Chapter 1

Introduction

1.1 Introduction

An adequate safe and accessible water supply is an important global issue and a challenge to be addressed in the new millennium.

Both groundwater and surface water can be a source of safe drinking water if they are not polluted and the water is adequately treated. Groundwater is reliable during droughts, whereas surface water can quickly deplete. Groundwater is generally easier and less expensive to treat than surface water because it is less polluted. Groundwater can be tapped where it is needed via wells, whereas surface waters are concentrated in lakes and streams.

Groundwater pollution occurs when contaminants are discharged, deposited or leached from the land surface above the groundwater. For example, fluoride is commonly found in groundwater due to weathering and leaching of fluoride-containing minerals from rocks and sediments and has become one of the most serious environmental hazards in the world.

Further, organic substances such as nitrophenols, dyes, pigments, pesticides, polychlorinated biphenyls, chlorinated solvents, etc. are found in waste water from various chemical operations such as petrochemical units, dye and dye intermediate production companies and textile units. Dyes and nitroarene containing effluents are of special concern globally due to their toxic effects on flora, fauna and humans.

1.2 Dyes

1.2.1 Sources and pathways of dyes in the environment

The sources and pathways of various dye pollutants in water bodies are depicted in figure 1.1. and classification of dyes in figure 1.2.

The release of the industrial dye effluent into water causes adverse effect on human health as well as lowers the light penetration and photosynthetic activity in aquatic ecosystems (Lellis et al., 2019). The presence of metal ions and aromatics in these dyes and hence in the effluent generates teratogenic or mutagenic effects on aquatic organisms and fish species (Deering et al., 2020).

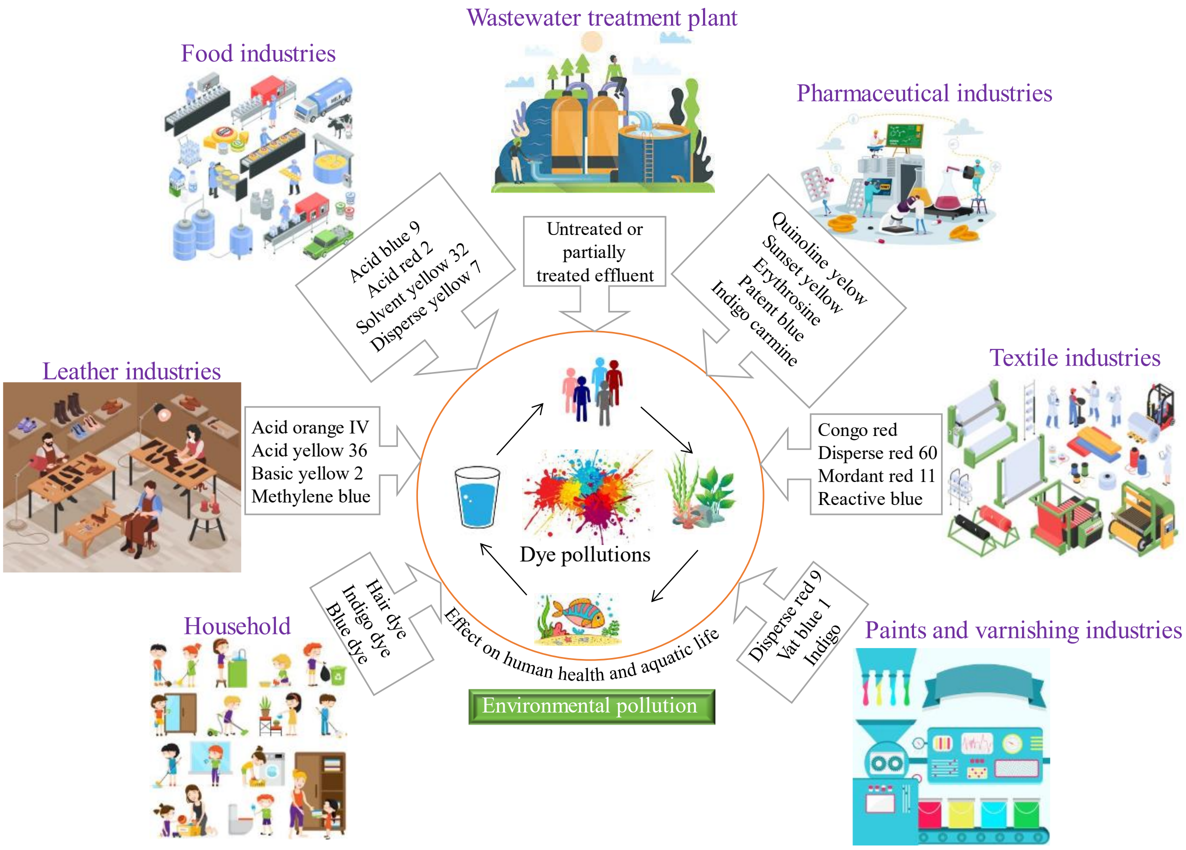

Figure 1.1. Sources and pathways of different dye pollutants

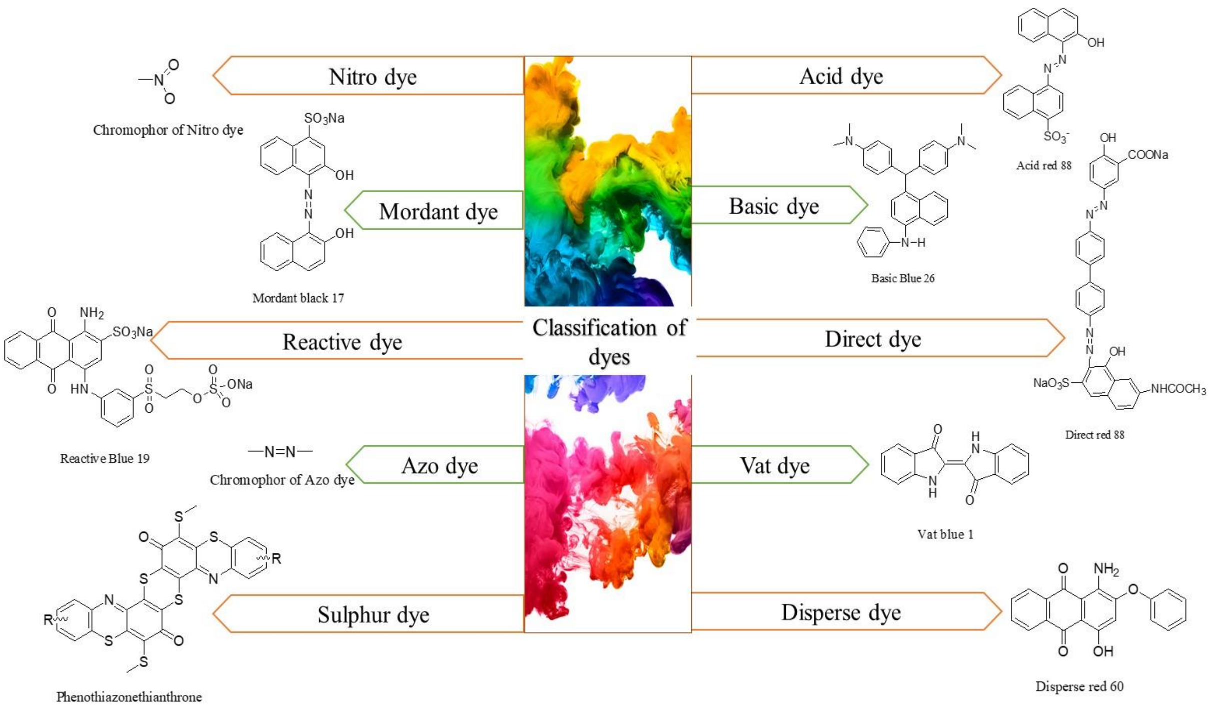

Figure 1.2. Classification of dyes

The presence of dyes in the environment has mild to severe toxic effects on human health, which include carcinogenic, mutagenic, allergic, dermatitis effects, and kidney disease (Lellis et al., 2019). Thus, the treatment of waste water from textile and manufacturing industries is a major challenge for environmental managers (Lellis et al., 2019) as dyes are water soluble and produce very bright colours in water with acidic properties. Dyes are stable to light and are biologically non-degradable. They are resistant to aerobic digestion and are one of the most difficult molecules to be removed from the industrial wastewater. Discharge of dye contaminated wastewater without proper treatment can also increase the Chemical Oxygen Demand (COD) of the water body.

1.2.2 Wastewater treatment techniques for dye removal

Dyes are typically categorized depending on their chemical structure, namely-anionic, cationic, and non-ionic (Heidari et al., 2019). The increasingly used dyes are methylene blue (MB), rhodamine B (RhB), methyl orange (MO), Congo red (CR), Disperse Violet 26, methyl red, and crystal violet. Table 1.1 summarizes the availability of various dye removal technologies that have been used to remove and recover toxic contaminants from industrial effluent. These technologies include chemical precipitation, reduction, oxidation, coagulation, ion-exchange, reverse osmosis, solvent extraction, flocculation, membrane separation, filtration, evaporation, electrolysis, and adsorption (Afroze & Sen, 2018). Each of the aforementioned procedures has advantages and disadvantages (Table 1.1) that must be carefully considered before adapting the technique for dye removal processes.

In electrocoagulation method, iron or aluminium electrodes are submerged in dye containing water and direct current source is applied. Thus, the metal hydroxides are formed at a particular pH, which then form suspended particles/agglomerates which adsorb dye particles. Besides this, in filtration technique, sieving and particle capturing process is done to separate suspended and dissolved particles (Sonal et al., 2021). In ion exchange technique, the dye removal takes place through the strong interactions between the functional groups on ion exchange resins and charged dye molecules. The use of ultraviolet/hydrogen peroxide (UV/H_2O_2), ozonation, Fenton, ultrasound, photocatalytic processes and anodic oxidation have been efficiently employed to treat dye wastewater. The active radical formed in these processes degrades contaminants (Gupta et al., 2021)(Kuila et al., 2021).

Table 1. 1 Existing and emerging processes for dye removal (Dutta et al., 2021)

Physical/chemical Methods	Method description	Advantages	Disadvantages
Fenton reagents Advanced Oxidation Process	Oxidation reaction using mainly H_2O_2-Fe (II)	Effective decolorization of both soluble and insoluble dyes	Sludge generation
Ozonation	Oxidation reaction using ozone gas	Application in gaseous state: no alteration of volume	Short half-life (20 min)
Photochemical Advanced Oxidation Process	Oxidation reaction using mainly H_2O-UV	No sludge production	Formation of by-products
NaCl	Oxidation reaction using Cl^+ to attack the amino group	Initial and acceleration of azo bond cleavage	Release of aromatic amines
Electrochemical destruction	Oxidation reaction using Cl^+ to attack the amino group	Breakdown of compounds are non-hazardous	High cost of electricity
Activated carbon	Dye removal by adsorption	Good removal of a wide variety of dyes	Regeneration difficulties
Membrane filtration	Physical separation	Good removal of a wide variety of dyes	Concentrated sludge Production
Ion exchange	Ion exchange resin	Regeneration: no adsorbent loss	Concentrated sludge Production
Electrokinetic coagulation	Addition of ferrous sulphate and ferric chloride	Economically feasible	High sludge production

Adsorption methods involve the transfer of a gas or liquid solute to the surface of the adsorbent. It is considered to be the most efficient technique for dye removal.

Methylene blue (MB) is a common dye mostly used in industries like plastics, cosmetics, textile, paper, leather, rubber, pharmaceutical and food industries. It is the most commonly used substance for dying wood, cotton and silk. It can cause eye burns and is responsible for permanent injury to the eyes of human and animals. When ingested through mouth it cause profuse sweating, vomiting, nausea, methemoglobinemia mental confusion (Gureev et al., 2020). Therefore, the treatment of effluent containing methylene blue dye is of interest due to its harmful impacts and has thus been used extensively by researchers as a model pollutant to study the efficiency of adsorbents under study.

1.3 Fluoride

1.3.1 Sources and pathways for fluoride in the environment

There are various minerals such as fluorite, biotite, topaz and their associated host rocks such as granite, basalt, syenite and shale which contain fluoride that can be released into the groundwater (Lavalle-Carrasco et al., 2021). Apart from this, industries like semiconductor industries, coal fired power stations, brick and iron works, photovoltaic solar cells, industry steel production, uranium enrichment facilities, beryllium extraction plants, oil refineries, aluminium-zinc smelters glass and ceramic industries and superphosphate fertilizer industries are responsible to cause fluoride pollution in environment (Lavalle-Carrasco et al., 2021). The incineration plants of municipal waste, fluorinated plastic and fluorinated textiles are also involved in occurrence of fluoride pollution to a great extent (Neuwahl et al., 2019).

The effluents from these industries have much higher concentration of fluoride than that of natural waters which is in the range of ten to thousands of mg/L. The fluoride enters in the body via the gastrointestinal tract through the ingestion of drinking water having naturally occurring fluorides or added fluoridated salts (Grandjean, 2019).

It is evaluated that more than 200 million people globally depend on drinking water containing fluoride concentrations which exceed the WHO guideline of 1.5 mg/L (Herschy, 2012). The population of India, China, Pakistan and Thailand are found to be affected by fluorosis where the concentration fluoride is found to be > 5.0 mg/L. Table 1.2 show the biological effect of different concentrations of fluoride on human health.

Table 1.2 Biological effect of fluoride on human health (Kumar et al., 2019)

Biological effect on human health		
Fluoride conc. (mg/lit)	**Source**	**Effects**
1	Water	Prevention of dental caries
2	Water	Effect of dental enamel
3 to 6	Water	Osteoporosis
8	Water	10% osteoporosis
20 to 80	Air & Water	Skeletal fluorosis
50	Food & Water	Affects thyroid
100	Food & Water	Defective development
>125	Food & Water	Affects kidney
>2500	Acute dose	Death

In view of toxic effects of fluoride on human health, there seems an urgent need to find out an effective and robust technology for the removal of excess fluoride from drinking water.

1.3.2 Wastewater treatment techniques for fluoride removal

Defluoridation is the process of removal of fluoride ion in drinking water and is the only practicable option to overcome the problem of excessive fluoride in drinking water, where alternate source is not available.

Some defluoridation techniques developed to control fluoride content in water are reverse osmosis (Sekhara et al., 2017), adsorption (Onyango & Matsuda, 2006), ion-exchange (S. Singh et al., 2020), precipitation–coagulation (Wambu et al., 2022), membrane separation process (Wambu et al., 2022), electrolytic defluoridation (Sai et al., 2019) and electrodialysis (Gmar et al., 2015). The adsorption of fluoride has been attempted using holly Oke, burnt bone powder, sunflower plant dry powder, stem of phytomass, neem bark powder, activated cotton jute carbon, bagasse ash, phosphate-treated saw dust, bone char, etc. as adsorbents in past (Jamode et al., 2004), Nalgonda technique, activated alumina process and ion exchange process (Sekhara et al., 2017). However, due to high cost or lower efficiency or non-applicability on mass scale these techniques are not much in use.

Initially precipitation is done by dosing of lime followed by addition of alum to obtain coagulation. In this process, alum reacts with water forming insoluble [$Al(OH)_3$]. This process can remove only a smaller portion of fluoride (18–33%) in the form of precipitates and converts a greater portion of ionic fluoride (67–82%) into soluble toxic aluminium fluoride complex ion and therefore this technology is inaccurate. The final concentration of fluoride treated by this method can only reach 10-20 mg/L. So, the precipitation method is only suitable for fluoride-containing water with high concentration such as wastewater produced from electronic industry, which is not suitable for drinking-water purposes and a subsequent defluoridation process need to be carried out. However, CaF_2 precipitation becomes difficult when fluoride concentration in the wastewater is <100 mg/L because of the solubility of fluorite ($K_{sp} = 3.46\times10^{-11}$) (Wambu et al., 2022). The fluoride removal is accomplished at pH range of 5.5–7.5. Due to use of alum as coagulant, the sulphate ion concentration increases tremendously and, in some cases, it crosses the maximum permissible limit of 400 mg/L resulting into the cathartic effect in human beings. The aluminium residue >0.2 mg/L in treated water can cause dementia and can cause neurobehavioral and pathophysiological effects. The respiratory, reproductive, endocrine, cardiovascular, musculoskeletal systems are also adversely affected (Kanduti et al., 2016). In this technique, large space for sludge drying is required. Even the maintenance cost is high. It is not an automatic process and requires attendance for chemical addition and after treatment process.

Membrane process/ reverse osmosis has emerged as preferred alternative to provide safe drinking water without posing the problems associated with other conventional methods. It is a physical process in which pressure is applied and the purification and concentration of different components occurs through the semipermeable membrane selective separation function. This process is reverse of natural osmosis because the pressure is applied to the concentrated side of semipermeable membrane which then takes over the natural osmotic pressure. There are two types of membranes that are known to remove fluoride from water: Nano filtration and reverse osmosis. Nano filtration is a relatively low-pressure process that removes primarily the larger dissolved solids as compared to reverse osmosis. On the other hand, reverse osmosis works at higher pressures with greater rejection of all dissolved solids. Fluoride removal efficiencies upto 98% have been reported by these processes. The impact of inorganic carbon and humic acid (HA) on fluoride retention over a broad range of pH values (2-12) by these processes had been studied by Owusu-Agyeman et al (Owusu-Agyeman et al., 2017). It was found that retention of fluoride increases with increase in pH. But since the

CO_3^{2-} ions were predominant inorganic carbon species at pH > 10, they get retained more easily than the monovalent fluoride. The use of HA changes the surface charge of membranes and thus enhances the fluoride retention. The use of membrane technology for drinking water purpose was considered as uneconomical as compared to the conventional methods. The water quality standards and the problems associated with the existing methods demands reconsideration of membrane technology for water purification due to increase in demand and contamination of water.

In comparison with the above-mentioned technology, adsorption has always been an attractive choice by the society at large and researchers due to its cost effectiveness, ease of operation, high removal capacity and ability to reuse the adsorbent. Research may thus be directed towards development of a cheap, efficient and environment-friendly, but highly selective adsorbent with high effective adsorption capacity.

1.4 Nitroarenes

Nitroarenes are nitro-substituted derivatives of monocyclic and polycyclic aromatic hydrocarbons (arenes) and the majority of them are believed to have been introduced into the environment by human activity rather than by natural process. Nitroarenes are one of the main mutagens and carcinogens produced during combustion and are also widely present in the environment. The substitution of a nitro moiety on cyclic carbon atoms in monocyclic and polycyclic aromatic hydrocarbons is known to induce nitroarenes (Capperucci & Tanini, 2022). They are not only toxic but also inhibitory and anthropogenic in nature so their reduction is a major concern.

The 4-Nitrophenol (4-NP) is frequently used to make medications, colours, fungicides, insecticides, and to darken leather. 2-nitrophenol and 4-nitrophenol may also be released onto the surface by textile industry effluents and waste waters from other industries, including iron and steel manufacture, foundries, pharmaceutical manufacturing, processing, and electrical/electronic component production. It causes irritation and inflammation in eyes. It combines with blood and results in the formation of methemoglobinemia. This effect causes unconsciousness, confusion and cyanosis. It causes vomiting and abdominal pain when ingested. 4-nitrophenol and its derivatives has an application in the synthesis of pesticides, herbicides and insecticide which turns out to be a threat to environment and human being (Godain et al., 2020).

2-nitroaniline (2-NA) is an environmental pollutant which is originated from the anthropogenic activities like production of dyes pharmaceutical products and explosives (Naseem et al., 2017). It is used as a precursor for synthesis of latex, pesticides and medicine. The waste effluents of textile industries and military plants also contains 2-NA (Naseem et al., 2017).

2-NA is also found sometime in waste effluents of military plants and textile industries. Its presence even at low levels can show highly toxic, carcinogenic and mutagenic effects (Naseem et al., 2017). 2-NA gets accumulated in food chains and thus disturbs the biological cycle. It has been considered as toxic pollutant and harmful waste by Unites States Environmental Protection Agency (Z. Dong et al., 2014).

1.4.1 Sources of phenol and phenolic derivatives

Phenol and phenolic derivatives are released from many industries such as pharmaceutical, petroleum and petrochemical, pesticides, plastic, paper and other manufacturers (Mainali, 2020). Furthermore, an important method to remove nitrophenols from industrial waste water is to carry out their reduction to aminophenols. Aminophenols are one of the important starting materials in the synthesis of many industrial dyes (Wyasu et al., 2020), pharmaceuticals and some biologically active compounds (Khandavilli et al., 2020). Aminophenols are also used as corrosion inhibitor in paints and as anti-corrosion lubricant in fuels. Many methods are available for the reduction of nitrophenols to aminophenols such as electrolytic reduction (Polat et al., 2002), metal/acid reduction (Pozun et al., 2013), homogenous and heterogeneous catalytic hydrogenation (Arora et al., 2018), photo reduction (Abdul Nasir et al., 2018), etc. Among the various methods, the use of $NaBH_4$ has proved to be a promising method as it is milder and thermally stable chemical hydride. Reduction reactions using $NaBH_4$ have been known to accelerate in the presence of suitable catalysts such as transition metals (Hervés et al., 2012).

To reduce the potential adverse effects of pollutants on the environment their removal at trace levels in aqueous solutions and removal from industrial effluents are the challenges faced by the world today. Consequently, the development of effective remediation techniques for the removal of such pollutants has become the focus of environmental research. It is also important to develop simple and reliable methods for their determination in environmental water samples. **Adsorption and Advanced Oxidation Processes** (AOPs) are more efficient, cheap and eco-friendly in the remediation of any kind of toxic pollutants including cations, anions, organic pollutants including nitroarenes, dyes, etc.

The remediation techniques of choice for fluoride, dyes and organics have been adsorption, Advanced Oxidation Processes and catalytic reduction. In the present work we have concentrated on adsorption and catalytic reduction. The two techniques are described in detail in the upcoming section.

1.5 Remediation techniques for pollutants

1.5.1 Adsorption

Adsorption outperforms other approaches in terms of ease of operation, affordability, and simplicity of design. It is also insensitive to harmful compounds. Adsorption is one of the most efficient physical methods for removing pollutants, works with all varieties of dyes, cation, anions and organic pollutants. Various adsorbents can be used to remove the pollutants from the environment. Several common adsorbents include:

1.5.1.1 Activated carbon

The most popular adsorbent is activated carbon (powdered or granular), which has excellent chemical adsorption potential. However, activated carbon that is sold commercially is highly expensive. Due to its high porosity, substantial surface area, and high catalytic activity, activated carbon is regarded as an effective adsorbent. However, activated carbon has a limited affinity for inorganic contaminants like fluoride and a small capacity for adsorption. Recent studies have concentrated on altering activated carbons with various chemical species to address these challenges. Activated carbon is now affordably prepared using a variety of low-cost materials as precursors (He et al., 2020).

1.5.1.2 Carbon nanotubes

Carbon nanotubes have been shown to exhibit a high potential as adsorbents for absorbing many different types of organic and inorganic pollutants from aqueous solution because of their large specific surface area, tiny pore size, hollow and layered architectures (Peng et al., 2021). Through a hydrothermal reaction with glucose solution, colloidal carbon nanospheres (CNS) have been created, which were then activated by NaOH solution and employed as adsorbents for basic dyes (Upadhyayula et al., 2009). On the other hand, carbon nanotubes and their nanocomposites are also observed to be used in adsorption of aromatic nitro compounds (Litts et al., 2018). It has been observed that the aromatic characteristics of the carbon nanotubes weaken by the attachment of polar groups that eventually reduces its the surface area and thus lowers the adsorption capacity. However, oxidation (introduction of hydroxyl, carbonyl, and carbonyl groups) has the potential to open carbon nanotubes which boost their adsorption capacity due to increased surface area and the emergence of hydrogen bonds between oxidized carbon nanotubes and adsorbates. It has been found that carbon nanotubes have a high water flow capacity, low biofouling activity and excellent fluoride filtering performance (Chufa et al., 2021). The carbon nanotube- based materials are shown in figure 1.3.

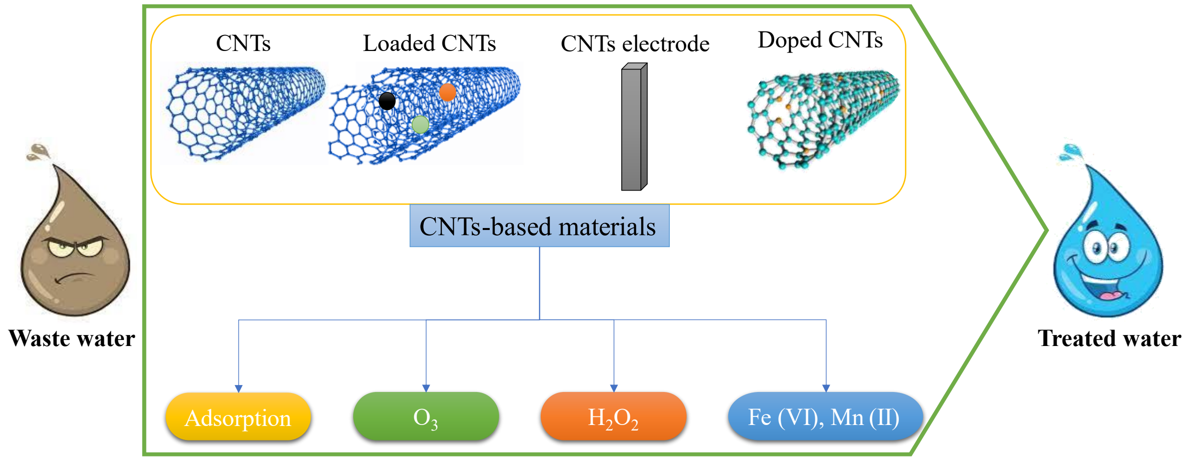

Figure 1. 3. CNT-based materials (Peng et al., 2021)

1.5.1.3 Graphene

Due to its special characteristics, graphene, a two-dimensional, one atom thick nanomaterial made of sp^2 - hybridized carbon, has drawn a lot of attention from scientists (figure 1.4.). As a zero-band gap semiconductor with new electrical properties, graphene is highly conductive for storing and moving electrons. According to M. Kaur et al. (2012), graphene produced via a modified Hummers' process (containing $KMnO_4$, $NaNO_3$, and H_2SO_4) has the greatest capability for methylene blue adsorption (Kaur et al., 2018). By grafting polyacrylamide chains with reduced graphene oxide, Hadi Hosseini et al. were able to enhance the adsorption capacity of methylene blue (Hosseini et al., 2022). To boost graphene's ability to adsorb materials, functionalizing it with polymers containing heteroatoms is an option. Due to its great porosity and potential as a very effective adsorbent, 3D graphene sponges or foams have received a lot of interest.

The graphene-based carbon nanomaterials have the potential to accelerate the transformation of nitroaromatic compounds. By surface modification of these carbon nanomaterials, the conversion efficiency of contaminants could be enhanced (L. Li et al., 2016). Some researchers have supported reduced graphene oxide with metals. Xiaolong Zhang et al. used CoPt and Ag nanoparticles to support graphene oxide and used it for the reduction of nitrophenols (X. Zhang et al., 2021). Zhiqiang Xu et al. used Cu@Ni bimetallic nanowires for support and nitrophenol reduction (Xu et al., 2019).

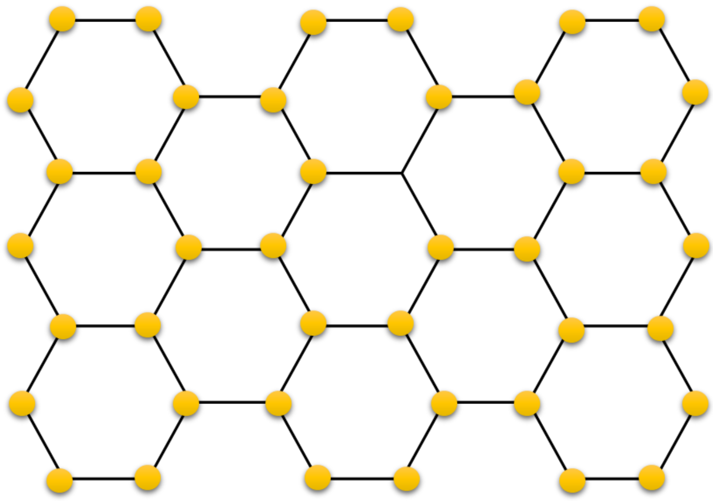

Figure 1. 4. Structure of graphene

Drinking water tainted with fluoride can be made safe again by using graphene nanosheets generated from brown seaweed biomass. These nanosheets can be used to make water safe because they are non-toxic. Metal salts of iron and tin can change the properties of graphene, giving it sheet-like structures and interconnecting nanopore networks (Sharma et al., 2017).

1.5.1.4 Low-cost adsorbents

1.5.1.4.1 Non-carbonized agro-waste

Agricultural waste is a broad term for organic substances discarded by humans during the agricultural production process. The main components of agricultural waste are plant waste, poultry manure and agricultural waste. The agricultural waste primarily consists of crop stalks and animal manure (Dai et al., 2018). Agro-waste by-products have emerged as a viable option for developing cost-effective and environmentally friendly waste water treatment processes (Sivaperumal et al., 2019).

Agrowaste has porous and loose structure which consists of hydroxy, carboxyl and other reactive groups due to which they can be a good option as adsorbents for pollution remediation and thus reduce environmental burden. The examples of the agrowaste materials used so far are avocado skin (Palma et al., 2016), palm shell (Soni & Padmaja, 2014), walnut shell (Uddin & Nasar, 2020), bagasse (Sarker et al., 2017), olive powder (Khalil et al., 2021), wheat straw (Qian et al., 2019), banana skin (Akpomie & Conradie, 2020), coconut shell (James & Yadav, 2021), cucumber (Wyrwicka et al., 2019), earthworm faeces (Xiao et al., 2022), mustard (Mitra, 2017) etc. to name a few.

Due to the abundance, affordability and environmental friendliness of cellulosic and lignocellulosic biomasses, researchers have tried to broaden their fields of application. One such application is as a bio-filter for the remediation of water that has been contaminated with various hazardous pollutants (Song et al., 2012).

1.5.1.4.2 Biochars

Biochar is a by-product of the pyrolysis of biomass during controlled thermal processes and gasification of biofuel. Pyrolysis process increases the surface density of functional groups. Due to this, it has capacity to act as an adsorbent for the micropollutants removal from the waste water. The properties of biochar are affected by various factors like pyrolysis temperature, time and type of feedstock. At low temperature, higher number of aliphatic carbons and functional groups get produced whereas at high temperature polyaromatic carbons are observed. As polyaromatic carbons contains high microporosity, it can be potentially used for the removal of organic pollutants (Qiu et al., 2022)(Zeghioud et al., 2022).

1.5.1.5 Biopolymers

Different strategies have been looked into for the creation of more affordable and efficient adsorbents. Among these, biopolymers and natural polysaccharides are of particular interest. Due to their structure, physico-chemical properties, chemical stability, strong reactivity and remarkable selectivity towards aromatic compounds, metals and other contaminants that cause water pollution, these materials have proven to be superior alternatives to their synthetic equivalents. Chitin, Chitosan, Alginates, Guar gum, etc. are a few of them (Russo et al., 2021). Because chitosan contains protonated amino groups, which interact with pollutants in solution through ion exchange at the optimum pH, it has the best anionic dye adsorption characteristics of all the biopolymers. The polymer's high amino group content also makes it easier to modify it chemically to increase its adsorbent capabilities.

1.5.1.6 Layered materials

Inorganic layered materials such as clay, hydrotalcites etc. are excellent options as adsorbents because they have large surfaces, great accessibility and limited interlayer spaces at the nanometre and micrometre scales.

1.5.1.6.1 Clay

Due to its large supply, low cost, excellent chemical and mechanical stabilities and high adsorptive characteristics, clay has become one of the most promising natural adsorbents. In the past ten years, applications of clay-based adsorbents for the removal of dye have drawn more and more attention (T. Zhang et al., 2021). For the creation of inexpensive adsorbents that might be helpful in environmental clean-up, clay minerals constitute a cheap and environmentally safe source of raw material.

1.5.1.6.2 Layered double hydroxides

Layered double hydroxides (LDHs), also known as hydrotalcite like compounds or anionic clay, have received a lot of interest lately because they feature large interlayer gaps, positively charged layers and exchangeable anions in the interlayers (figure 1.5). Chemically, LDHs can be represented by the formula $[M^{2}_{1-x}\ M^{3+}_{x}\ (OH)_2]^{x+}[A^{m-}_{x/m}].nH_2O$ (Q. Li et al., 2010). The trivalent cations M^{3+} (Al^{3+}, Fe^{3+}, Co^{3+}, Mn^{3+}, Ni^{3+}, Cr^{3+}, etc.) substantially replace the divalent cations M^{2+} (Ca^{2+}, Mg^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, etc.) to produce a positively charged layer (Y. Zhang, 2021). Anions can be intercalated into the LDHs' interlayer area to maintain charge neutrality.

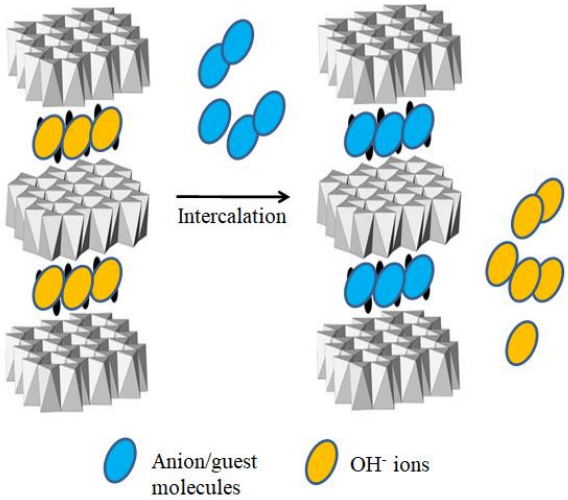

Figure 1. 5. Structure of layered double hydroxide

1.5.1.6.3 Zeolites

A network of $[SiO_4]_4^-$ and $[AlO_4]_4^-$ tetrahedrally linked to one another by the sharing of an oxygen atom forms the basis of zeolites, which are crystalline, microporous and hydrated aluminium silicates. $M_{x/n}[AlO_2]_x$. $[SiO_2]_y.mH_2O$ M is an alkali or alkaline earth cation, in which n is the valence of the cation, y is the amount of water molecules per unit cell, x is the total number of tetrahedra per unit cell and the ratio y/x (atomic Si/Al ratio) typically has values of 1 to 5, though for the silica zeolite, y/x can range from 10 to 100.

Zeolites make up a distinct class of solid materials with numerous uses in industrial operations and the reduction of environmental pollutants. They can be applied to both preventative decontamination plans and the clean-up of different sorts of harmful spills. A zeolite's functional structure consists of a microporous, aluminosilicate framework with a formal negative electric charge and the precise quantity of cations needed to balance that charge. Zeolites are efficient ion-exchange materials because different types of cations that are added in the solution phase can exchange the cations out of the zeolite (Rhodes, 2010).

Zeolites can serve as microreactors for a variety of "green" chemical reactions because they are microporous i.e., they have a honeycomb-like structure with pores that are typically less than 1.3 nm in diameter and can thus easily accommodate simple organic molecules (Rhodes, 2010).

Zeolites with characteristics including high BET surface area, ion exchange property, shape selectivity, native-charged lattice and strong thermal and chemical durability are potential options for adsorption of pollutants such as metal ions, dyes, phenol and phenol derivatives (Tasić et al., 2019). Zeolite with ordered mesopores demonstrated outstanding methylene blue adsorption performance (Ji et al., 2021).

Zeolites typically contain negative surface charges at all pH levels, which results in a high capacity for adsorbing cations but a low capacity for adsorbing anions due to electrostatic repulsions. To increase the adsorption capacity of zeolites, various researchers treated zeolite surfaces with multivalent metallic cations (He et al., 2020).

1.5.1.6.4 Tetravalent Metal Acids (TMAs)

TMAs are a type of multilayer inorganic ion exchangers that includes zirconium phosphate and zirconium tungstate. Due to their robust properties, thermal and chemical stability, ion exchange properties and absolute insolubility in water, they have been widely used as adsorbents for metals and dyes (Velusamy et al., 2021). Layered zirconium phosphate has drawn a lot of interest recently as a versatile material having phosphate groups that can be exchanged with inorganic and organic cations for remediation purposes (Pica, 2021). Titanium phosphate, Zirconium tungstate, Cerium phosphomolybdate, sodium vanadate orthovanadate, sodium metavanadate, vanadyl sulphate are other examples of TMAs (figure 1.6.).

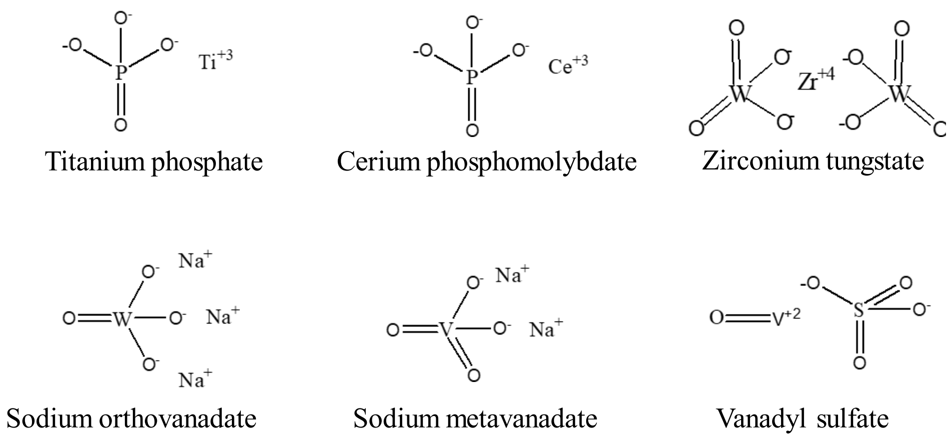

Figure 1.6. Examples of tetravalent metal acid salts

Through ionic interactions, van der Waals forces and hydrogen bonds, special organic groups can be grafted or inserted, allowing for the modification of interlayer distances as well as the introduction of selectivity, adsorption capacity and reactivity to enhance adsorption capacity towards metal ions and dyes (Pica, 2021).

1.5.1.7 Composites

Adsorption properties are improved when an adsorbent is combined with additional substances using techniques such grafting, impregnation, chelation and crosslinking (Wei et al., 2022). For the remediation of gases, metals, pharmaceutical wastes, dyes and pesticides, the synergy of adsorbent materials as composites has been specifically designed. Composite adsorbents are known to have improved surface chemistry, greater mechanical strength, increased surface area and enhanced selectivity (Valdez-Alegría et al., 2020). Nanocomposites are materials in which the distributed particles (nanofillers) have at least one dimension in the nanometre range.

The term "bio nanocomposite" has gained popularity in recent years to describe nanocomposites that contain a naturally occurring polymer (biopolymer) along with an inorganic moiety and have at least one nanometre-scale dimension. Because of their functional properties, bio nanocomposites based on layered inorganic materials mentioned above are of singular importance, as described in a review (Journal, 2017)(Karadag et al., 2008). Since the advent of nanocomposites, materials scientists are making huge efforts in this direction because of the excellent features of these nanohybrids as structural or functional materials, with interesting applications as components in heterogeneous catalysts and optical, magnetic and electrochemical devices (Darder et al., 2006). Bio nanocomposites show improved mechanical properties, higher thermal stability and gas-barrier properties as shown by synthetic polymer composites as well as the remarkable advantage of exhibiting biocompatibility, biodegradability and in some cases, functional properties provided by either the biological or inorganic moieties. Living organisms are known to produce natural nanocomposites that show an amazing hierarchical arrangement of their organic and inorganic components from the nanoscale to the macroscopic scale. Nacre in pearls and shells (Gerhard et al., 2017) and enamel and dentine in teeth (Balhuc et al., 2021) are well known examples of bio nanocomposites found in nature. There are many natural biomacromolecules such as starch, cellulose (and its derivatives), guar-gum, chitosan and poly (lactic acid) (PLA) that can be used in the preparation of green bio nanocomposites (A. A. Singh et al., 2020).

Numerous hybrid nanocomposites made of conducting polymers like polypyrrole, polyaniline and polythiophene and semiconductor nanoparticles have been synthesized in recent years and are widely used for eliminating environmental pollution. PANI, one of these conducting polymers, has drawn the most interest for adsorption, energy storage, sensors and electrochromic devices due to its high conducting properties compared to metals. PANI is helpful in photodegradation due to its high absorptivity and excellent redox properties (Ahmad et al., 2018). Because of this, polyaniline has been blended with different biomaterials to get bio nanocomposites. For example, Ashvinder K. Rana synthesized Cellulose/polyaniline hybrid nanocomposites (Rana et al., 2022). In-situ polymerization of aniline with cellulose and Ni nanoparticles was attempted by Nafeeds Ahmed et al. This hybrid bionanocomposite was used for the photocatalytic activity and antifungal activity (Ahmad et al., 2019).

1.5.1.7.1 Metal cholates

The possibility of using low molecular weight hydrogels as tunable functional materials in composites has generated a great deal of interest to design sensors and in biomedicine, which includes various fields like drug delivery, regenerative medicine and tissue engineering (Bhowmik et al., 2010).

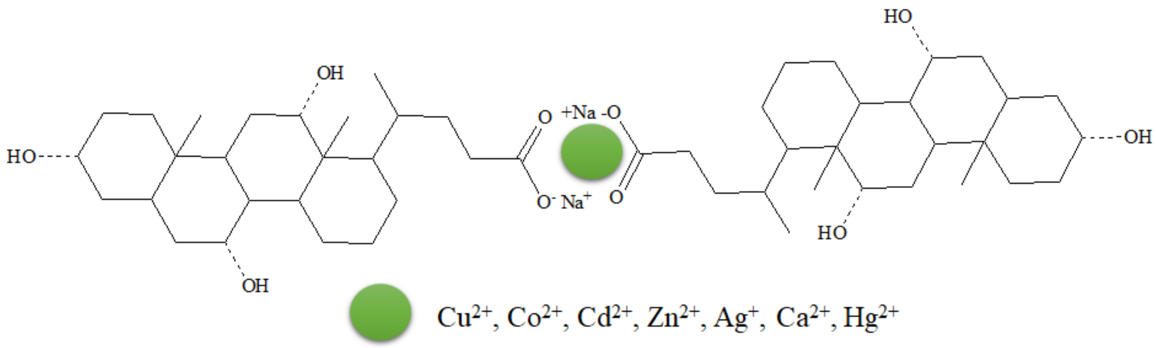

Figure 1. 7. Chemical structure of metal cholates

Several bile salts are known to form hydrogels. For example, sodium deoxycholate (3α- and 7-α dihydroxy) and sodium salt of lithocholic acid (3 α-hydroxy) (Chem, 2012). Sandip Bhowmik et al. firstly reported the supramolecular hydrogelation of sodium cholate driven by lanthanides (Bhowmik et al., 2010). They stated that the hierarchical nanostructures can be used as templates for fabricating size and shape-controlled nano objects with specific functions. The rigid helical superstructures of the hydrogels are advantageous for the controlled growth of novel nanomaterials that could be used in a variety of applications such as biosensors, chiral catalysts, non-linear optics and materials science. The chemical structure of metal cholates is shown in figure 1.7. Arkajyoti Chakrabarty et al. developed metal cholates using copper, cobalt, cadmium, zinc, silver, mercury and calcium (Bhowmik et al., 2010).

1.5.2 Catalytic reduction by $NaBH_4$

In past, Brown et al. found that sodium borohydride reacted with certain metal salts to form finely divided black precipitates of borides which can be useful for the catalytic hydrogenation (Brown, 1970). This process was applied for the catalytic conversion for nitroarenes to their respective amino compounds. Monometallic catalysts (Pd, Pt, Ru, Ag, Cu), bi or multimetallic nanocatalyst (Cu-Pd, Pt-Ni. Pt-Ni-Fe), supported catalysts (with supports such as carbon nanotube, mesoporous silica, graphene oxide, carbon nitride, polymer), supported magnetic nanocatalysts (iron oxide, carbon coated magnetic NPs, polymer encapsulated magnetic NPs) have been used for the reduction of nitroarenes (K. Zhang et al., 2019).

Silver nanoparticles are of high interest in catalysis because of having significant characteristics like their unique optical and electronic properties, antimicrobial activity, environmental friendliness and low cost (X. Y. Dong et al., 2015).

The high catalytic activity of silver nanoparticles partially originates from their large specific surface area owing to their small sizes. Silver in the form of colloids and nanofluids is more reactive. Nanofluids of silver are obtained by dispersing/suspending nanoparticles with dimensions in order of 10 nm. It is a new class of technology based heat transfer fluids (M. S. Ahmed, 2019). Ag NPs loaded Al_2O_3 and SiO_2 in NF as catalysts towards reduction of nitrophenol has been evaluated (M. et al., 2021).

Interaction of unprotected small particles however, will lead to agglomeration or aggregation from the cohesive surface energy. In addition, the soluble/dispersible nano catalysts suffer from problems associated with the separation, recovery and instability at high temperatures. These general problems can be overcome by using a framework to support the nanoparticles, which keeps them separated and also makes them recyclable. Carbon-based materials, polymers and mesoporous silica metal organic frameworks and magnetic metal organic frameworks have been used as supports for metal nano catalysts (K. Zhang et al., 2019). For example, magnetic chitosan-supported silver nanoparticles were synthesized by Kamrul Hasan et al. for reduction of 4-nitrophenol (Hasan et al., 2019). Hem Prakash Karki et al. prepared silver nanoparticle loaded on magnetic Fe_3O_4/ATO nano-composite (Karki et al., 2018). Neelu Chouhan et al. developed silver nanoparticles using *Trachyspermum ammi* (Ajwain) seeds for reduction of nitrophenol to aminophenol (Chouhan et al., 2017). The ultrasmall core-shell silver nanoparticles were synthesized by an upscaled modification of the polyol process (Kästner & Thünemann, 2016). S. Shanmuga Priya et al. developed simple and rapid method for the synthesis of silver nanoparticles using *Areca catechu* root extract as reducing and stabilizing agent (Priya et al., 2015). Akshay Shankar demonstrated Sporotrichum thermophile culture extract-mediated greener synthesis of silver nanoparticles for functional group transformation of nitro to amino (Shankar, 2020). Silver nanoparticles supported on cellulose polymer paper and other matrices have been used for catalytic degradation of dyes and nitrophenols (Albukhari et al., 2019).

The illustrative representation of the catalytic reduction of nitro compounds by $NaBH_4$ is described in figure 1.8.

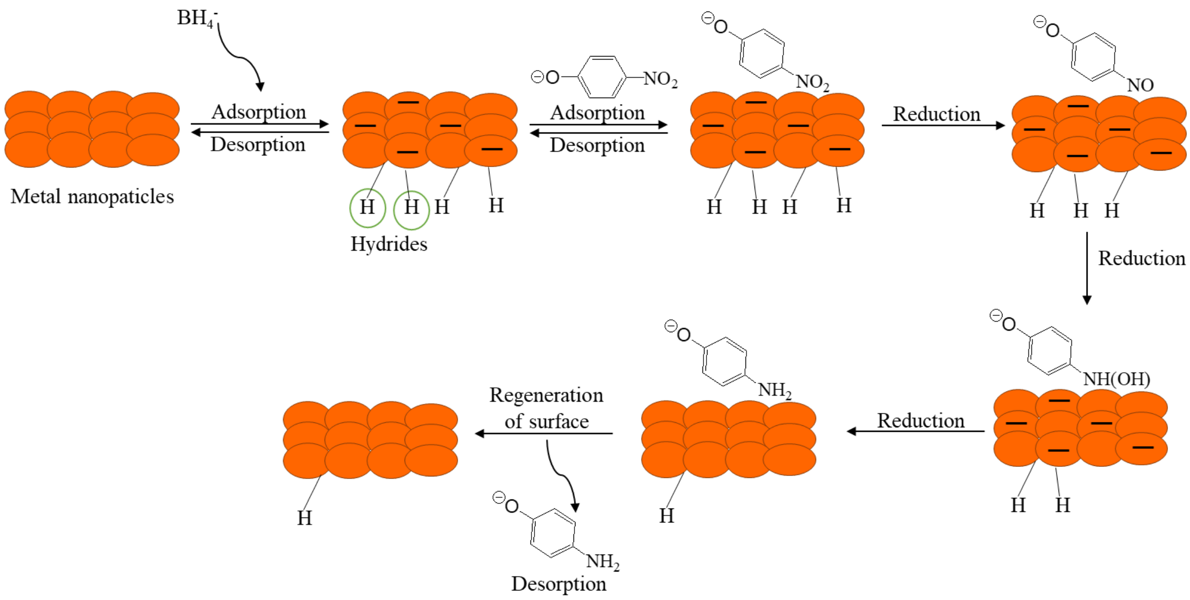

Figure 1.8. Mechanism of reduction of nitro to amino group

The common mechanism of reduction follows the Langmuir–Hinshelwood (L-H) adsorption model followed by catalytic reduction (De Oliveira et al., 2016). The catalytic reduction generally takes place using excess $NaBH_4$ because significant portion of the activated hydride on catalyst surface is being lost as gaseous molecular hydrogen. Initially the surface of the catalyst is activated by hydrides of $NaBH_4$ which are then transferred to nitro group. The nitro group receives electron and converts it to amino group. Then the product is desorbed from the metal nanoparticle surface and released into the aqueous medium (Imran et al., 2019).

1.5.2.1 Metal organic frameworks (MOFs)

Metal organic frameworks have emerged as a diverse class of crystalline materials with extremely high porosity (up to 90% free volume) and massive internal surface areas exceeding 6000 m^2/g (Reviews, 2012). These properties, combined with the extraordinary degree of variability in both the organic and inorganic components of their structures, make MOFs appealing for potential applications in clean energy, most notably as storage media for gases such as hydrogen and methane and as high-capacity adsorbents, membranes, thin film devices, catalysis and biomedical imaging to meet a variety of separation needs.

The combination of a MOF's two components, the metal ion or cluster and the organic linker, opens up an infinite number of possibilities (figure 1.9). By combining magnetic nanoparticles and MOFs to build up magnetic MOF composites have attracted various area of adsorption and separation (A. Ahmed & Mchugh, 2022). Due to their superparamagnetic properties, quick adsorption/separation and reusability, they have found extensive use in photo electrocatalysis, adsorption/separation, drug delivery, sensor detection and other processes. In recent years, magnetic MOFs (MMOFs) have been used in sample collection and pre-enrichment, solid-phase extraction and solid-phase microextraction due to their effectiveness as adsorbents (Gao et al., 2020). The sum of the physical properties of respective inorganic and organic components, as well as the possible synergistic interaction between the two, provide intriguing properties for MOFs.

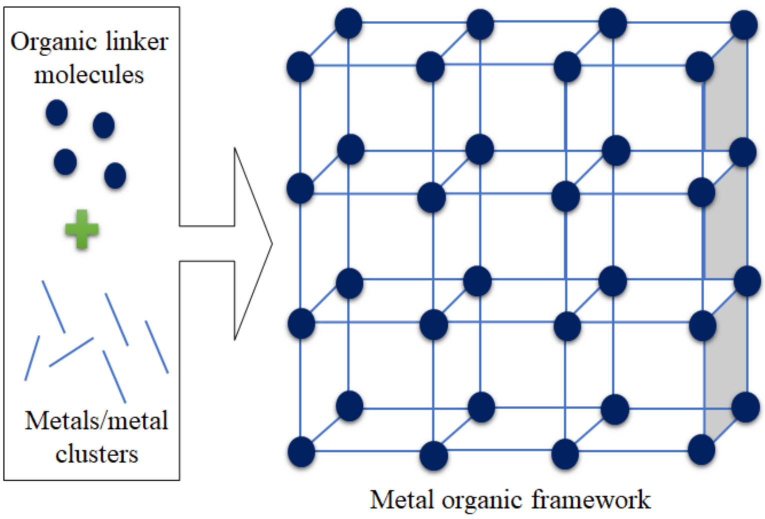

Figure 1.9 Structure of metal organic frame work

There are several examples available in literature where MOF is widely used as catalyst for the nitroarene reduction. F. Julian Martín-Jimeno et al. developed carbon supported Ni nanoparticles derived from metal organic framework for reduction of nitroarenes (Martín-Jimeno et al., 2021). Shuliang Yang et al. synthesized metal organic framework derived Co_3S_4/nitrogen-doped carbon hollow nanoboxes for chemoselective reduction of nitrophenol (Shuliang Yang et al., 2018). Sen Yang et al. prepared Cu-BTC@Fe_2O_3 metal organic framework for nitroarene reduction (Sen Yang et al., 2018).

1.6 Aim

The goal of this research is to synthesise novel materials from sources amenable for removal of toxic and mutagenic micropollutants by adsorption or by catalytic reduction by imbibing the green chemistry and sustainability principles to the best possible extent.

The main objectives thus are

- To produce biochar from agro waste with potential for adsorptive removal of pollutants such as fluoride and dyes.
- Synthesis of cholate-based gels and hydrotalcite with defluoridation potential.
- Microwave synthesis of silver nanoparticle based nanofluids and MMOFCs and evaluation of their reductive remediation potential of nitro derivatives.
- To synthesize Zirconium tungstate by sol-gel method and study its potential for methylene blue removal.

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