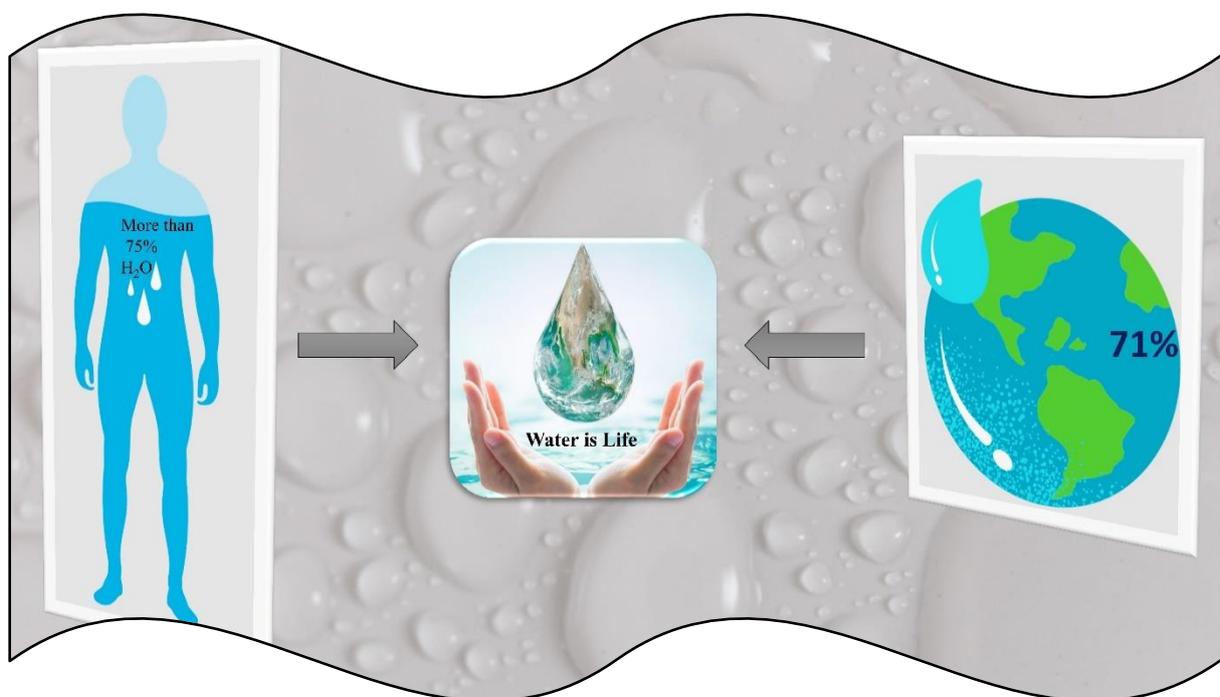


The present chapter focuses on the basic needs of water, water pollution and specifically, on the strategies to remove of organic and inorganic pollutants from water. Employing adsorbents for the removal of pollutants.

## 1.1. Water

Water is one of the most precious possessions that God has bestowed upon us; the life of many biotas on Earth depends on it. The existence of life requires water. The word “water” is the true equivalent of the word “life”. Water covers over 71% of the Earth's surface, giving many of the organisms in the ecosystem a place to live [1,2]. All living organism, especially humans, depend mainly on the water as a means of life and growth. Water is crucial for energy, food, drink, and agriculture. It represents more than 75% of the human body composition (**Figure 1.1**). It is the only substance that exists in all three of its natural physical states on Earth. Because of its versatility as a factory coolant and universal solvent, it has also been believed to have had the greatest impact on the evolution of any society. The availability of clean drinking water is paramount to maintain a healthier life [3]. But due to various anthropogenic activities, water is being polluted or destroyed. Any alteration to the chemical, biological, or physical qualities of water that could have an undesirable effect on any living organism is referred as water pollution.



**Figure 1.1.** Water – a natural resource.

## 1.2. Water Pollution

Water pollution is defined as the presence of exorbitant concentrations of a danger (pollutants) in water to the point where it is no longer appropriate for cooking, bathing, drinking, or other purposes [4]. Water pollution occurs when unsafe substances-often chemicals or microorganisms-contaminate a stream, river, lake, ocean, aquifer, or other body of water, degrading water quality and rendering it toxic to humans or the environment (**Figure 1.2**). We cannot disregard the critical necessity for clean water. Sadly, the unrestrained industrial invasion and population growth over the past few decades have put extreme strain on the water resources that are limited. Worse still, innumerable water pollutants are synchronously released into aquatic bodies. It causes the quality of the water to rapidly and drastically deteriorate [5].



**Figure 1.2.** Water pollution.

Conversely, one of the most pressing issues facing the modern world is water pollution. From various printed media and surveys reports, over one-sixth of the global population is suffering from drinkable water crisis. Moreover, the World Health Organization reports that 748 million people globally lack access to safe drinking water, 2.5 billion people lack access to sanitation, and 3,900 children die every day due to unhealthy drinking water and disease.

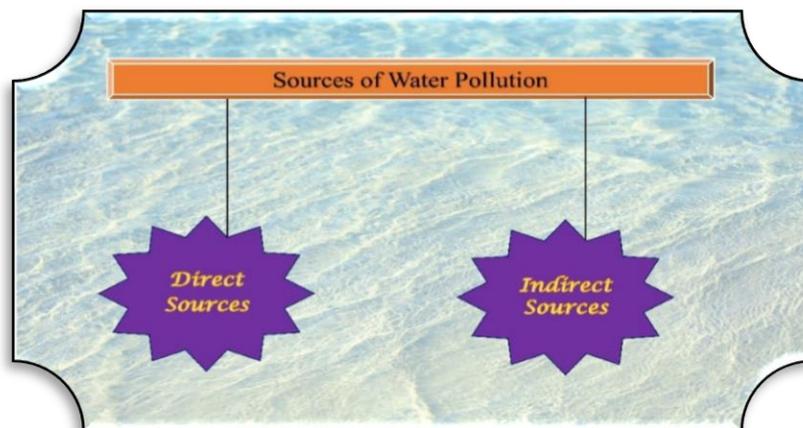
Based on a World Health Organization investigation, only 5% of the world's water supply is suitable for human consumption. It is estimated that, in comparison to the current levels, consumer demand for water would rise by 50% by 2050 [6]. First and foremost, it's critical to understand its characteristics, primary sources, and proven effects on both human health and the ecosystem. As a result, getting access to clean water is still seen as one of humanity's most fundamental aspirations and an ongoing worldwide concern in the 21<sup>st</sup> century. Good quality of water determines the healthy life of living beings on this earth [7].

### 1.3. Sources of Water Pollution

Water pollution can arise from distinct sources, both natural and human-induced. Several of the most prominent pollutants in water include,

- Industrial Effluents
- Domestic Waste
- Agriculture Run-off
- Urban Run-off
- Oil Spills
- Mining Activities
- Atmospheric Deposition
- Natural Sources

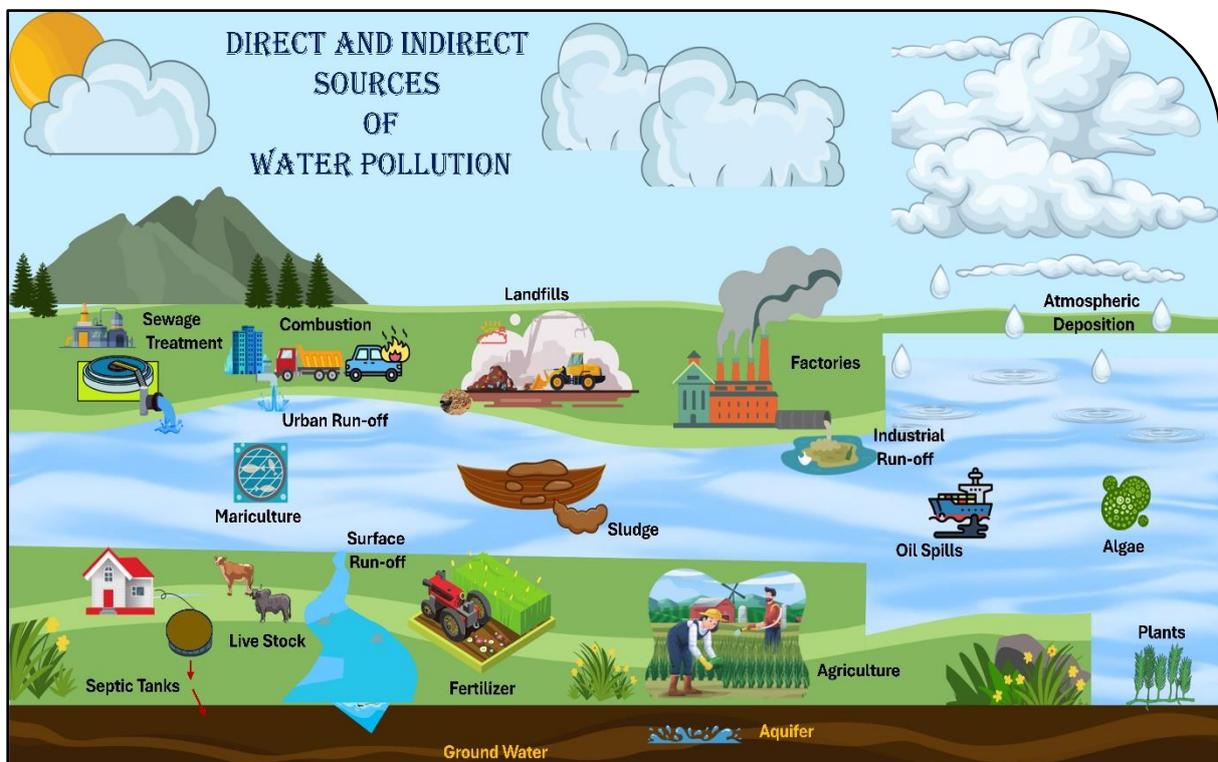
There are two main sorts of induces that lead to water pollution: direct and indirect sources (**Figure 1.3**).



**Figure 1.3.** Two sorts: Sources of water pollution.

Direct sources are organizations that discharge waste and hazardous byproducts into the nearest water supply without beforehand treating them, such as factories, waste management facilities, refineries, etc. This makes the water poisonous, every so often resulting in death, for fish and other aquatic creatures. Nevertheless, animals also consume this water, which also bring to them ill health or death. It can also affect to humans. In developed countries, people no longer depend on drinking water from the stream or river. There is still a risk for those who swim in or participate in activities such as canoeing on polluted water, as some of them can cause illness and even death.

Pollutants that enter water indirectly arise from indirect sources. Chemical pesticides and fertilizers, for instance, seep into the soil, enter groundwater, and eventually enter other streams. Rainwater is a crucial natural source of water pollution because it dissolves suspended particles and air pollutants and carries them down with it. For instance, the appearance of acid rain results from the dissolution of acidic gases such as oxides, sulphur, and nitrogen. Whether it's direct or indirect sources of water pollution (**Figure 1.4**), the results can still be the same, i.e. disease and possibly death to any living organism that inhabits in it or consumes in water.



**Figure 1.4.** Sources of water pollution.

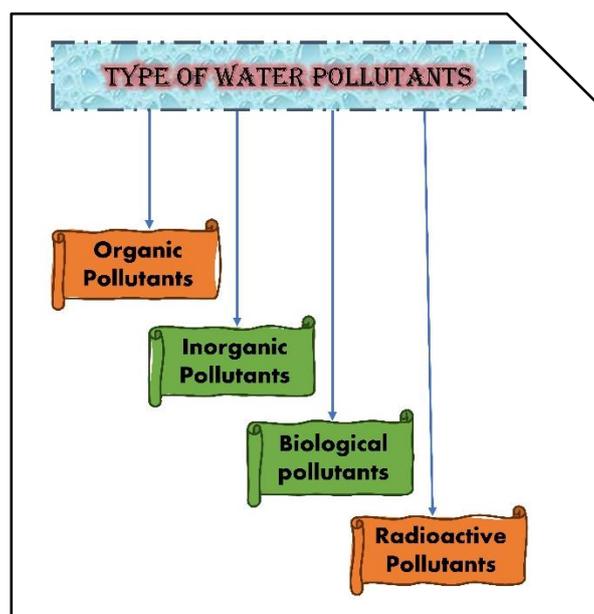
Therefore, it is essential that people and organizations take action to reduce their pollution levels and environmental impact. The most frequent sources of water pollution can vary from fully natural to man-made sources such as release of domestic and industrial waste water. However, the impact of natural sources on water pollution is generally overshadowed by human activities. Addressing water pollution requires concerted efforts from government agencies, industries, communities, and individuals to implement effective pollution prevention and control measures [8,9].

We will focus herein on the anthropogenic sources of pollution, that is, pollution arising from human activities.

## 1.4. Types of Water Pollutants

Water pollution arises when one or more additional components cause negatively alter in its colour, taste, or odour. Even while certain pollutants don't change the physical characteristics of water, they can nonetheless turn it poisonous. The different sorts of water pollutants can be characterized into the following categories as are depicted in (Figure. 1.5) [2]. Here in these focuses on the two categories, namely,

1. Inorganic water pollutants
2. Organic water pollutants



**Figure 1.5.** Types of Water Pollutants.

### 1.4.1. Inorganic Pollutants

Inorganic pollutants are chemically and biologically nonbiodegradable and persist in the water systems for longer periods of times. They include pigments, mineral acids, alkalis, cyanides, fluorides, and heavy metals [10,11]. They become pollutants when they build up in water. This could be the consequence of enhanced human mobility, mechanical errors, or draining from landfills. According to several research studies, inorganic pollutants are components that occur in nature but have been altered by people to multiply several times in water sources. Untreated waste effluents from anthropogenic activities such as waste mining especially electronic waste mining, refining, and metallurgical operations lead to the release of inorganic pollutants into waterways. Developing nations are concerned about pollution of harmful chemical such as heavy metals in drinking water. This sort of water pollution, particularly at higher concentrations, can cause serious health problems in humans and have terrible impact on aquatic life and other creatures [12].

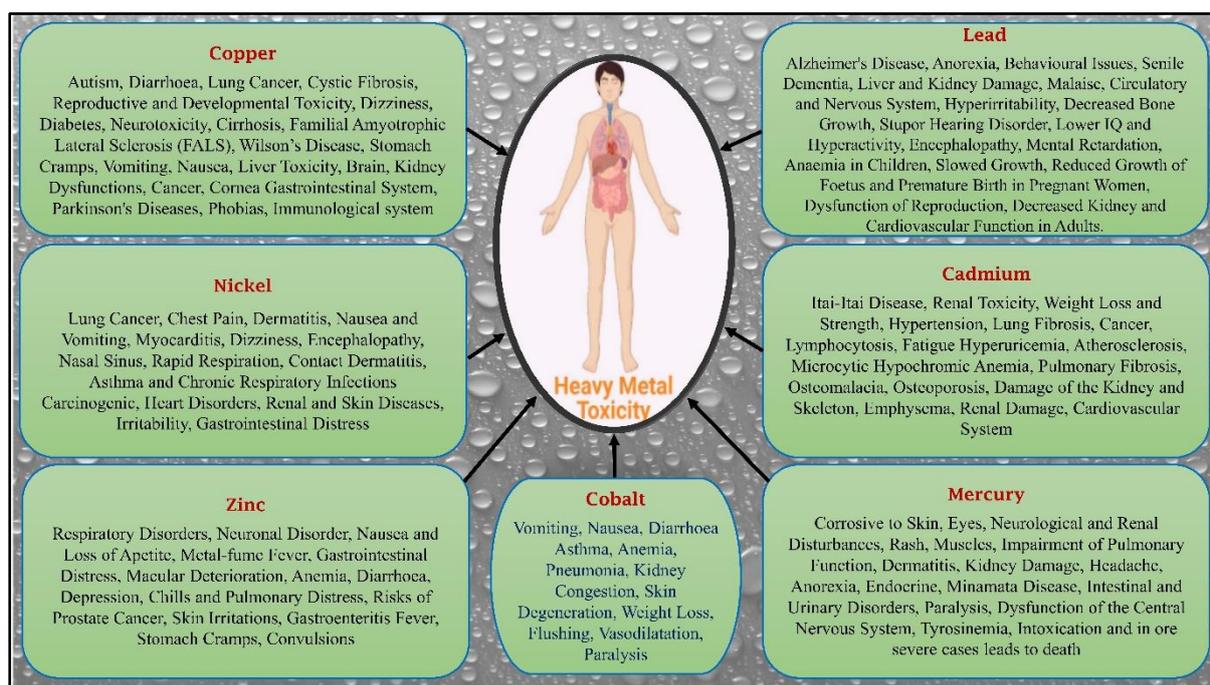
#### 1.4.1.1. Heavy metal ion sources and human impact

Excessive heavy metals ingestion of surface and groundwater has been identified as a major global risk to a variety of water resources and is referred to as an inorganic pollutant. The term "heavy metals" describes naturally occurring elements that are denser than water, have a high bulk density and atomic weight, and have a specific density of more than  $5 \text{ g/cm}^3$  [13,14]. They enter the environment through natural and anthropogenic sources. Natural water contains impurities of rare elements/heavy metals in solution. In addition, anthropogenic sources such as the large-scale use of pesticides, fertilizers in agriculture, paints, and ongoing rapid industrialization and municipal waste add these metal ions to surface and groundwater is continuously increasing and causing grave consequences. Heavy metal pollutants include ion species  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ . Heavy metals contamination in water is extremely hazardous and gained paramount attention in recent years. They are indispensable, relatively poisonous at very low concentrations and cannot biodegrade [15,16]. **Table 1.1** exhibits the several sources of different types of heavy metals [17–21]. Additionally, mediated by water, air, and food, they enter into a human body they cause serious health problems. Exposure to heavy metals has been linked to a number of illnesses, including cancer, autoimmune diseases, developmental retardation, renal damage, and in extreme circumstances, even death [22,23].

**Table 1.1. The main sources of common heavy metal ions in water.**

Metal ion	Sources
<b>Copper (Cu)</b>	Fertilizers, Electronics Plating Industries, Metal Plating, Paint-Pigments Manufacturing, Photovoltaic cells, Tanning and mining processes, Copper polishing, Wood Preservatives, Corroded Plumbing Systems, Smelting, Cu-based Agri-chemicals, Welding Processes, Sewage Treatment Plants, Alloys, Cables.
<b>Zinc (Zn)</b>	Cosmetics, Mining, Pigments, Manufacturing Processes, Soldering, Cosmetics, Rubber Industry, Zn Alloys, PVC Stabilizers, Cyanide Solution-Based Gold Precipitation in Chemicals and Pharmaceuticals, Anti-corrosion Coating, Cans, Batteries, Galvanizing.
<b>Cobalt (Co)</b>	Electroplating, Alloys, Metallurgical, Petrochemical, Coal Industries, Mining, Paint Industries.
<b>Nickel (Ni)</b>	Discharges of Silver Refineries, Printing, Mining Processing, Smelting Operations, Domestic Wastewaters, Landfill Leachate, Stainless Steel, Molds for Catalysts and Glass, Electroplating Batteries using Nickel-Cadmium, Prosthetics for Surgery and Dentistry, Arc-Welding, Rods and Pigments.
<b>Mercury (Hg)</b>	Weathering of Mercuriferous Areas, Volcanic Emissions, Ignition of Coal, Metallurgical, Incineration, Solid waste, Combustion of Coal, Municipal Solid Waste Incineration and Volcanic Emissions, Gold Mining, Cement Production, Chloro-Alkali Industry, Pharmaceuticals, Vapor Lamp for Hg, X-Ray Tubes, Erosion of Natural Deposits, Emissions from Refineries and Factories, Landfill Runoff and Croplands.
<b>Cadmium (Cd)</b>	Photovoltaic Cells, Municipal Waste Incineration, Paint Sludge, Pigments, Batteries made up of Cadmium and Nickel, Plastic Stabilizers, Electroplated Parts, Synthetic Rubber, Engraving Process, Photoconductors, Metal Processing, Mining, Smelting, Phosphate Fertilizers, Coal Combustion, Alloying Industries, Steel Industry, Corroded Galvanized Pipes.
<b>Lead (Pb)</b>	Electroplating, Pigments and Paints Sectors, Sanitation PVC Pipes and Reused of PVC, Jewellery, Manufacturing of Lead Batteries, Lunchboxes, Agriculture, Mining Activities, Metal Processing, Tanneries, Textile Production, Fertilizers, Pesticides, Agriculture, Oil-Refining Industries and Motor Vehicles that Use Petrol, Thermal power plants supplied by coal, Ceramics, Solder, Rust Inhibitors.

As per the World Health Organization (WHO), consuming polluted water is the main trigger of 80% of diseases that affect people globally. Some of the health risks connected with heavy metal toxicity [are summarized in **Figure 1.6**] [22–25]. Many legislations and regulations have been imposed across the world for management and control of heavy metal pollution in water. So, it is necessary for eliminating heavy metal ions from the waste water. Additionally, it can facilitate the development of effective strategies and policies to manage and mitigate the adverse effects of heavy metal pollution on aquatic ecosystems and public health.



**Figure 1.6.** Toxicological effects of various heavy metals.

#### 1.4.2. Organic Pollutants

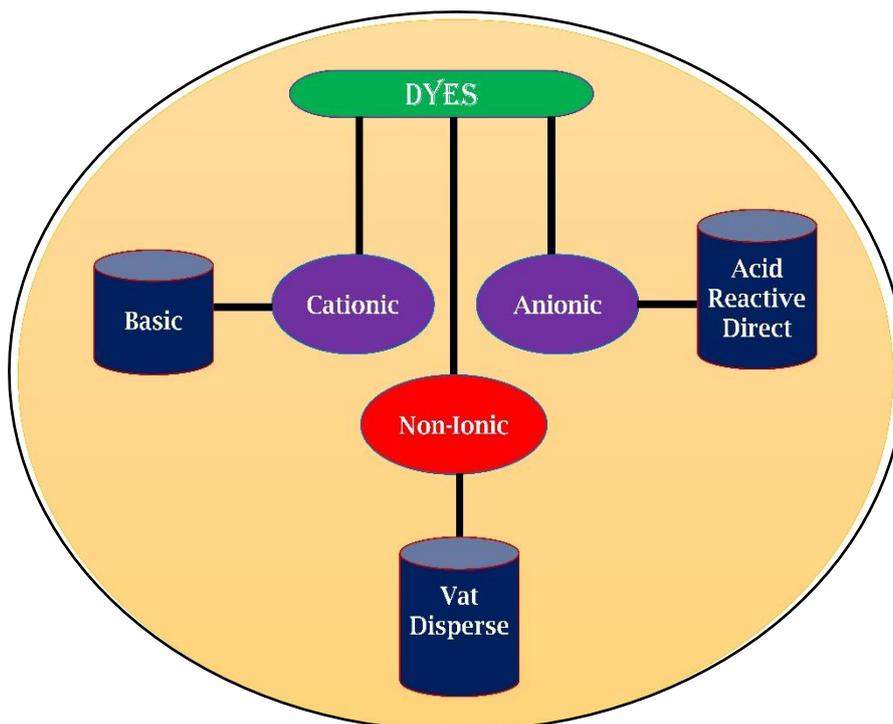
The elements of carbon, hydrogen, oxygen, nitrogen, and sulfur constitute organic molecules. Organic pollutants emitted via sewage, urban waste water, industrial effluent and agricultural waste, canning enterprises, food processing premises, slaughterhouses, paper and pulp mills, tanneries. The entire consumption of oxygen in the water body through these pollutants creates anaerobic conditions in the ecosystem. However, artificial beings organic pollutants do not biodegrade and linger in the water for a very long period. Among the artificial organic pollutants includes synthetic pesticides, detergents, food additives, medications, insecticides, dyes, synthetic textiles, plastics, solvents, and volatile organic compounds [26].

## 1.4.2.1. Dyes sources and toxicology effect

Dyes are one of the most widely used intensely coloured organic materials in our industry and life. It's predominantly derived from two significant sources, including natural and anthropogenic. Natural sources comprise of plants, insects, animals, and minerals; on the other hand, synthetic dyes are created by humans utilizing a variety of chemical compounds [27]. Synthetic dye is one of those effluents that has increased consumption amounts in the industrial procedures, because of its vast applications as in paint, cosmetics, textile, paper, printing, leather, plastics, electroplating, fur, hair, wool, waxes, greases and pharmaceuticals [28,29]. The world uses over 7 million tons of synthetic colours annually. Textile industries are one of the biggest nationally recognised sources of organic pollutant. Every year, the textile industries release 10-15% of their manufactured dyes into the environment. However, water pollution problems are also on the grow. The untreated effluents of these industries are continuously polluting the water. Dyes are lately considered to be one of the essential and alarming sources of organic pollution of water and are a reason for great concern [30].

The molecular structures of commercial dyes are typically complicated, vast, and frequently unreported mixtures with a wide range of chemical compositions and attributes. Commercial dyes can be classified in several kinds of approaches. Every dye class has an extremely distinct chemistry, structure, and bonding mechanism. The primary class of dyes utilized in industrial applications are azo dye derivatives.

Generally, dyes are categorized as cationic (which includes all basic dyes), anionic (which includes direct, acid, and reactive dyes), or non-ionic (which includes vat and dispersed dyes) depending on the particle charge they exhibit when dissolved in an aqueous application media. The colour index is an organized technique for classifying dyes based on their molecular constitution. The charge-based dye categorization is displayed in **Figure 1.7**. The severely toxic and dangerous industrial effluents that are carcinogenic to both human health and the environment are also taken into account in this classification [31,32].



**Figure 1.7.** Classification of dyes according to ionic charges.

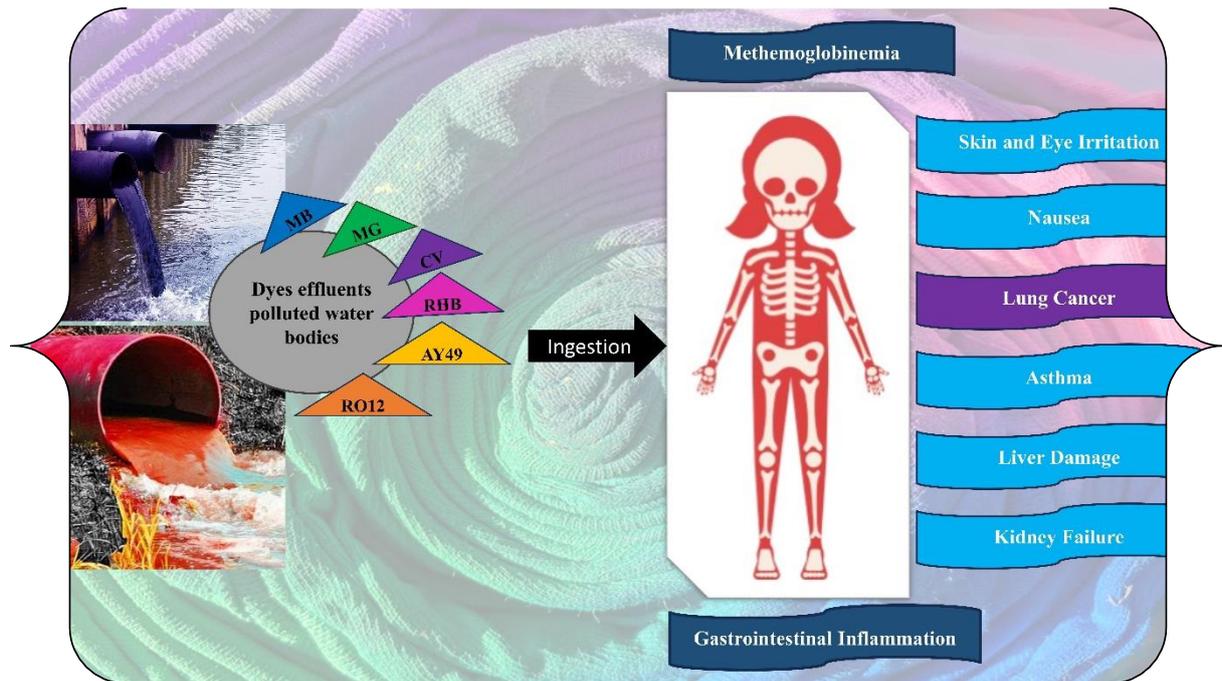
The majority of the time, cationic dyes are used to colour silk, wool, acrylic, and nylon. Their chemical structures differ based on the replaced aromatic groups within them [33]. The positive ion is primarily necessary for these dyes. Their aqueous solution contains coloured cations due to their water solubility and positive charge. Catalytic dyes are often visible and exhibit high colour intensity and brilliance [34,35]. Considered hazardous colouring agents, these cationic dyes have the potential to cause severe health risks, including dermatitis, cancer, genetic disorders, and skin irritation [36].

The negative ion is primarily necessary for anionic dyes. These azo dyes are of various varieties, each exhibiting unique structural differences, yet they all share characteristics like ionic groups and water solubility. Strong covalent bonds are created between the reactive groups of the reactive dyes and the wool and cotton through interaction. Since reactive dyes have a low degree of fixation owing to the hydrolysis of reactive groups in water, it is not advised to release them into the ecosystem [37]. Wool, silk, acrylic, polypropylene, and polyamide fibers are used to apply the acid dyes. They are well soluble in water. Furthermore, the organic sulphonic acids present in these are hazardous to humans [38,39]. The release of the acidic, reactive, direct, vat, and disperse dyes can cause damage to organisms like allergic reactions, carcinogenic effects, rhinitis, allergic conjunctivitis and occupational asthma [40].

Aquatic toxicity is exacerbated by highly dispersible aesthetic pollutants called dyes. Sunlight, which is essential for photosynthesis, is obstructed by the soluble dyes in the wastewater, which appear in the stream as their colour. Dyes are not intended to degrade when exposed to light, chemicals, biochemicals, or other exposures; rather, they are incredibly stable molecules by design. The increasingly used cationic (basic) dyes including Methylene blue (MB), Rhodamine B (RHB), Malachite green (MG), Crystal violet (CV), and anionic dyes including Acid yellow 49 (AY 49) and Reactive orange 12 (RO 12) dyes are the most important sources of industrial pollutants emanating from different industries are representing in **Table 1.2** and some toxicological effects on human beings are shown in **Figure 1.8** [41–45]. Waste water from dyes is regarded as a chemical that can lead to cancer and mutations. About 10% (up to 15%) of the dyes are released into aquatic spaces unrestricted during the dyeing process. Thus, it becomes imperative to create a colour removal method that is both affordable and widely recognized [46]. Consequently, research in this area is ongoing.

**Table 1.2. Sources of different types of dyes.**

Dyes	Sources
<b>Methylene Blue</b>	Dyeing Cotton, Wood and Silk, Pharmaceutical, tannery
<b>Malachite Green</b>	Paper Formulation, Ceramics Production, Leather, Textile Industry, Food Colouring and Cell Staining
<b>Crystal Violet</b>	Veterinary Medicine Textiles, Pens and Printers
<b>Rhodamine B</b>	Leather/textile Processing Plants
<b>Acid Yellow 49</b>	Wool, Silk and Polyamide Fiber or Wool Blended Fabrics, Textile, Printing and Dyeing, Paper, Leather Colouring, Pharmaceutical
<b>Reactive Orange 12</b>	Textile, Pharmaceutical, Leather, Food, Printing and Paper Industries



**Figure 1.8.** Impact of toxic dye effluents on the human body

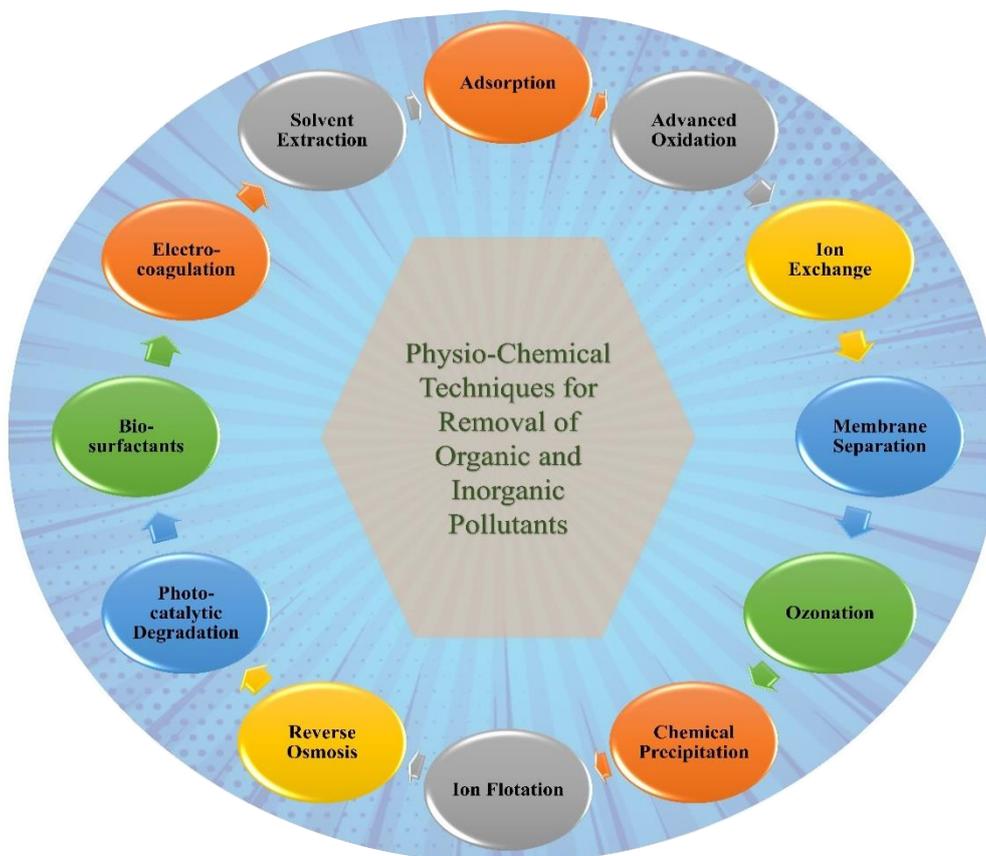
Therefore, it is essential that an efficient technique be developed to eliminate these colours from wastewater in order to safeguard the environment and future generations. Literature addresses the topic of colour, the quest for solutions, and the status of new as well as outdated technologies [47,48]. Studying these aspects has led to an ongoing discussion about the development of water monitoring technologies. Following technologies illustrates the various approaches to remove both organic and inorganic pollutants -

### 1.5. Strategies to remove of organic and inorganic pollutants

Controlling water pollution due to the existence of heavy metals and dyes is a problem that is going to endure for years to come. Consequently, it is crucial to concentrate on water treatment in order to design a practical and economical approach that permits resource recovery. Numerous techniques, including chemical, physical and biological processes like the physio-chemical process, have been developed and put into practice in recent decades to remove organic and inorganic pollutants from wastewater. The goal is to increase the possibilities of water resources and lessen problems and concerns associated with water pollution [49].

### 1.5.1. Physio-chemical process

The expression "physio-chemical treatment" describes a group of procedures that use chemical compounds and reactions to purify water. Chemical injection is one of the primary techniques for treating wastewater, since it allows for the removal of colorants and heavy metal ions. Literature reported the application of various treatment techniques in eliminating organic and inorganic pollutants from wastewater, such as adsorption [50,51], advanced oxidation [52,53], ion exchange [54,55], membrane separation [56], ozonation [57], chemical precipitation [58], ion flotation [59], reverse osmosis [60], photo-catalytic degradation [61], bio-surfactants [62], electro-coagulation [63], solvent extraction [64]. **Figure. 1.9** illustrates the current techniques, such as physio-chemical procedures, for the elimination of heavy metal ions and dyes. Given the foregoing, treating water polluted with metal ions and dyes prior to discharge is crucial. Due to their high cost, poor efficiency, sludge disposal, and limited applicability to a variety of contaminants, the majority of these technologies are not widely employed [65].

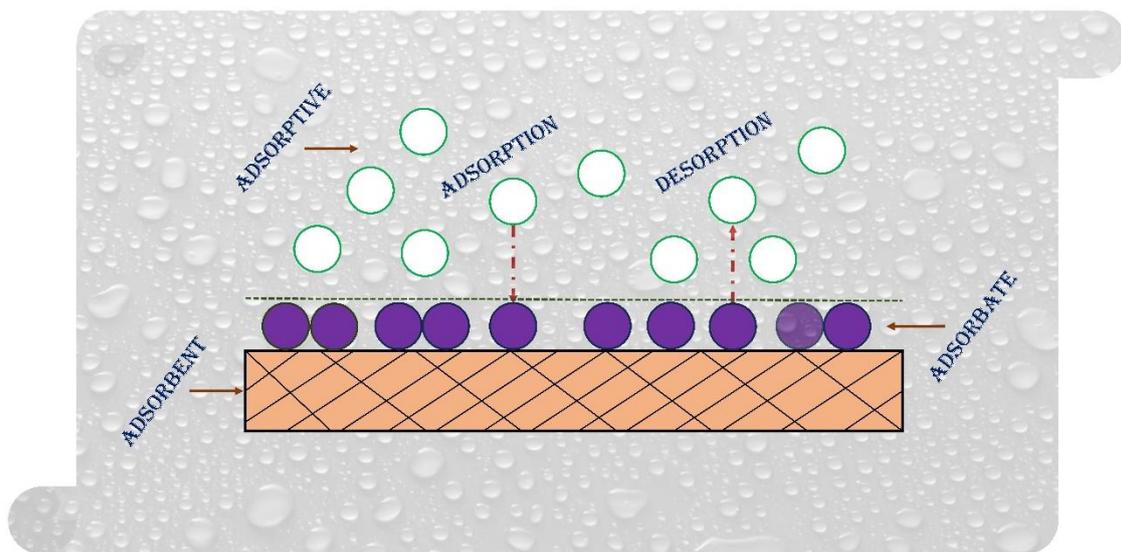


**Figure 1.9.** Physico-chemical strategies for removal of heavy metal ions and dyes.

Nevertheless, the ion exchange and adsorption techniques, which will be addressed below these two approaches, are currently the most efficient since of their quick kinetics and high removal efficiency of harmful substances [66].

### 1.5.1.1. Adsorption process

Adsorption, a surface phenomenon, is the technique used in laboratories and industries to separate mixtures; it is characterized by an increase in a specific component's concentration at the interface between two phases. It is universally acknowledged as a successful technique for eliminating both inorganic and organic pollutants from their matrices [67,68]. Adsorption is essentially a mass transfer process wherein compounds from a liquid phase, known as adsorbates, are specific moved to the surface of a solid phase, known as adsorbents. The type of forces that exist between the adsorbent and the adsorbate determines the precise form of adsorption [69]. The process of concentrating a material from its liquid or gaseous environment over a solid surface is known as "adsorption," as **Figure. 1.10** illustrates.



**Figure 1.10.** Adsorption process.

This method has the following three stages [70];

- I. Pollutant diffusion from solution to the adsorbent surface
- II. The contaminant's adsorption on the adsorbent surface
- III. Diffusion within the structure of the adsorbent

An essential explanation of adsorption on porous carbon for medical uses was provided by Hippocrates and Pliny the Elder, and it dates back to an Egyptian papyrus from 1550 B.C. However, Scheele (1773) provided an explanation of the adsorption phenomenon for gases exposed to carbon in scientific records. Lowitz carried on the process in 1785, using wood charcoal to remove colour and smelly substances from water in a reversible manner. Similar behavior was noted by Larvitz (1792) and Kehl (1793) with regard to vegetable and animal charcoals, respectively. Nonetheless, Kayser coined the term "adsorption" for the first time in 1881 to distinguish between intermolecular penetration and surface accumulation [71–73]. Physical and chemical adsorption are the two broad categories into which adsorption goes. Pollutants are deposited on the adsorbent surface during physical adsorption, or physisorption, due to physical factors such as Van der Waals forces, hydrogen bonding, polarity, dipole-dipole interaction, and  $\pi - \pi$  interaction, among others. Adsorption of this kind is a reversible process. Conversely, chemical adsorption, also known as chemisorption, produces a strong interaction between the adsorbate and the adsorbent that might cause the adsorbate molecules to adhere to a particular functional group on the adsorbent surface as a result of an electron exchange. The adsorbed species are particularly difficult to remove from the solid surface due to the strong connection that forms during the chemisorption process between the adsorbent and adsorbate. Permeable structure is generally desirable in an adsorbent [65,74].

An assortment of phenomena, including chemical complex formation at the adsorbent's surface, electrical attraction, and the exclusion of the adsorbate from the bulk solution as a result of hydrogen bonding between the molecules of adsorbate and adsorbent, can all contribute to the mechanism of adsorption. The nature of the adsorbent (synthetic or biomass derived); the presence of basic or acidic functional groups on the adsorbent surface; and the doping of the metal ions/dyes of specific functionality on the adsorbent surface can all affect the roles that physisorption, chemisorption, and electrostatic attraction play in the removal of toxic metals and dyes [75,76].

Furthermore, he investigated the advantages that the adsorption process has, which lead to its widespread application in a variety of industries, natural materials, and agricultural waste. Among the major advantages are [77]:

- ❖ Simple installation and maintenance
- ❖ Low operating cost
- ❖ High efficiency and ease of use
- ❖ Flexibility in design and operation
- ❖ Insensitivity to toxic pollutants
- ❖ High adsorption capacity due to large surface area
- ❖ Reversibility
- ❖ Robustness

Due to its efficiency in eliminating impurities, separating components, and promoting chemical reactions, the adsorption process has a wide range of applications in a variance of sectors. Adsorption has substantial applications in the following areas [77]:

- ❖ Water Purification and Treatment
- ❖ Air Purification
- ❖ Gas Separation and Purification
- ❖ Chemical and Petrochemical Industries
- ❖ Pharmaceutical and Biomedical Applications
- ❖ Environmental Remediation

Overall, the benefits of adsorption processes make them an attractive choice for a wide array of applications where efficient contaminant removal, selective separation, and cost-effective treatment solutions are required. Since adsorption occurs on surfaces, a high surface to volume ratio is necessary for the perfect adsorbent. This can be achieved by decreasing the adsorbent particle size and by creating a network of pores within the adsorbent particles. In order to remove pollutants from wastewater in an economically viable manner, a number of low-cost adsorbents have been explored below.

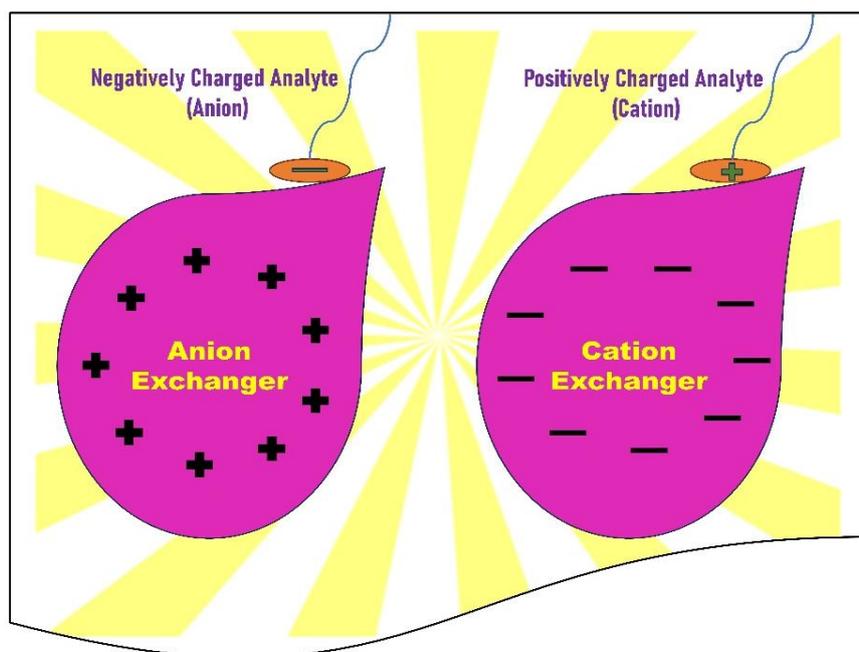
## 1.5.1.2. Ion-Exchange process

The history of the ion-exchange process is intriguing; it is a centuries-old method that has been recorded in literature for over a century now. References to the explanation of ion exchange processes can be found in some of the earliest writings. The Holy Bible contains the first mention of the concept, stating that "Moses" was able to successfully employ ion exchange to turn brackish water into potable water [78]. Aristotle [79] proposed filtering water through specific kinds of soil. The first ion exchange was found in soil over a century ago by agricultural chemists Thompson, Roy and Way from England [80,81]. Without a scientific awareness of the phenomenon, humans in the past improved the quality of drinking water via plants, sands, soils, and natural zeolites. The first synthetic zeolites were developed in 1903 by Harms and Rumpel to extract potassium from sugar juices [82,83]. Afterwards, in 1917, Follin and Bell suggested a synthetic zeolite for urine collection and ammonia separation that could be sold commercially [84]. Gans pioneered the industrial application of ion exchangers early [85]. Several scholarly articles have been written regarding the application of inorganic ion-exchange materials that are natural, processed, and developed. Still, the synthesis of the first organic ion exchangers, known as ion-exchange resins, by Adams and Holmes (England Chemists) in 1935 marked a significant advancement in the field [86]. Subsequently, ion exchange has been significantly investigated in a number of disciplines, including engineering, organic chemistry, analytical chemistry, and agriculture. By counting the number of articles on ion exchangers utilized in chemistry, engineering, and environmental science, Alexandratos et al. [87] assessed improvements in ion-exchange research. Subsequently, a variety of sectors and technological processes have adopted this water softening process.

In recent years, ion exchange strategy has been used more often to remove lethal organic and inorganic pollutants from wastewater [88,89]. The reversible exchange of ions with the same polarity is the core of the ion-exchange technique, a crucial analytical technique. It is stoichiometric chemical reaction that preserves overall electroneutrality by exchanging an ion from a solution, electrolyte, or molten salt for an ion with a similar charge that is bonded to an immobile, insoluble solid. Insoluble compounds having charged functional groups on their surface, known as "counter ions," are linked to the solid material, also known as resin/ion exchangers [80,90].

When these ions arrive into connection with one another, they can exchange for ions that have the same sign in solution. Since these counterions are used in ion-exchange processes, one of an ion exchanger's most crucial features is its counterion content [91,92]. The basis of the separation is the electrostatic interaction between polar and ionic analytes that transport different species in separate directions while having an equivalent number of ions with the same charge. According to fixed groups, it can be split into two categories of ion exchangers (**Figure 1.11**) [92]:

- A. Cation Exchanger: It has groups that are negatively charged, and these will draw groups that are positively charged.
- B. Anion Exchanger: It has positively charged groups, which will draw molecules with negatively charged.



**Figure 1.11.** Type of Ion Exchangers.

During the process, the ion exchanger's structure is not changed. Sometime during the exchange process, the ion exchange equilibrium is attained. An instance of an ion exchange that frequently occurs during water softening is as follows:



where R stands for the structural unit of the ion exchanger. The exchanger transforms from its  $\text{Na}^+$  form to its  $\text{Ca}^{2+}$  form in this case. The exchanger can be completely converted to the  $\text{Ca}^{2+}$  form by treating it with a sufficiently excess solution of a  $\text{Ca}^{2+}$  salt.

The ion exchange mechanism is reversible with relatively few exceptions. An exhausted cation exchanger in water softening can be replenished by adding a sodium salt solution, such  $\text{NaCl}$ , after all of its  $\text{Na}^+$  ions have been lost. Regeneration reverses the process, returning the ion exchanger to its  $\text{Na}^+$  state. These days, many industrial processes and chemical labs use ion exchange as an ordinary technique.

Compared to other physico-chemical processes, this one has several of advantages, including,

- ❖ Excellent efficacy in eliminating pollutants that are harmful
- ❖ Less sludge volume
- ❖ Very effective for recovery of metals
- ❖ High selectivity
- ❖ Rapid results
- ❖ Specific structure of resin during the whole process
- ❖ Possibility to regenerate resin that's used
- ❖ pH Tolerance
- ❖ Scalability

All things considered, the ion exchange process has multiple benefits, such as selectivity, efficiency, sustainability, and versatility, which makes it is the preferred technique for many industrial applications involving purification and separation, such as waste water treatment, pharmaceutical technology, metal purification, food and beverage production, the nuclear and chemical industries, and agriculture. The restoration of risky heavy metal ions and dyes from industrial wastes, sewage, tannery effluents, and other sources, as well as the creation of purifying solutions, can be accomplished with this effective, adaptable, and environmentally friendly extraction method [93].

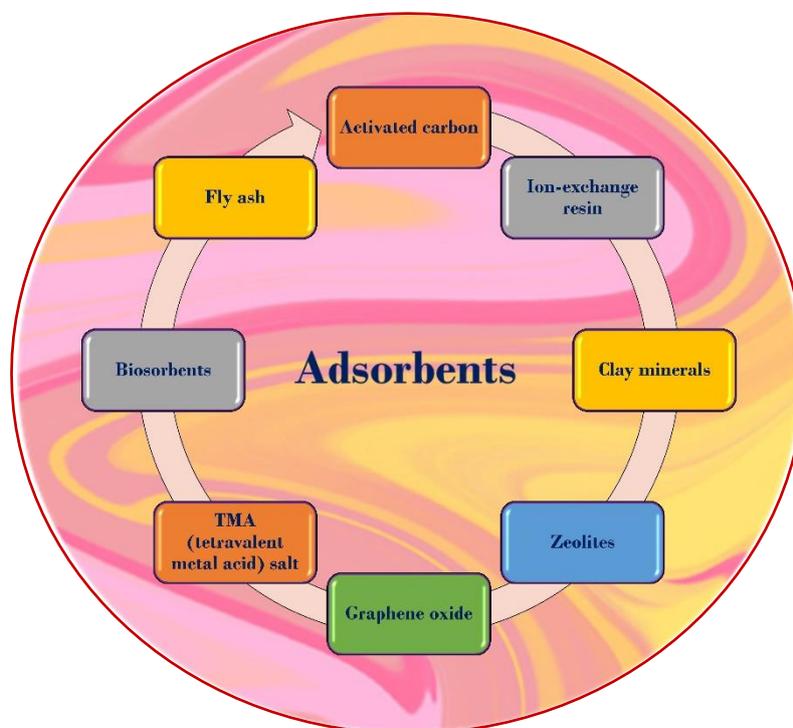
## 1.6. Theoretical aspects on sorption

Adsorption and ion exchange can be combined under the term "sorption" for a single treatment because they have so many traits in common when it comes to use in batch and fixed-bed processes. However, because of their rapid kinetics and high removal effectiveness, sorption techniques are currently quite successful. These techniques are classified as sorption processes because specific adsorptive materials are packed in a column or suspended in a vessel and are specifically transferred from the phase of fluidity to the surface of insoluble, stiff particles [94]. Molecules to concentrate on sorbent's surface through a physio-chemical process called sorption. Two phases make up the separation process of sorption, wherein certain components may become differently distributed. It occurs into one of three categories: electrostatic, chemical, or physical sorption. Adsorption isotherms, notably Langmuir and Freundlich, are utilized to elucidate the connection between the equilibrium concentration of the adsorbate in the solution and the quantity of adsorbate existing. Kinetic models can be employed to illustrate the adsorption rate and the transport mechanism, such as pseudo-first and second order, pseudo-second-order and intraparticle diffusion. Temperature, pH, along with the sort of adsorbent all have an impact regarding the adsorption of metal ions and dyes. These approaches are the primary and most economical ways to remove dyes and metal ions [93,95–98].

## 1.7. Adsorbents for removing of organic and inorganic pollutants

Adsorbents of numerous kinds have been employed recently by researchers to remove dyes and metal ions from aqueous media. Plenty of investigations have been conducted on the utilization of several low-cost adsorbents, including activated carbon [99], synthetic materials like ion-exchange resins [100,101], clay minerals [102], zeolites [103], graphene oxide [104], TMA (tetravalent metal acid) salt (metal phosphonate) [105,106], biosorbents [107], fly ash [108] as demonstrated in **Figure 1.12**. Despite the fact that most sorbents have the capacity to achieve relatively high removal efficiencies, one of the main obstacles to their expanded implementation is the expense of their use. In order to remove both organic and inorganic impurities from water with the goal of employing them in technologies down the road, the development of specialized solid-phase sorbents has become a challenging endeavour. Discovering affordable and more efficient adsorbents, including Ion-exchange resin and TMA (tetravalent metal acid) salt (metal phosphonate), has become progressively

more widespread over time. Research on ion exchangers that can provide improved composite qualities in terms of chemical, mechanical, and thermal stabilities as well as superior selectivity for metal ions and dyes has been encouraged by the restricted capabilities of both exchangers [109,110].

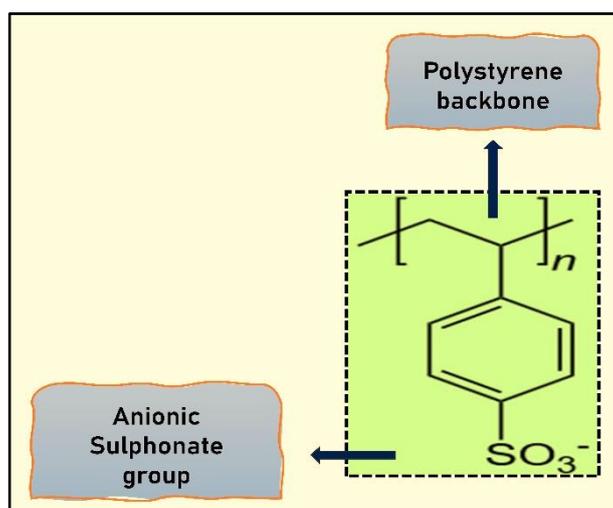


**Figure 1.12.** Adsorbents to remove heavy metals and dyes.

### 1.7.1. Ion exchange resin as sorbent

The first organic ion exchangers, known as ion-exchange resins, were created in 1935 by Adams and Holmes, marking a significant advancement in the field [86]. Among the many varieties of ion exchangers, synthetic ion exchangers, also known as ion exchange resins are extremely useful. Resins are amorphous particles of organic components which are composed of polystyrene and divinyl benzene. Polystyrene contains sites for exchangeable functional groups. Divinyl benzene acts as a cross-linking agent and offers adequate strength i.e., mechanical stability. Ion exchange resins are employed in the process of separating tiny molecules. They may selectively exchange ions from their backbone to the ionic form in solution because of their special structure. Nowadays, synthetic resin is regarded to be the most viable adsorbent material because to its chemical stability and surface chemistry controllability [111].

Ion exchange resins are an insoluble polymeric matrix that usually takes the shape of tiny, crosslinked organic polymers with a radius of 0.25-1.43 mm. These microbeads are typically white or yellowish and help to enhance ion exchange reactions. The beads are usually porous, stable both chemically and physically, and have a wide surface area on which ions can be trapped and other ions can be released. An array of ion-exchange resin types exists. Usually, they are made of polystyrene and other crosslinked polymers, including polyacrylate. The majority of commercial resins are derived from polystyrene sulfonate [112], as illustrated in **Figure 1.13**.



**Figure 1.13.** Structure of polystyrene sulfonate.

There are five specific events that are predicted to make up the actual ion exchange mechanism [113]:

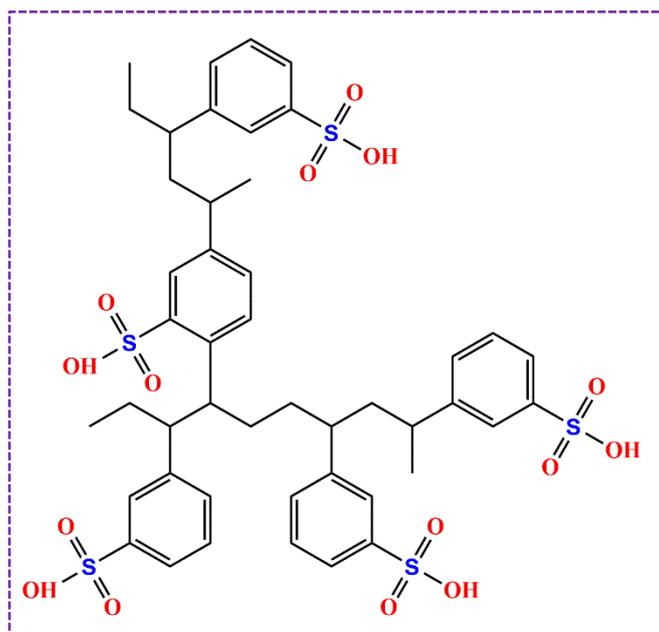
1. The ion's diffusion onto the exchanger surface. This happens in homogeneous solutions quite quickly.
2. Ion diffusion to the exchanger site via the matrix. This depends on the solution's concentration as well as the exchanger's extent of cross-linking.
3. At the exchange point, ions are exchanged. This arises instantly during an equilibrium process:



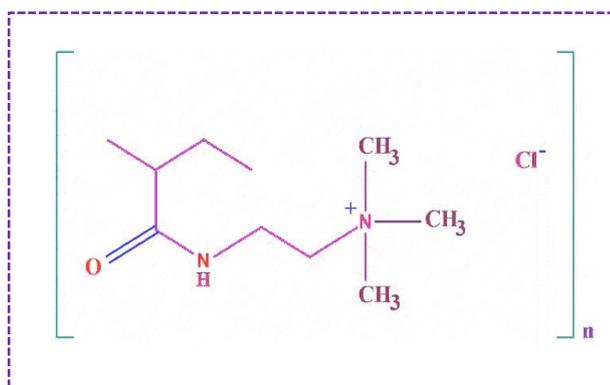
4. Diffusion of the exchanged ion to the surface through the exchanger.
5. Selective desorption by the eluent and diffusion of the molecule into the external solution occurs.

We can classify the ion exchange resins as follows based on their functionalities [114];

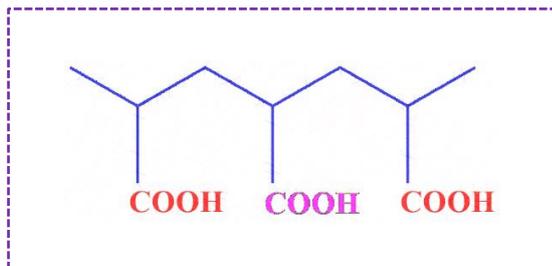
- A.** Strong acidic cation exchange resins (SAC), containing groups of sulfonic acid, which are utilized for demineralization and softening processes. (Amberlite IR 120, Dowex HCR, Lewatit S 1500).



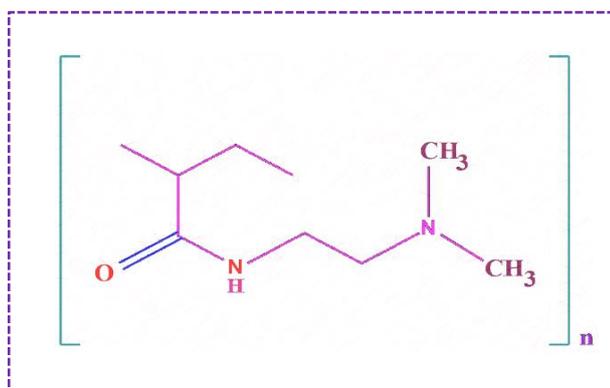
- B.** Strong basic anion exchange resins (SBA), featuring quaternary ammonium groups, are deployed for demineralization, dealkalization, and removal of total organic carbon (TOC). (Quaternary Amine (Amberlite IRA 458)).



- C.** Weak acidic cation exchange resins (WAC), having carboxylic acid groups, are less frequently used but can be selective in certain applications. (Amberlite IRC 86, Lewatit CNP).



**D.** Weak basic anion exchange resins (WBA) comprising amine functional groups, are used for adsorbing free mineral acidity ( $\text{Cl}$  and  $\text{SO}_4$ ). (Tertiary Amine (Amberlite IRA 67)).



**E.** Chelating resin

A wide range of pollutants, such as natural organic matter (NOM), heavy metal ions, anions, boron, surfactants, medications, and colours, are widely removed using ion exchange resins. One prominent technique to remove heavy metals from wastewater is sorption through ion exchange resin. Over the past few decades, ion exchange resins have emerged as a significant wastewater treatment strategy. A great deal of research has been done on the implications of complex formation on the distribution of metal ions between the liquid and resin phases, as well as on the ion exchange sorption equilibrium [115].

A sort of polymer-based material known as chelating resins has particular functional groups (iminodiacetic acid (IDA), ethylene diamine tetra acetic acid (EDTA) or amino phosphonic acid (APA)) that can converse with metal ions to create coordination complexes [116-118]. These resins exhibit higher adsorption capacities, efficiencies, and high selectivity to certain metal ions, making them useful in a variety of industrial processes, especially in purification and separation applications where metal ions need to be removed from solutions. They are also easily handled and reusable. It involves binding functional groups to the polymer backbone, such as carboxylic acids, amines, or imines. Owing to the lone pair

electrons in these functional groups, metal ions can form coordinate bonds with them. As a result, the metal ion and resin combine to form a stable complex. Depending on the type and sequence of functional groups that are present on the resin, these resins can be configured to bind particular metal ions only. This selectivity is essential in applications where it's necessary to remove or separate metal ions intentionally. Regenerating the chelating resin involves washing it with a regenerate solution, which removes the bonded metal ions from the resin, once it has been saturated with metal ions. Because of this, the resin is more affordable and could be employed repeatedly [119,120].

Diverse polymeric materials have been explored for the sorption and recovery of metal ions in recent years, as evidenced by literature [121,122]. The literature currently in focus centers on our most recent investigation, which reports on the removal of metal ions using ion exchange resins involving Dowex A-1 [123], Amberlite 252 ZU [124], Amberlite XAD 16 [125], Purolite C 100 [126], Amberlite IRC-718 [127] and Amberlite IR 120 [128,129]. The recovery and separation of heavy metals has been proven to be extremely effective when using ion exchange resins.

Selecting an ion exchanger requires consideration of the resin beads' internal structure, namely their macroporous or microporous (gel-type) composition. Macroporous resins assist in ion exchange because of their large effective surface area. They can also be utilized with nearly any solvent, regardless of whether it is suitable for the uncross-linked polymer, and they absorb the solvent with little to no volume change. Furthermore, they provide access to the exchange sites for deeper ions. This helps to make the beads more easily removed from the reaction system since they are stiffer. To interact with exchange sites, solute ions diffuse through the particle in microporous resins because they lack distinct pores [130].

Strong sorption outcomes with anion exchangers based on various basicity and matrix designs imply that they might be effective sorbents for the removal of acid and reactive dyes. Styrene-divinylbenzene crosslinked copolymers are still used to create the majority of ion exchange resins. Consequently, this specific type of matrix remains the most essential. Styrene and divinylbenzene copolymers are excellent arrays for ion exchange resins because of their numerous advantages. Styrene monomer is widely accessible and reasonably priced. During temperatures of relevance in treating aqueous solutions, the polystyrenic matrix exhibits outstanding chemical and physical stability and is resistant to hydrolysis and

oxidation. Due to the electronegative sulfonic groups in their molecules, anion-exchange resin can readily remove acid dyes by electrostatic attraction. These resins have certain benefits, irrespective of diffusion constraints on the reaction rates: they respond more quickly in functionalization and application reactions, have larger loading capacities, and are less delicate, needing less handling care [131]. Given their excellent capacity and dye-specific selectivity, ion exchange resins appear to be suitable materials for the sorption of dyes from wastewater from textile factories. Three model reactive dyes, C.I. Reactive Black 5, C.I. Reactive Red 2, and C.I. Reactive Red 120, were chosen in the literature to investigate the adsorption potential of anion exchangers based on the styrene–divinylbenzene copolymers, specifically Amberlite IRA-900 for reactive dyes removal [132]. Adsorption of the anionic textile dye Acid Orange 10 onto Amberlite IRA-400 from an aqueous solution [133]. Examining and contrasting gel anion exchangers for removing Acid Orange 7 from aqueous solutions [134]. Studies of the gel anion exchanger's equilibrium and kinetics during the adsorption of acid Green 9 dye [135]. Referring to some literature, many research investigations have been carried out to remove acid and reactive dyes from wastewater employing ion exchange resins [136,137].

Ion exchange resin has distinctive advantages [112], including;

- ✱ Simplicity of application
- ✱ Inexpensiveness
- ✱ Reusable renewal
- ✱ Organic polymer stability

The capacity of ion exchange resins to remove ions from solutions selectively makes them useful materials for a wide range of commercial, industrial, and residential applications [120] (**Figure 1.14**).

A couple of usual applications are as follows:

- Softening of Water
- Water Purification
- Wastewater Treatment
- Chemical Processing
- Hydrometallurgy
- Food and Beverage Industry
- Nuclear Industry
- Pharmaceutical and Biotechnology



**Figure 1.14.** Application of Ion exchange resin.

These are examples of the wide-ranging applications of ion exchange resins across various industries, highlighting their importance in water treatment, chemical processing, environmental remediation, and many other fields. Ongoing research and development efforts continue to expand their utility and optimize their performance for diverse applications. Even if there are several industrial applications for organic ion exchange resins, numerous organizations are trying to create new ones in order to enhance the water treatment process. In the last decade, there has been a growing focus on the potential of ion exchange resins and the integration of diverse water treatment procedures to attain more economical and effective separation of inorganic and organic pollutants [120]. The technological usefulness of

synthetic ion exchangers is identified by a number of features, among them: particle size, bulk density, chemical resistance, selectivity.

### 1.7.2. Tetravalent metal acid salt as sorbent

Since the onset of the industrial maturity, there has been a conscious strive to combine the benefits of inorganic units and organic moieties in a single composite material. Livage's "Chimie Douce" unlocked the entrance to a whole new universe of materials known as inorganic–organic hybrid materials [138]. At the present time, there is a lot of curiosity in designing mixed materials, or organic/inorganic composites via Sol-gel technique, where the qualities of the inorganic and organic components work well together to develop new materials with novel composite properties and solid-state structures. The rigid inorganic backbone and the flexible organic groupings that provide a variety of features are two of the main benefits of inorganic–organic hybrid materials. This adaptability makes it possible to construct compounds with certain characteristics. Special attention should be paid to organic derivatives of inorganic ion exchangers belonging to the TMA salt class [139].

Over the past half-century, numerous investigators have been derived to these materials. Recently, "Tetravalent Metal Acid (TMA) Salts" have gained recognition as promising advanced materials due to their high thermal and chemical stability, adaptability to ionizing radiation, resistance to change the organic group's makeup, and significant applications as ion exchangers. Four books have examined and discussed the vast body of research on TMA salts that is currently available [140–143]. The desirable ion-exchange behaviour and potent selectivity of TMA salts for specific metal ions or dyes have rendered the synthesis of inorganic ion exchangers the focus of much research.

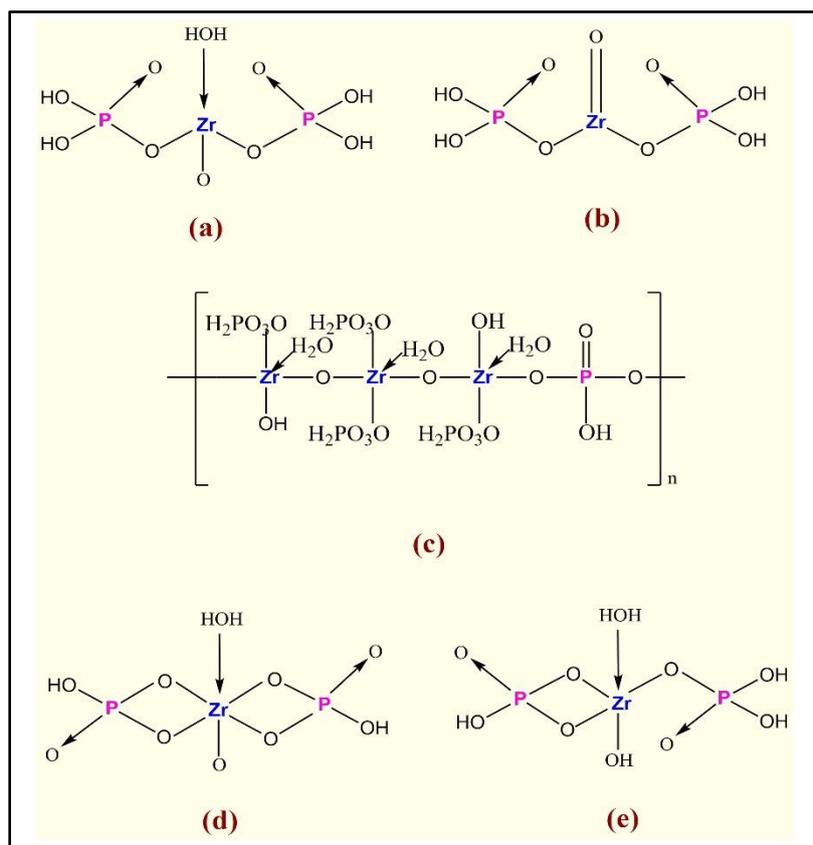
#### 1.7.2.1. Salient aspects of tetravalent metal acid (TMA) salts

Tetravalent metal acid salts are among the most significant and extensively researched classes of inorganic ion exchangers and some noteworthy features specific to this class. Under a number of circumstances, they can be produced by mixing tetravalent metal salts with anions such as phosphate, molybdate, arsenate, tungstate, etc. This category includes zirconium (IV), thorium (IV), cerium (IV), tin (IV) as well as other well-researched metals. With  $M = \text{Zr, Th, Ce, Sn, etc.}$  and  $X = \text{P, As, W, Sb, etc.}$ , they have the universal expression  $M(\text{IV})(\text{HXO}_4)_2 \cdot n\text{H}_2\text{O}$ .

TMA salts are composed of an M–O–P structure with structural hydroxyl groups; the cation exchange sites are the H<sup>+</sup> ions of the –OH groups. The cation-exchange capabilities of TMA salts are due to their ability to exchange multiple cations for H<sup>+</sup>. Affinity for specific metal ions can be observed in both amorphous and crystalline forms of it. The reality that amorphous materials are easily created and available in a variety of mesh sizes appropriate for column operations makes them the preferable form over crystalline materials. The drawbacks of tiny grain size in crystalline materials have restricted their use in column operation. The materials differ in physical appearance from completely opaque to translucent and are often rigid. One can obtain TMA salts with different composition, water content, and crystallinity by adjusting parameters like the mole ratio of reactants M: X (where M is a tetravalent metal and X is a polyvalent anion), temperature, mixing mode (converting metal salt solution to anion salt solution or vice versa), pH, and mixing rate. Materials with distinct qualities are produced by varying any of these parameters. The structural hydroxyl groups are impacted by the preparation process, which is reflected in their capability to move ions. Owing of their strong chemical, thermal, and radiation durability and ion exchange behaviour, those acid salts predominantly act as cation exchangers [144,145].

### 1.7.2.2. Structural aspects of TMA salts

Nearly every possible pairing of polybasic acids (which comprise P, W, Mo, As, Sb, and other elements) and Zr, Ti, Ce, Sn, and Th (Tetravalent metals) has been investigated. Amorphous materials were used in earlier research. Previous investigations mostly concerned zirconium phosphate (ZP) [146]. Amphlett C.B. has evaluated a wealth of information regarding ZP's structure [147]. Zirconium monohydrogen phosphate (Zr(HPO<sub>4</sub>)<sub>2</sub>) was the structure of ZP as noted by De Boers, despite some researchers stated that zirconyl salt (ZrO(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>) be the original structure. The following structural formula for ZP [147] was proposed by Bluementhal (**Figure. 1.15 (a)**), Paterson (**Figure. 1.15 (b)**), Baestle and Pelsemakers (**Figure. 1.15 (c)**), Nancollas and Pekarek (**Figure. 1.15 (d)**) and (**Figure. 1.15 (e)**).



**Figure 1.15.** Structural Formula for ZP.

These configurations indicate that the exchangeable protons are represented by the H of the structural -OH groups. K A Kraus's research team at Oak Ridge National Laboratory [148] and C B Amphlett's team in the UK [147] conducted a large portion of the significant work in this field. Clearfield and Stynes were the first to prepare crystalline  $\alpha$ -zirconium phosphate [149]. The first structural elucidation was done in 1969 [150]. ZP is organized into layers. As seen in (Figure 1.16), zirconium atoms are situated just above and below the ab plane and are connected by phosphate groups. These are located above and below the plane of the metal atoms, respectively. Three oxygen atoms in each phosphate are linked to three nearby metal atoms to form a deformed equilateral triangle [151]. Therefore, oxygens coordinate each zirconium atom octahedrally. Figure 1.17 shows an idealized image of a section of the layer.

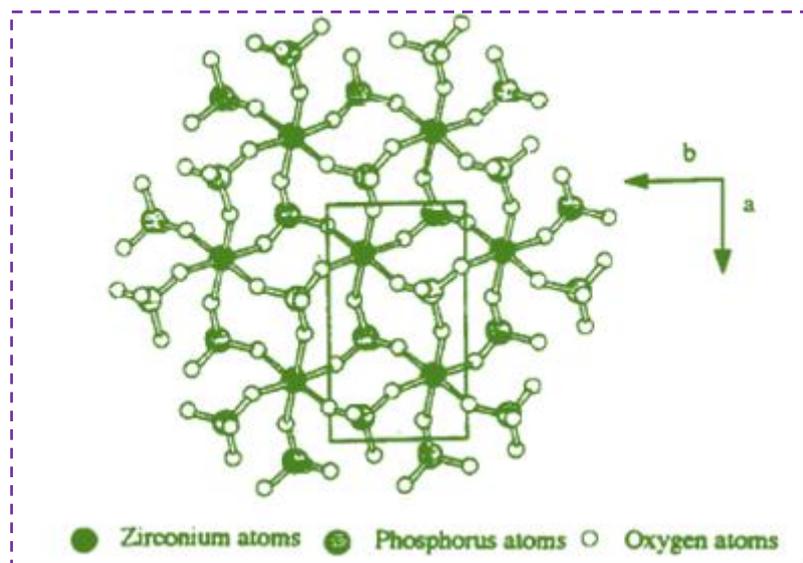


Figure 1.16. ab layer of  $\alpha$ -zirconium phosphate

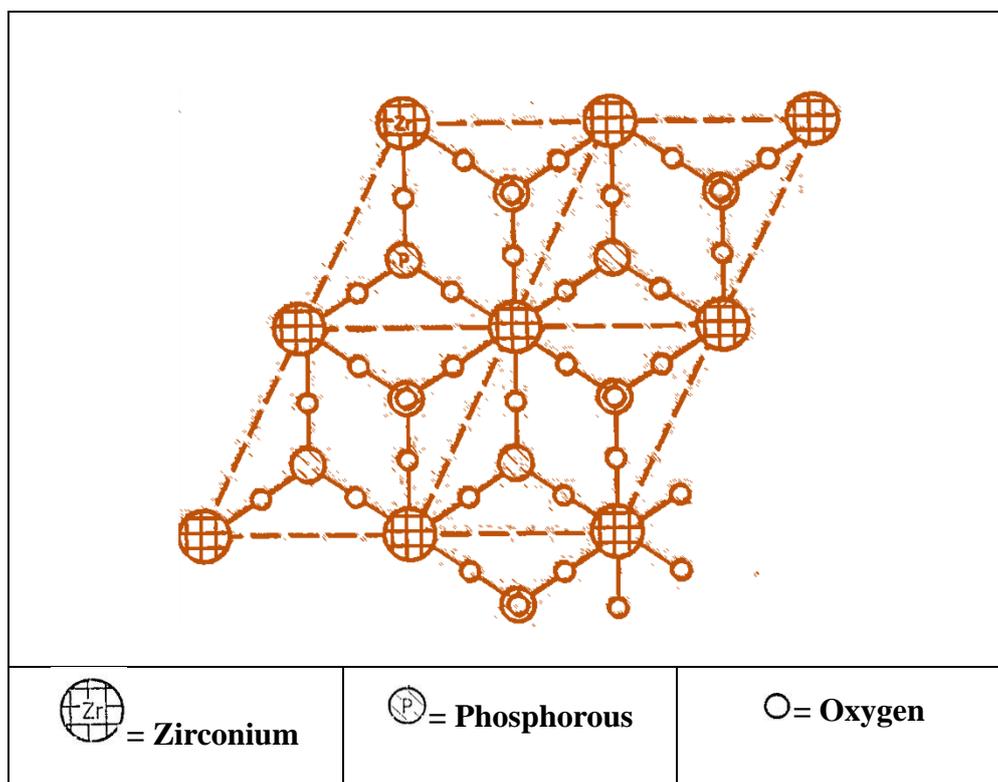
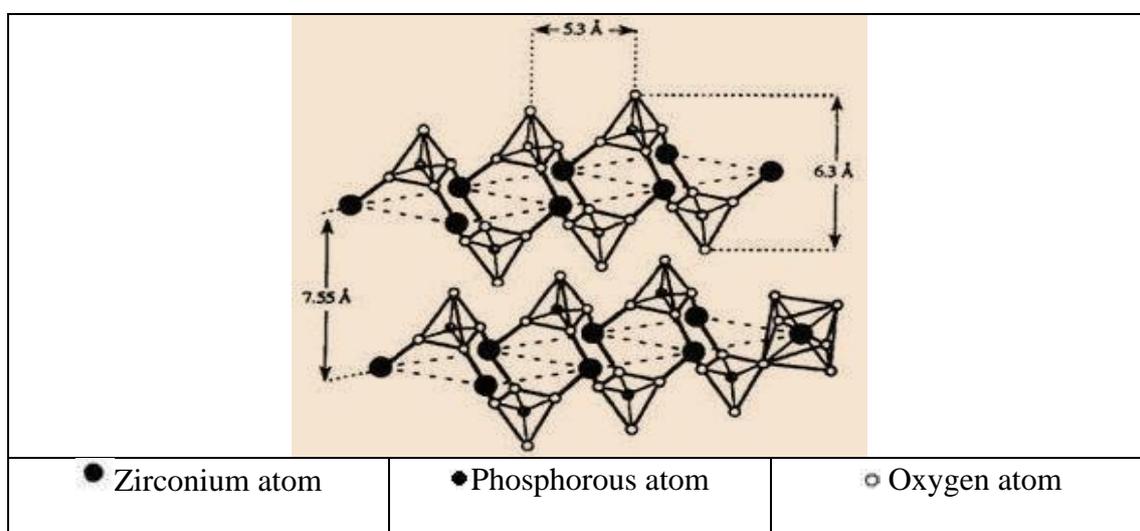


Figure 1.17. Idealized diagram showing arrangement of Zr and P (portion of layer)

The most researched tma salt of the crystalline type, zirconium phosphate, can be made into three-dimensional, layered, or fibrous structures [149]. In turn, the layered acid salts can be produced in at least two distinct modifications, commonly referred to as  $\alpha$ -ZP and  $\gamma$ -ZP, with the formulas  $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  and  $\text{Zr}(\text{PO}_4)(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$  [152]. The  $\alpha$ -ZP's structure (Figure 1.18) results from the ABAB stacking of layers, whereby zirconium atoms

are arranged in almost a perfect plane between  $-O_3POH$  groups, with the exchangeable proton pointing as  $P-OH$  into the interlayer region [151]. Ion exchange is brought about by these protons [153]. Zirconium atoms are arranged in two parallel ideal planes and connected by  $-PO_4$  groups to create the layers of the  $\gamma$ -ZP, with  $-O_2P(OH)_2$  groups oriented toward the interlayer region [154]. Because of this, the  $\gamma$ -ZP layers are thicker (0.92 nm) than the  $\alpha$ -ZP layers (0.64 nm), and the acidities of the  $-OH$  groups attached to the identical phosphorous atoms differ. Books and reviews have accumulated a wealth of knowledge on the chemistry of metal (IV) phosphates with  $\alpha$  and  $\gamma$  type structures [155,156]. From our lab, TMA salts as sorbents have been thoroughly explored as cation exchangers [157].



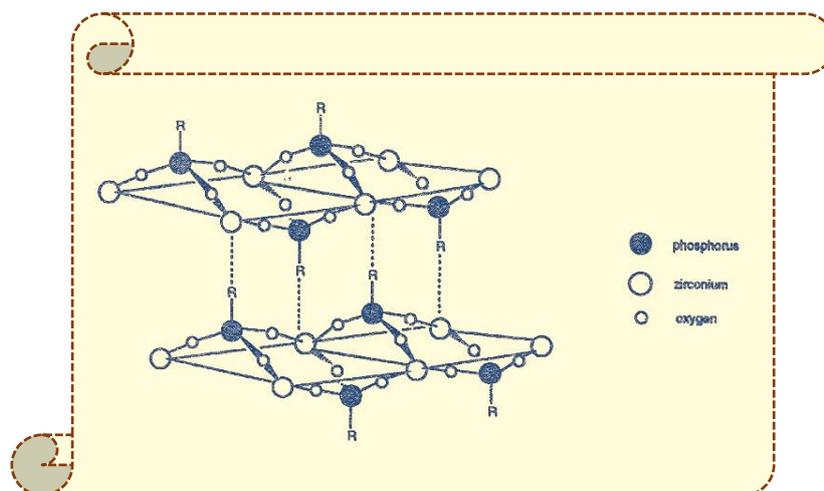
**Figure 1.18.** Schematic diagram of the arrangement of two adjacent macro anions in  $\alpha$ -ZP

### 1.7.2.3. Metal phosphonates as novel hybrid materials

Engineering mixed materials is very prominent these days because it may be used to construct novel lattice or solid-state structures by allowing the two interacting components to work concurrently. These materials could have a wide range of interesting properties and new properties not found in pure compounds. TMA salt materials, or compounds with two distinct cations and an anion, are intriguing in this instance since they might possess superior qualities compared to their single salt equivalents. Particularly interesting are the organic derivatives of the TMA salt class of inorganic ion exchangers. These inorgano-organic hybrid materials have a rigid inorganic backbone, which is one of their main advantages. This versatility makes it possible to construct compounds with particular characteristics. For example, the surface area and, consequently, the surface acidity can be changed when the organic functionalities contain ionogenic groups ( $-OH$ ,  $-COOH$ ,  $-SO_3H$ , etc.) Titanium

phosphate and cerium phosphate of the class of TMA Salts are now well-known inorganic ion exchange materials and have displayed a number of advantages as ideal host lattices [158,159].

M(IV) phosphonates of the class of TMA salts were mentioned for use as ion exchangers. Phosphonates are frequently layered hybrid organic compounds, with organic groups hanging on each side of the inorganic element that forms the layer's centre [160]. Nearly 25 years ago, Yamanaka et al. presented the first report on metal phosphonates [161]. A significant number of articles on layered M(IV) phosphonates were published, with Yamanaka's work being the first. It was based on the work of Clearfield, Smith, Alberti, et al. on layered zirconium hydrogen phosphonates.  $\alpha$ -zirconium Phosphonates (**Figure 1.19**), of general formula  $Zr(O_3PR)_2$  are known since 1978. Specifically, the layered structures of organic phosphonate  $[RPO_3]_2$ -salts of tetravalent metals, like zirconium, have the organic functions R located in the inter-layer space between quasi-two-dimensional metal-oxygen sheets. (**Figure 1.19**) [162]



**Figure 1.19.** Structure of Zirconium Phosphonates.

The emphasis has been on elucidating the structure, despite the synthesis and characterization of many metal phosphonates. An extensive literature on metal phosphonates exists today, which have been reviewed and detailed [163,164]. The potential use of these materials as sorbents to remove dyes and metal ions makes them intriguing. Claw molecules of the type HEDP (1-hydroxyethylidene-1,1-diphosphonic acid) ATMP (amino tris (methylene phosphonic acid)) EDTMP (ethylenediamine tetra (methylene phosphonic acid)), and DETPMP (diethylenetriamine penta (methylene phosphonic acid)) are phosphonic acids

containing structural hydroxyl ( $-OH$ ) groups of five, six, eight, and ten, respectively. These molecules contain Lewis bases and extra coordinating sites that, when coupled with tetravalent metal ions, can induce cross linking, the dimensionless of which can be customized by picking the appropriate interlinking organic groups. The various binding properties of amino phosphonic acids have attracted significant interest for the reason of their donor groups' effectiveness in binding tetravalent metal ions. Furthermore, employing a "Sol-gel *Chemie Douce*" technique, the organic species included in an inorganic phase provides regulation of porosity, hydrophobicity/hydrophilicity, and ion exchange properties (organic moiety including ionogenic groups). The characteristics of the metal can be combined with phosphonate anions, or the latter with the former, to create new materials in an efficient way. Hydrogen ions that are easily exchanged and connected to the anionic groups of salt give birth to the cation exchange characteristics. The ion-exchange behaviour of these compounds is caused by surface hydroxyl protons [163-165]. Typically, the structures of dyes (MB, MG, CV, RHB) include one or additional of the following functional groups:  $-OH$ ,  $-COOH$ ,  $-SO_3H$ ,  $NO_2$ ,  $N=N$ , etc. In adsorption, the functional groups indicated above are thought to interact with the matrix material or sorbent in various ways, such as covalent, coulombic, hydrogen bonding, or weak Van der Waals forces. The type and degree of the interaction between the dye and sorbent determines how well the dye may be adsorbed out. The use of TMA salts in the treatment of dye-containing wastewater was considered interesting. Since the dye contains structural hydroxyl groups, it is anticipated that it will be bound by weak van der Waals forces or by hydrogen bonds [166].

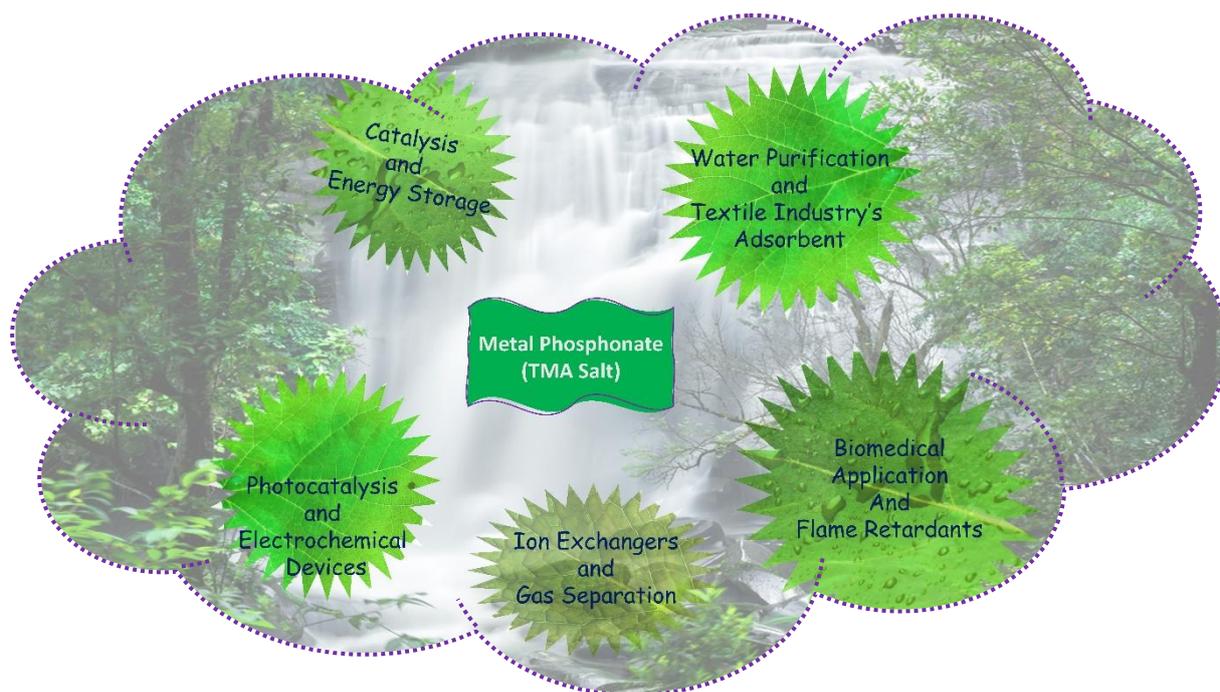
A survey of the literature on the subject of the study shows that different metal phosphonates have been utilized for metal ion sorption in the areas of mesoporous titanium phosphonates, coded as PMTP-1, PMTP-2, TPPH [167-169]. Ti-EDTMPA [170], Ti-ATMP [171], Zr-HEDP [172], NTAZP [173] and Zr-DETPMP [174]. Though the cation-exchange characteristics of TMA salts are well-established, not much effort has been placed on the adsorption characteristics of these materials. There are a few publications in the present region of the study, where ion exchange materials have been used as sorbents for removal of dyes [166,175-177]. The sorption behavior of cationic dyes by using sorbent as Titanium phosphonate [178]. Adsorption of methylene blue by periodically occurring mesoporous titanium phosphonate materials in aqueous solution [179], Mesoporous organic-inorganic hybrid improved qualities of its organic and inorganic components [180].

Sol-gel derived composite substance have several advantages due to their unique properties and structural characteristics [159];

- ✿ Chemical Stability
- ✿ Thermal Stability
- ✿ Ion Exchange Capacity
- ✿ Tunable Properties
- ✿ Structural Diversity
- ✿ Biological Compatibility
- ✿ Environmental Friendliness
- ✿ Catalytic Activity

Overall, the combination of chemical, thermal, and structural properties make metal phosphonates attractive for a broad range of applications across industries including catalysis, environmental remediation, materials science, and biomedicine (**Figure 1.19**) [138]. Metal phosphonates, have various applications across different fields in include:

- ✿ Catalysis
- ✿ Ion Exchangers and Gas Separation
- ✿ Energy Storage
- ✿ Water Purification
- ✿ Textile Industry's Adsorbent
- ✿ Biomedical Applications
- ✿ Flame Retardants
- ✿ Photocatalysis
- ✿ Electrochemical Devices



**Figure 1.19.** Application of metal phosphonate (Tetravalent metal acid Salt).

Ongoing research efforts continue to explore novel synthesis methods and applications to further harness their potential across various sectors.

### **1.8. Aim and scope of the present work**

The release of industrial wastewater that contains intricate metals and dyes compounds into aquatic environments has emerged as a critical concern, endangering both human health and ecosystems. The relevance of ion exchange resin (Polymeric resin) and metal phosphonates (TMA salt) their possible use as adsorbents in the research for the removal of organic and inorganic pollutants detailed in the current thesis work. This study's primary intent is to evaluate these adsorbents to modified and after that utilized in metals and dyes removal from the aqueous solution. The utilization of modified cationic resin, anionic resin and metal phosphonate offers a novel and promising avenue to overcome these challenges. The aim of this research is to offer workable ways to lessen the harm that metal and dye pollution due to aquatic environments. The ultimate goal is to provide a sustainable, efficient, and cost-effective solution for wastewater treatment, contributing to environmental protection and the reduction of water pollution.

## 1.9. Key Objectives of the work

The specific objectives of the study for metals and dyes removal are as follows:

- 1. Synthesis (Modification) and Characterization Ion Exchange Resin and Metal Phosphonate:** To synthesize ion exchange resin modified with  $\text{Na}_2\text{EDTA}$  and metal phosphonates modified with distinct metal ions (Cerium and Tin) and phosphonic acid (ATMP). Perform a thorough characterization of these adsorbents, focusing on their structural and chemical properties.
- 2. Optimization of Adsorption Conditions:** To evaluate the optimal circumstances conditions for maximum metal ion and dye removal.
- 3. Adsorption Isotherms, Sorption of Kinetics and Thermodynamics:** To investigate the adsorption behavior of the modified resin using isotherm models and kinetics.
- 4. Reusability Studies and Comparison with Other Adsorbents:** To appraise the reusability of the metal phosphonate over multiple adsorption-desorption cycles for metal and dye. To compare the adsorption performance of the both adsorbent with that of unmodified adsorbents and commercial adsorbents.

## 1.10. Constitution of the thesis

The thesis entitles “**Removal of Organic and Inorganic Pollutants by Modified Adsorbents**” consists of seven chapters including: I) **Chapter 1:** Introduction; II) **Chapter 2:** Materials, Methods, and Characterizations; III) **Chapter 3:** Removal of Transition and Heavy Metal Ions by Using Modified Chelating Resin (MCR) as an Adsorbent; IV) **Chapter 4:** Adsorption of Acid Yellow 49 and Reactive Orange 12 by Using Amberlite IRA-400( $\text{Cl}^-$ ) Resin; V) **Chapter 5:** Removal of Transition and Heavy Metal Ions by Using Cerium Amino Tris-(Methylene Phosphonic Acid) (Ce-ATMP); VI) **Chapter 6:** Adsorption of Cationic Dyes by Using Tin Amino Tris-(Methylene Phosphonic Acid) (Sn-ATMP); VII) **Chapter 7:** Overall Conclusion.

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