 3, **2013**, 1223.
59. P.A. Carneiro, G.A. Umbuzeiro, D. P. Oliveira, M.V.B. Zanoni, *J. Hazard. Mater*., 174, **2010**, 694-699.
60. D. Bhatia, N.R. Sharma, R. Kanwar, J. Singh, *Appl. Water Sci*., 8, **2018**, 1-12.
61. T.M. Farook, S. Manderia, K. Manderia, *Int. Res. J. Environment Sci*., 1, **2012**, 41-45.
62. M.A.S. Jiku, A. Singha, M. Faruquee, M.A. Rahaman, M.A. Alam, M. Ehsanullah, *Acta Ecol. Sin*., 41, **2021**, 358-364.
63. E.S. Armengol, A.B. Kerezsi, F. Laffleur, *Int. Immunopharmacol*., 110, **2022**, 109043.
64. J. Sharma, S. Sharma, V. Soni, *Reg. Stud. Mar. Sci*., 62, **2023**, 102911.
65. S. Velusamy, A. Roy, S. Sundaram, T.K. Mallick, *Chem Rec*., 21, **2021**, 1570-1610.
66. D.M. Leme, F.L. Primo, G.G. Gobo, C.R.V. da Costa, A.C. Tedesco, D.P. de Oliveira, *Journal Toxicol Environ Health A*., 78, **2015**, 466-480.
67. S. Sudarshan, V.S. Bharti, S. Harikrishnan, S.P. Sukla, G.R. Bhuvaneswari, *Arch. Microbiol*., 204, **2022**, 658.
68. O.V. Ayebidun, A.O. Ajibare, *Bulletin of the National Research Centre*., 47, **2023**, 86.
69. R. Sinha, R. Jindal, C. Faggio, *Appl. Sci*., 11, **2021**, 3507.
70. M. Alaguprathana, M. Poonkothai, *Environ. Sci. Pollut. Res*., 28, **2021**, 17602-17612.
71. H.B. Siama, A.C. Bouket, Z. Pourhassan, F.N. Alenezi, A. Silini, H. Cherif-Silini, T. Oszako, L. Luptakova, P. Golinska, L. Belbahri, *Appl. Sci*., 11, **2021**, 6255.
72. L. Pereira, M. Alves, Environmental Protection Strategies for Sustainable Development, Strategies for Sustainability, ed. A. Malik, E. Grohmann, Springer, Dordrecht, **2011**, ch. 4, pp. 111-162.
73. P. Saharan, V. Kumar, I. Kaushal, A. Mittai, S.K. Shukla, D. Kumar, A.K. Sharma, H. Om, *Environ. Sci. Pollut. Res*., 30, **2023**, 45677-45700.
74. S. Ahuja, Separation Science and Technology, ed. S. Ahuja, **2019**, Elsevier, vol. 11, ch. 1, pp. 1-12.
75. Commission Regulation (EC) No 552/2009 OF 22 June 2009 amending Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards Annex XVII, Official Journal of European Union, 164, **2009**, 7-31.
76. I. Jasmin, P. Mallikarjuna, *Environ. Monit. Assess*., 186, **2014**, 935-948.
77. K. Xu, G. Tian, *Int J Environ Res Public Health*., 19, **2022**, 9978.
78. U. Nimkar, *Curr. Opin. Green Sustain. Chem*., 9, **2018**, 13-17.
79. Textile Industry Wastewater Discharge Quality Standards: Literature Review-Zero Discharge of Hazardous Chemicals Programme, **2015**.
80. M. Roy, R. Saha, Intelligent Environmental Data Monitoring for Pollution Management, ed. S. Bhattacharyya, N.K. Mondal, P. Kromer, Elsevier, **2021**, ch. 6, pp. 127-160.
81. E. Idaka, T. Ogawa, H. Horitsu, C. Yatome, *Eur. J. Appl. Microbiol*., 15,**1982**, 141-143.
82. R. Majumdar, W.K. Shaikh, S. Chakraborty, S. Chowdhury, Microbial Biodegradation and Bioremediation-Techniques and Case Studies for Environmental Pollution., ed. S. Das, H.R. Dash, Elsevier, **2021**, ch. 12, 241-261.

83. M.M. El-Sheekh, M.M. Gharieb, G.W. Abou-El-Souod, *International Biodeterioration & Biodegradation*., 63, **2009**, 699-704.
84. J.M. Khaled, S.A. Alyahya, R. Govindan, C.K. Chelliah, M. Maruthupandy, N.S. Alharbi, S. Kadaikunnan, R. Issac, S. Murugan, W.J. Li, *Environ. Res*., 207, **2022**, 112211.
85. L. Xu, J. Sun, M.A. Qaria, L. Gao, D. Zhu, *Catalysts*., 11, **2021**, 955.
86. R.V. Khandare, S.P. Govindwar, *Biotechnol. Adv*., 33, **2015**, 1697-1714.
87. A. Movafeghi, A.R. Khataee, Z. Moradi, F. Vafaei, *Int. J. Phytoremediation*., 18, **2016**, 337-347.
88. G. Bal, A. Thakur, *Mater Today: Proc*., 50, **2022**, 1575-1579.
89. X.R. Xu, H.B. Li, W.H. Wang, J.D. Gu, *Chemosphere*, 59, **2005**, 893-898.
90. L. Bilinska, K. Blus, M. Bilinska, M. Gmurek, *Catalysts*., 10, **2022**, 611.
91. P.V. Nidheesh, R. Gandhimathi, S.T. Ramesh, *Environ. Sci. Pollut. Res*., 20, **2013**, 2099-2132.
92. B. Viswanathan, *Current Catalysis*., 7, **2018**, 99-121.
93. S. Ammar, M. Asma, N. Oturan, *Curr. Org. Chem*., 16, **2012**, 1978-1985.
94. S. Singh, V.C. Srivastava, I.D. Mall, *J. Phys. Chem. C*., 117, **2013**, 15229-15240.
95. M.M. Hassan, C.M. Carr, Chemosphere., 209, 2018, 201-219.
96. S.S. Moghaddam, M.R.A. Maghaddam, A. Arami, *J. Hazard. Mater*., 175, **2010**, 651-657.
97. A.K. Badawi, M.A. Elkodous, G.A.M. Ali, *RSC Adv*., 11, **2021**, 36528-36553.
98. P. Moradihamedani, Polym. Bull., 79, **2022**, 2603-2631.
99. M. Suzuki, Fundamentals of Adsorption, ed. M.D. Levan, Springer, Boston, MA, **1996**, vol. 356, ch. 1, pp. 3-15.
100. W.J. Thomas, B. Crittenden, Adsorption Technology & Design, Elsevier, **1998**, ch. 1, 1-7.
101. E. Robens, *Stud. Surf. Sci. Catal*., 87, **1994**, 109-118.
102. S. Dutta, B. Gupta, S.K. Srivastava, A.K. Gupta, *Mater. Adv*., 2, **2021**, 4497-4531.
103. P. Pourhakkak, A. Taghizadeh, M. Taghizadeh, M. Ghaedi, S. Haghdoust, Interface Science and Technology., Elsevier, **2021**, vol. 33, ch. 1, pp. 1-70.
104. H.B. Patterson, Bleaching and Purifying Fats and Oils-Theory and Practice, ed. G.R. List, Elsevier, **2009**, ch. 2, pp. 53-67.
105. T.A. Saleh, Adsorption technology and surface science, Elsevier, **2022**, vol. 34, ch. 2, pp. 39-64.
106. J. He, M. Wei, B. Li, Y. Kang, D.G. Evans, X. Duan, Layered Double Hydroxides, ed. X. Duan, D.G. Evans, Springer, Berlin, Heidelberg, **2005**, vol. 119, ch. 1, pp. 89-119.
107. G. Arrabito, A. Bonasera, G. Prestopino, A. Orsini, A. Mattoccia, E. Martinelli, B. Pignataro, P.G. Medagilia, *Crystals*, 9, **2019**, 361.
108. G. Mishra, B. Dash, S. Pandey, *Appl Clay Sci*., 153, **2018**, 172-186.
109. Z. Chen, Q. Fan, M. Huang, H. Colfen, *CrystEngComm*., 24, **2022**, 4639-4655.
110. L. Jin, X. Zhou, F. Wang, X. Ning, Y. Wen, B. Song, C. Yang, D. Wu, X. Ke, L. Peng, *Nat. Commun*., 13, **2022**, 6093.
111. X. Fang, C. Chen, H. Jia, Y. Li, J. Liu, Y. Wang, Y. Song, T. Du, L. Liu, *J. Ind. Eng. Chem*., 95, **2021**,16-27.
112. D. Tonelli, I. Gualandi, E. Musella, E. Scavetta, *Nanomaterials*., 11, **2021**, 725.
113. Z. Jiang, J. Wu, X. Liu, H. Yu, C. Jiao, J. Shen, Y. Pei, *New J. Chem*., 45, **2021**, 14580-14588.

114. Z. Liu, R. Ma, M. Osada, N. Iyi, Y. Ebina, K. Takada, T. Sasaki, *J. Am. Chem. Soc.*, 128, 2006, 4872-4880.
115. L. Dubnova, R. Danhel, V. Meinhardova, V. Korolova, L. Smolakova, T. Kondratowicz, O. Kiktyanin, L. Capek, *Front Chem*., 9, **2021**, 803764.
116. A. Inayat, M. Klumpp, W. Schwieger, *Appl Clay Sci*., 51, **2011**, 452-459.
117. Z.P. Xu, G.Q. Lu, *Chem. Mater*., 17, **2005**, 1055-1062.
118. Z. Yang, F. Wang, C. Zhang, G. Zeng, Z. Yu, Y. Zhong, H. Wang, F. Cui, *RSC Adv*., 6, **2016**, 79415-79436.
119. N. Almoisheer, F.A. Alseroury, R. Kumar, M. Aslam, M.A. Barakat, *RSC Adv*., 9, **2019**, 560-568.
120. G. Darmograi, B. Prelot, G. Layrac, D. Tichit, G. Martin-Gassin, F. Salles, J. Zajac, *J. Phys. Chem. C*., 119, **2015**, 23388-23397.
121. D. Yuan, L. Zhou, D. Fu, *Appl. Phys. A*., 123, **2017**, 146.
122. J. Nie, D. Zhi, Y. Zhou, Sorbents Materials for Controlling Environmental Pollution-Current State and Trends, ed. A. Nunez-Delgado, Elsevier, **2021**, ch. 8, pp. 163-187.
123. I. Haziri, D. Chebli, A. Bouguettoucha, S. Rohani, A. Amrane, *Arab. J. Sci. Eng*., 44, **2019**, 5245-5261.
124. M. Shamim, K. Dana, *Int J Environ Sci Technol*., 15, **2018**, 1275-1284.
125. R.M.M. dos Santos, R.G.L. Goncalves, V.R.L. Constantino, C.V. Santilli, P.D. Borges, J. Tronto, F.G. Pinto, *Appl. Clay Sci*., 140, **2017**, 132-139.
126. N.D. Setti, N. Jouini, Z. Derriche, *J. Phys. Chem. Solids*., 71, **2010**, 556-559.
127. C. Lei, M. Pi, P. Kuang, Y. Guo, F. Zhang, *J. Colloid Interface Sci*., 496, **2017**, 158-166.
128. D. Bharali, R.C. Deka, *Colloids Surf A: Physicochem. Eng. Asp*., 525, **2017**, 64-76.
129. B. Zhang, Z. Dong, D. Sun, T. Wu, Y. Li, *J. Indus. Eng. Chem*., 49, **2017**, 208-218.
130. S. Lei, S. Wang, B. Gao, Y. Zhan, Q. Zhao, S. Jin, G. Song, X. Lyu, Y. Zhang, Y. Tang, *J. Colloid Interface Sci*., 557, **2020**, 181-190.
131. M. Bouraada, M. Lafjah, M.S. Ouali, L.C. de Menorval, *J. Harzard. Mater*., 153, **2008**, 911-918.
132. M. Bouraada, M. Lafjah, M.S. Ouali, L.C. de Menorval, *J. Harzard. Mater*., 163, **2009**, 463-467.
133. D. Zhang, M.Y. Zhu, J.G. Yu, H.W. Meng, F.P. Jiao, *Trans. Nonferrous Met. Soc. China*., 27, **2017**, 2673-2681.
134. H. Starukh, S. Levytska, *Appl. Clay Sci*., 180, **2019**, 105183.
135. A. Kheradmand, M. Negarestani, S. Kazemi, H. Shayesteh, S. Javanshir, H. Ghiasinejad, *Sci. Rep*., 12, **2022**, 14623.
136. M. Zubair, I. Ihsanullah, H.A. Aziz, M.A. Ahmad, M.A. Al-Harthi, *Bioresour. Technology*., 319, **2021**, 124128.
137. M. Zubair, M.S. Manzar, N.D. Muazu, I. Anil, N.I. Blaisi, M.A. Al-Harthi, *Appl. Clay Sci.*, 190, **2020**, 105587.
138. M. Zubair, I. Ihsanullah, H.A. Aziz, M.A. Ahmad, M.A. Al-Harthi, *Environ. Technol. Innov*., 23, **2021**, 101614.
139. L. Meili, P.V. Lins, C.L.P.S. Zanta, J.I. Soletti, L.M.O. Ribeiro, C.B. Dornelas, T.L. Silva, M.G.A. Vieira, *Appl. Clay Sci*., 168, **2019**, 11-20.

140. N.R. Palapa, T. Taher, B.R. Rahayu, R. Mohadi, A. Rachmat, A. Lesbani, *Bull. Chem. React. Eng*., 15, **2020**, 525-537.
141. J. Missau, D.A. Bertuol, E.H. Tanabe, *Appl. Clay Sci*., 214, **2021**, 106297.
142. X.F. Li, R.X. Li, K.X. Wang, *J. Ind. Eng. Chem*., 126, **2023**, 270-282.
143. H. Wang, W. Zhao, Y. Chen, Y. Li, *Bioresour. Technol.*, 315, **2020**, 123834.
144. S. Natarajan, V. Anitha, G.P. Gajula, V. Thiagarajan, *ACS Omega*., 5, **2020**, 3181-3193.
145. R. Tabatabaeian, M. Dinari, H.M. Aliabadi, *Carbohydr. Polym*., 257, **2021**, 117628.
146. Q. Yan, Z. Zhang, Y. Zhang, A. Umar, Z. Guo, D. O′Hare, Q. Wang, *Eur. J. Inorg. Chem*., 2015, **2015**, 4182-4191.
147. T. Taher, R. Putra, N.R. Palapa, A. Lesbani, *Chem. Phys. Lett*., 777, **2021**, 138712.
148. Q. Sun, M. Tang, P.V. Hendriksen, B. Chen, *J. Alloys Compd*., 829, **2020**, 154552.
149. L. Adlnasab, M. Ezoddin, M.A. Karimi, N. Hatamikia, *Res. Chem. Intermed*., 44, **2018**, 3249-3265.
150. N. Ghanbari, H. Ghafuri, *Environ. Technol. Innov*., 26, **2022**, 102377.
151. M. Abbasi, M.M. Sabzehmeidani, M. Ghaedi, R. Jannesar, A. Shokrollahi, *Mater. Sci. Eng. B*., 267, **2021**, 115086.
152. F. Mohamed, M.R. Abukhadra, M. Shaban, *Sci. Total Environ*., 640-641, **2018**, 352-363.
153. J. Zhao, Q. Huang, M. Liu, Y. Dai, J. Chen, H. Huang, Y. Wen, X. Zhu, X. Zhang, Y. Wei, *J Colloid Interface Sci*., 505, **2017**, 168-177.
154. R. Khalili, M. Ghaedi, M. Parvinnia, M.M. Sabzehmeidani, Surf. Interfaces., 23, **2021**, 100976.