

# ***CHAPTER 1***

## ***Introduction and Review of literature***

## 1.1 WATER: A NATURAL RESOURCE

Water, a vital substance for life maintenance, was revered as "a primary source of all that exists" by the ancient Greek philosopher Thales of Miletus over 2,600 years ago. Despite its long history of study and deep significance to human civilization, water remains one of the most remarkable and enigmatic compounds on Earth, with many of its unique properties and behaviors still not fully understood by science. Its exceptional characteristics, such as high melting, boiling, and evaporation points, as well as its unparalleled dissolving abilities, set water apart from other common substances and make it indispensable for sustaining life on our planet.

The water on Earth is predominantly found within the hydrosphere, which comprises oceans, seas, surface water bodies, groundwater reserves, as well as snow and ice formations. The hydrosphere encompasses around 70.8 % of the Earth's surface and totals around 1.39 billion km<sup>3</sup>. Oceans and seas represent the largest portion, accounting for 96.4 % of the hydrosphere. Ground water comprises 1.68 %, while snow and ice, primarily from polar regions, make up about 2 %. Surface freshwater bodies, including saline lakes and inland seas, constitute a relatively small fraction of 0.059 %. Although water exists within the Earth's atmosphere and living organisms, these amounts are relatively minor in comparison to the vast reservoirs of the hydrosphere.

The hydrological cycle, a globally occurring process driven by solar energy and gravity, facilitates the continuous transformations of water. This cycle encompasses the vaporization of water from the Earth's surface, the atmospheric transport of water vapor, the condensation of vapor into clouds, and the eventual precipitation of water back onto the Earth's landmasses and oceans. Remarkably, the annual precipitation closely matches the amount of water evaporated from land and seas, underscoring the dynamic and cyclical nature of water circulation on Earth, a phenomenon that is vital for sustaining life and replenishing freshwater supplies.

### 1.1.1 Types of water

The types of water can be broadly distinguished into the following types[1]:

➤ **Atmospheric water**

Atmospheric water is essential for the water circulation of nature, transitioning among different states. While moisture primarily exists in a gaseous form within the atmosphere, it diminishes with increasing altitude and latitude, exhibiting seasonal and surface-dependent variations. Although the atmosphere contains a relatively small amount of moisture, it serves as the prime source of fresh water replenishment through vaporization and precipitation. The total evaporation from oceans and continents amounts to a significant volume annually, contributing to the water cycle on Earth [2].

➤ **Oceanic water**

Accounting for the majority of the Earth's water, oceanic water constitutes approximately 70% of the planet's surface and contains nearly all of its free water. The chemical properties of seawater can differ significantly from ocean water due to runoff from land sources like rivers and springs. Evaporation and freshwater discharge influence the salinity of oceans and marginal seas, with seawater's chemical composition remaining relatively constant except in areas with significant river inputs [3].

➤ **Freshwater**

This category includes surface water (lakes, rivers, and streams) and groundwater. Surface water, such as rivers, lakes, and streams, makes up a relatively small fraction of the Earth's total water, while groundwater, stored in aquifers, represents a much larger portion.

i. **Surface Water:** Refers to water found continuously or at irregular intervals on the land surface in various forms such as rivers and streams, artificial water storage reservoirs, natural lacustrine water bodies like lakes, and wetland ecosystems such as swamps and bogs, as well as frozen water resources in the form of glaciers and snow cover. Rivers are watercourses flowing along self-formed channels, with contributions from surface runoff and groundwater discharge. They form river systems shaped by climatic conditions, topographical features, geological formations, and basin characteristics. Rivers can be classified into mountain rivers and plain rivers based on their flow characteristics. Lakes are natural water bodies contained within a basin, isolated from direct connection to the sea. Lakes can be categorized based on their mode of formation, including tectonic, glacial, fluvial, coastal, sinkhole, volcanic, and dammed lakes. Lakes can also be classified based on their hydrological connectivity, distinguishing between those with an outlet, allowing the flow of water out of the basin (exorheic), and those without an outlet, where water only leaves through evaporation or underground seepage (endorheic). Water Reservoirs are artificial water basins formed in river valleys to regulate water use for natural economy purposes. Reservoirs can be permanent or temporary and are classified based on their form into fluvial, lacustrine, and mixed types. Wetlands are regions characterized by persistent or excessive water saturation, facilitating the proliferation of water-loving flora and distinctive edaphic processes. Wetlands comprise various types, such as bogs, marshes, and water bodies that have developed due to excessive water saturation or nutrient enrichment within a reservoir. They play a crucial role in the ecosystem.

ii. **Groundwater**

This underground component of the water cycle is stored in aquifers, which are permeable geological formations capable of yielding significant quantities of water.

Aquifers can be classified according to their extent, depth, water-bearing properties, and relationships with surface water. Groundwater encompasses water present in the Earth's subsurface in diverse physical forms within sedimentary strata and fractured crystalline bedrock. It is classified based on factors like infiltration, distribution, lithological composition, geological age, hydrodynamics, temperature, and chemical composition. Groundwater can be categorized based on its physical and chemical characteristics. This includes free gravitational water that is primarily recharged by infiltration, water that is physically bound within sedimentary or fractured rock structures, water that is chemically bound in mineral complexes, and water in a supercritical state at high temperatures and pressures. Gravitational groundwater is primarily recharged by infiltrating rainfall, water vapor condensation, and river runoff, and it interacts with surface water bodies and ecosystems. Groundwater is further categorized based on its water exchange capacity, leading to zones of active water exchange with fresh bicarbonate- and calcium-rich water, zones of reduced water exchange with brackish water, and zones of very reduced water exchange with saline water. The chemical composition of groundwater includes various chemical elements, ions, molecules, organic-mineral complexes, colloids, and isotopes. Groundwater can be classified based on its mineralization into fresh, saline, and brine types, with mineralization levels ranging from less than 1 g/l to over 25 g/l [4].

➤ **Frozen water**

This includes water stored in glaciers, ice caps, and permafrost, which make up important portion of the Earth's freshwater reserves. Glaciers, icebergs, and ground ice play significant roles in the Earth's hydrological cycle and have various implications for the environment and human life.

## 1.2 GROUNDWATER POLLUTION

Globally, groundwater constitutes as an essential source of potable water for numerous rural and urban communities [5]. However, intensifying industrial and agricultural activities have led to in the elevated production of toxic contaminants, including inorganic anions, metal ions, and synthetic organic chemicals, raising significant public health concerns regarding groundwater quality. In India, groundwater is particularly critical, as it supplies drinking water to a substantial portion of the population. Specifically, over 95% of the rural population and 30-40% of the urban population rely on groundwater for their domestic requirements [6].

Groundwater faces a growing threat from contamination. This contamination arises from a diverse array of pollutants, including inorganic and organic chemicals, radionuclides, and microorganisms. Inorganic chemicals, distinguished by their mineral origin and absence of carbon, can be naturally occurring within geological formations or introduced into the hydrological cycle through agricultural practices and industrial discharges [7]. Common examples of inorganic contaminants include nitrates, fluorides, and arsenic. Alarmingly, elevated concentrations of these and other toxicants are being increasingly detected in groundwater resources, rendering them unsuitable for human consumption.

The observed groundwater contamination can be attributed to two primary sources: geogenic and anthropogenic. Geogenic contaminants, such as arsenic, fluoride, and iron, pre-exist within the Earth's crust and can leach into groundwater naturally. Conversely, anthropogenic contaminants, encompassing nitrates, phosphates, and heavy metals, originate from human activities. These activities include domestic sewage disposal, agricultural practices involving fertilizers and pesticides, and the discharge of industrial effluents. The cumulative impact of modern civilization, characterized by industrialization, urbanization, and population growth, significantly exacerbates the degradation of groundwater quality [6].

Widespread investigations across India have documented the presence of a diverse array of hazardous contaminants within groundwater resources. These contaminants include fluoride, arsenic, nitrate, sulfate, pesticides, and a spectrum of heavy metals [8]. Particularly concerning are the escalating concentrations of arsenic, fluoride, and nitrate, which have rendered the groundwater increasingly unfit for human consumption.

The alarming presence of diverse contaminants in groundwater resources necessitates a paradigm shift towards water resources planning and development that prioritizes the mitigation and prevention of these threats [9]. In India, a prime illustration of this challenge is the widespread prevalence of fluoride, a naturally occurring inorganic pollutant within groundwater aquifers.

Furthermore, a substantial portion of India's groundwater resources suffers from the co-occurrence of nitrate and fluoride contamination. The intensification of agricultural practices, particularly the extensive deployment of inorganic nitrogenous fertilizers, is considered a key driver of nitrate contamination, especially in vulnerable hydrogeological regions [10].

### **1.3 WATER POLLUTION BY FLUORIDE AND NITRATE: DISTRIBUTION, SOURCES, AND HEALTH IMPLICATIONS**

#### **1.3.1. Fluoride contamination in drinking water**

Fluoride occurs naturally as an element found in the soil and aquatic environments; human activity can also affect its levels. Although fluoride plays an important role in maintaining dental health when ingested within the recommended limits [11,12], excessive intake results in fluorosis. Fluorosis poses a significant challenge to public health worldwide as it affects millions of individuals. The World Health Organization has established recommendations for the upper permissible level of fluoride in drinking water. As per the recommendations, the ideal

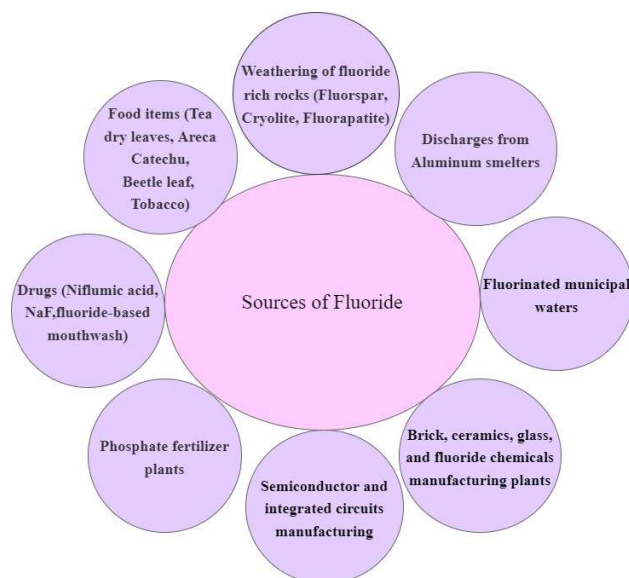
level of fluoride in drinking water should fall between 0.5–1 mg/L. However, it is worth mentioning that Sri Lanka suggests reducing the optimum concentration even further, to 0.6–0.9 mg/L, due to the emerging findings suggest a connection between fluoride and the long-term impairment of kidney functions [13]. Groundwater fluoride levels can exceed 67 mg/L, whereas the majority of surface waters have concentrations lower than 0.1 mg/L. In seawater, fluoride concentrations range from 1.2 to 1.4 mg/L [14].

Excessive consumption of fluoride has been associated with skeletal and dental fluorosis, conditions characterized by the deterioration of tooth enamel and bone strength. Dental fluorosis manifests as white streaks or brown discoloration on the teeth, while skeletal fluorosis can lead to joint pain and stiffness, as well as skeletal deformities [15]. In addition to dental and skeletal issues, fluoride has also been associated with neurological and developmental disorders [16,17] Several research findings suggest a possible association between exposure to fluoride and reduced IQ levels in children [18]. Moreover, fluoride has been implicated in disruptions to thyroid function, which can result in hormonal imbalances and impaired metabolism [19].

The alarming health hazards linked with excessive fluoride ingestion have led to a growing need for efficient methods to remove fluoride during water treatment processes. effective fluoride removal methods in water treatment processes. Numerous methods are existing for removing fluoride from water sources. Some of the most common approaches for the defluoridation of drinking water are coagulation and precipitation [20], membrane processes [21], ion exchange [22], electro-coagulation [23], and adsorption [24]. Adsorption is an effective method for removing elevated fluoride from potable water due to its low cost, simplicity of design, enhanced removal capacity, environmentally benign quality, and reusability of the adsorbent.

### 1.3.1.1 Sources of fluoride in water

Water can be contaminated with fluoride from natural sources as well as several human activities. Natural sources of fluoride include the weathering of rocks that contain fluoride-rich minerals. There is an abundance of fluoride in the geological environment [25]. Furthermore, it is typically discharged into water-table aquifers by weathering of fluorine-bearing rocks [26]. Fluoride can be released into the groundwater by several minerals like biotite, topaz, fluorite [27], and fluorapatite [28,29] in addition to the host rocks that they are found in like granite, basalt, syenite, and shale [14,30]. These rocks can release fluoride into the surrounding soil and water. Additionally, volcanic activity and geothermal springs can contribute to fluoride concentrations in water sources [31]. Human activities like industrial operations, mining, and farming practices may also be a source of fluoride contamination in water [32]. Industrial processes such as aluminium production and phosphate fertilizer manufacturing can release fluoride compounds into the environment [33,34]. Similarly, mining activities can introduce fluoride through the leaching of minerals containing fluoride. In agriculture, the application of fluoride-containing fertilizers can result in the accumulation of fluoride in soil and water [35]. Fig. 1.1 summarizes sources of fluoride in the environment.



**Fig. 1.1 Different sources of fluoride in water**

### 1.3.1.2 Global and Indian scenario of fluoride contamination in water

#### 1.3.1.2.1 International status of fluoride contamination in water

Fluoride contamination in groundwater presents a significant global health burden, impacting millions of people across numerous countries. The issue is not confined to specific regions. Over 100 countries grapple with groundwater exceeding the World Health Organization (WHO) guideline of 1.5 mg/L for fluoride concentration. This translates to a potential risk for an estimated 200 million people worldwide, with the highest burden concentrated in Africa, Asia, and Europe [36].

#### Asia

- i. **China:** High fluoride levels are prevalent in North China, particularly in areas with fluorite-rich geological formations. Studies by Wang et al. (2011) highlight the health concerns associated with this contamination, including dental fluorosis and skeletal fluorosis in severe cases [37].
- ii. **India:** Endemic fluoride contamination plagues various regions in India, impacting millions. Jacks (2016) emphasizes the severity of this issue in the country [38]. Millions

of people lack access to safe drinking water due to fluoride contamination, leading to chronic health problems.

- iii. **Africa:** The continent faces a substantial challenge with fluoride contamination. Firempong et al. (2013) and Osemwegie et al. (2013) report alarming levels in various African regions, highlighting the need for urgent intervention [39,40]. Geological factors like fluoride-rich volcanic rocks contribute to the problem. This contamination can disproportionately impact rural communities that rely heavily on groundwater resources.
- iv. **Latin America:** Countries like Mexico and Argentina are not exempt from this issue [41]. Here, arid and semi-arid regions are particularly vulnerable due to factors like limited water resources and reliance on groundwater.
- v. **Other Regions:** While the burden is concentrated in Africa, Asia, and Europe, fluoride contamination also affects countries like Turkey, Iraq, Iran, Afghanistan, Northern Thailand, Pakistan, Bangladesh, pockets within the United States, and even Japan [42].
- ❖ **Co-occurrence with Other Contaminants:** An additional concern is the co-occurrence of fluoride with other contaminants in groundwater. Joshi et al. (2012) reported the presence of fluoride alongside arsenic, lead, boron, and molybdenum in the groundwater of Nepal's Kailali district [43]. This necessitates a multi-pronged approach to address water quality challenges. The presence of multiple contaminants can exacerbate health risks and complicate water treatment processes.

#### 1.3.1.2.2 Indian status of fluoride contamination of groundwater

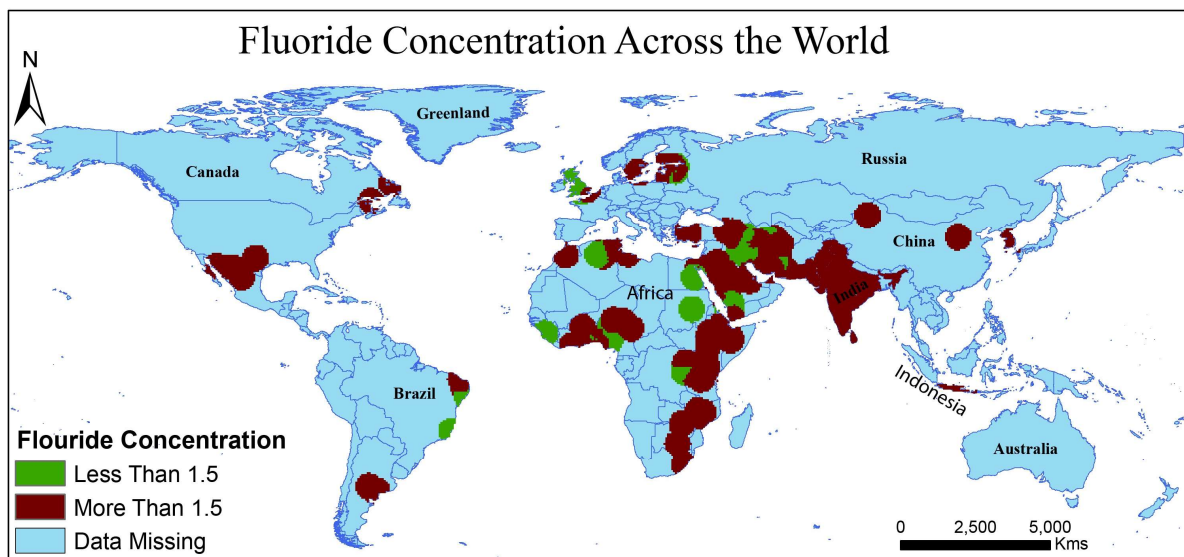
Most of India's rural residents drink groundwater, and 50% of the groundwater sources are fluoridated [44]. According to Susheela, the Three states with the highest endemic rates of chronic fluorosis are Rajasthan, Gujarat, and Andhra Pradesh [45]. Ten of India's 19 states—Andhra Pradesh, Rajasthan, Madhya Pradesh, Haryana, Maharashtra, Assam, Delhi, Gujarat,

Karnataka, and West Bengal [42] had groundwater fluoride concentrations that were more than ten mg/L [46]. Narsimha and Sudarshan analyzed groundwater samples in Telangana's Medak district [47]. They found that it has fluoride concentrations ranging from 0.2 to 7.4 mg/L, which is the primary drinking water source for the population. About 57% of groundwater samples were unfit for human consumption. Around 62 million people in 250 districts of India were in danger of developing endemic fluorosis, whereas 25 million people have dental fluorosis problems, mainly affecting the under-18 population [45]. Table 1.1 lists some districts in India where fluoride concentration is above 1/5 mg/L in water sources. Fig. 1.2 highlights fluoride contamination in various countries all over the world.

**Table 1.1 Fluoride in water incidences in Indian districts (CGWB 2022)**

State	Number of Districts Affected	Names of Affected Districts
Andhra Pradesh	16	All districts except Adilabad, Nizamabad, West Godavari, East Godavari, Vishakhapatnam, Srikakulam, Vizianagaram
Assam	2	Karbi Anglong, Nagaon
Bihar	5	Daltonganj, Gaya, Rohtas, Gopalganj, Paschim Champaran
Chhatisgarh	2	Durg, Dantewara
Delhi	7	Central, South, West, East, South-west, North-West, North-East zones
Gujarat	18	All districts except Dang
Haryana	11	Rewari, Faridabad, Karnal, Sonipat, Jind, Gurgaon, Mohindergarh, Rohtak, Kurukshetra, Kaithal, Bhiwani
Jammu & Kashmir	1	Doda
Jharkhand	1	Ranchi
Karnataka	17	All districts except Udupi, Kodagu, Dakshin Kannada
Kerala	3	Palghat, Alappuzha, Kottayam

State	Number of Districts Affected	Names of Affected Districts
Madhya Pradesh	17	All districts except Hoshangabad, Ujjain, Shajapur, Raisen, Katni, Sidhi, Jhabua, Mandla, Neemuch
Maharashtra	10	Amravati, Nanded, Nagpur, Chandrapur, Yavatmal, Latur, Jalgaon, Nandurbar, Beed, Buldana
Odisha	10	Balasore, Cuttack, Dhenkanal, Deogarh, Jaipur, Kalahandi, Keonjhar, Khurda, Nayagarh, Phulbani
Punjab	8	Hoshiarpur, Nawanshahr, Bathinda, Mansa, Faridkot, Patiala, Sangrur, Moga
Rajasthan	20	All districts except Bikaner, Jaisalmer
Tamil Nadu	12	Dharmapuri, Krishnagiri, Namakkal, Salem, Karur, Erode, Coimbatore, Thiruchirapalli, Madurai, Dindigul, Ramanathapuram, Sivagangai
Telangana	10	Nalgonda, Mahbubnagar, Warangal, Karimnagar, Medak, Ranga Reddy, Khammam, Nizamabad, Adilabad, Hyderabad
Uttar Pradesh	10	Agra, Mainpuri, Allahabad, Pratapgarh, Raebareli, Hardoi, Unnao, Banda, Mahoba, Sonbhadra
West Bengal	6	Purulia, Bankura, Birbhum, Malda, South Dinajpur, North Dinajpur



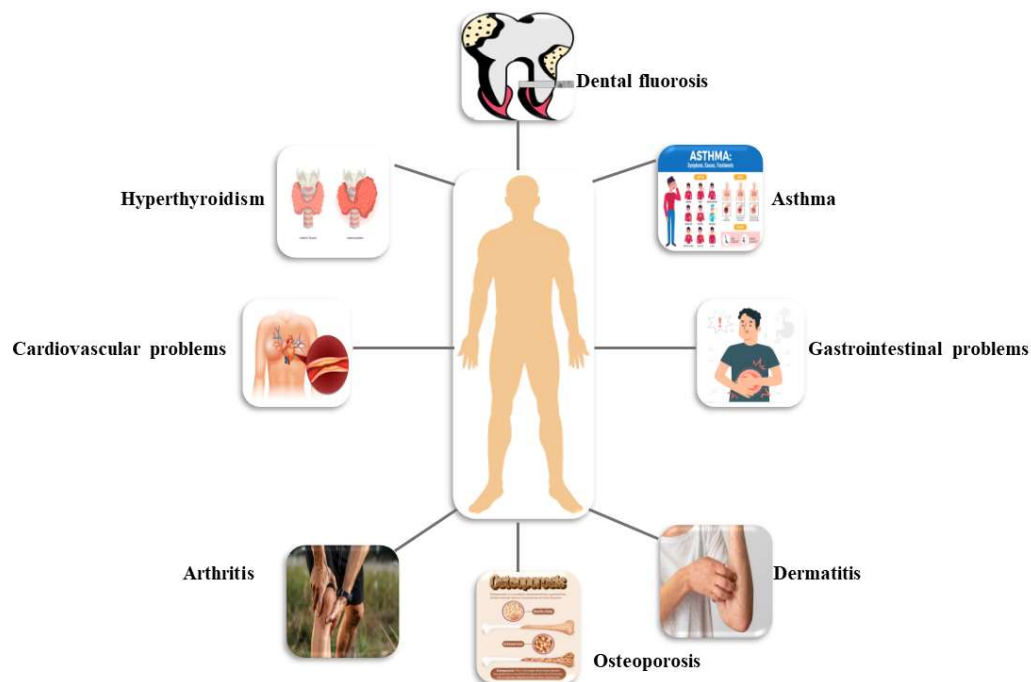
**Fig. 1.2** The distribution and levels of fluoride in aquifers ( $F^-$  mg/L) in various places of the world are depicted on a map

### 1.3.1.3 Health effects of consuming fluoride-rich water

- **Dental and skeletal health effects**

Dental fluorosis causes dental enamel to look opaque by causing porosity on its outer and inner surfaces. The clinical symptoms range from minor white lines running throughout the teeth on all areas of the enamel to complete chalky white teeth (Fig. 1.3). In the latter case, the enamel is hypo mineralized, and if the outer enamel breaks, its subsurface becomes dark in colour, losing its lustre completely [48,49].

Skeletal fluorosis is caused when excessive fluoride gets accumulates in bones. It can affect both children and adults. During the initial stage, a person shows arthritis-like symptoms such as severe pain in joints and stiffness of muscles. Later it restricts spine movements, and in the advanced stage, it results in osteoporosis [50].



**Fig. 1.3 Toxic effects of fluoride in potable water**

- **Non-skeletal health effects/other problems**

Excessive intake of fluoride may give rise to problems like cancer, infertility, cognitive impairment, Alzheimer's disease, and thyroid dysfunction [51,52]. Additionally, it can harm the neurological system [53], endocrine glands [54], reproductive system [55], kidney, liver [56,57] and other organs in terms of metabolic processes and structural integrity. Other problems that could arise due to the consumption of fluoridated water are muscle fibre damage, deformities in red blood cells, headache, skin irritation, anxiety, abdominal pain, numbness in hands and feet, weak immunity, recurrent miscarriages, male infertility, etc. [12]. Different organizations have established regulations regarding the acceptable levels of fluoride in drinking water, as outlined in Table 1.2.

- **Thyroid**

Numerous studies from various parts of the world, including India, have discovered changes in thyroid hormones in populations with high environmental fluoride concentrations, supporting the hypothesis that fluoride and hypothyroidism are related (Fig. 1.3). These changes include decreased T3 and increased TSH [58–63]. Hypothyroidism in a clinical setting is characterized by insufficient production of the thyroid hormones triiodothyronine (T3) and thyroxine (T4) by the thyroid gland [64]. As these hormones are necessary for all cells that are involved in metabolism, the absence of them can lead to a range of adverse effects, such as exhaustion, soreness in the muscles and joints, anxiety, obesity, menstrual cycle interruptions, problems in fertility, mental confusion, and trouble concentrating. The pituitary gland reacts to a drop in T3 and T4 levels by producing more "Thyroid Stimulating Hormone" (TSH) to stimulate the thyroid to create more T3 and T4.

TSH levels are high underlying subclinical hypothyroidism, although T3 and T4 levels remain healthy [65]. The latest study published in the Journal of the American Medical Association discovered that grown-ups with subclinical hypothyroidism seemed to have a considerably more significant risk of coronary artery disease (CAD).

- **Cardiovascular problems**

- **Hypertension**

Elevated fluoride levels in the water table have been linked to a rise in the incidence of hypertension, particularly among the male population. Those subjected to fluoride at work had an increased incidence of arterial hypertension [66].

- **Calcification of the Arteries**

Elevated artery calcifications have been documented often in people with skeletal fluorosis [67]. Fluoride build-up causes cellular damage, possibly in  $\text{Ca}^+$  deposition

[68]. According to one report, at 8,400 ppm F<sup>-</sup>, the aorta may acquire higher fluoride than any other tissue (Fig. 3). According to studies, the aorta and heart of animals exposed to fluoride over time have higher amounts of both Ca<sup>+</sup> and F<sup>-</sup> [69].

➤ **Arteriosclerosis**

According to several studies, people regularly exposed to fluoride are more likely to develop arteriosclerosis. For instance, it was discovered that patients with mild fluoride toxicity had impeded ascending aortic elasticity [70].

➤ **Myocardial damage**

According to Barbier et al. [56], fluoride has been shown to cause reactive oxygen species and an adverse reaction in both people and lab animals. These reactions are most likely to be to blame for the myocardial cellular damage [71]. Hazy swelling, degenerative vacuole, internal bleeding, interstitial swelling, fibre necrosis, disintegration of a nucleus, and congealing of the arterial wall in the muscle of the heart are some of the typical characteristics of this damage [72–76].

➤ **Gastrointestinal problems**

Combining with calcium and disrupting the action of proteolytic and glycolytic enzymes, high fluoride ingestion can have deleterious impacts. In the stomach, fluoride that has been consumed reacts with gastric acid to form hydrofluoric acid. The early symptoms of acute exposure to elevated concentrations of the most solubilized fluoride derivatives include nausea, vomiting, diarrhoea, and abdominal pain.

➤ **Hypersensitivity and Asthma**

The topical application of fluoride items, such as toothpaste, has been linked in studies to adverse skin effects. Urticaria, perioral dermatitis, and stomatitis are some of these skin reactions (Fig. 1.3). Contact with the skin or eyes could lead to severe burns or injuries. It is potentially lethal if breathed, swallowed, or exposed topically [77]. Initial

symptoms of hydrogen fluoride inhalation include severe respiratory tract itchiness, responses resembling asthma, and pulmonary oedema. Asthma may be brought on by recurrent exposure to aluminium fluoride through breathing, especially in work situations [77].

**Table 1.2 Standards of fluoride in drinking water by different agencies**

Agency/sources	Guideline (mg/L)	value
Bureau of Indian Standards (BIS)	Desired limit: 1.0 Permissible limit: 1.5	
EU Directives	1.5	
World Health Organization (International Standards for Drinking Water)	1.5	
United States Environmental Protection Agency (USEPA)	4.0	

### 1.3.2 Nitrate contamination in drinking water

Nitrate contamination in groundwater resources presents a significant global challenge due to its high solubility, making it one of the most widespread groundwater contaminants [78]. This contamination poses a grave concern for public health and safety and can contribute to the eutrophication of aquatic ecosystems. Understanding the context of nitrate contamination necessitates a deeper examination of the nitrogen cycle. Nitrogen is involved in a complex biogeochemical cycle encompassing a variety of biological and non-biological transformations [79]. These transformations result in a diverse array of inorganic and organic nitrogen compounds, which are all critical for the sustenance of various life forms. Within the specific context of wetlands, three key inorganic nitrogen forms are most relevant: ammonium ( $\text{NH}_4^+$ ), nitrite ( $\text{NO}_2^-$ ), and nitrate ( $\text{NO}_3^-$ ) [79]. Gaseous nitrogen can also exist in various forms within these ecosystems, including dinitrogen ( $\text{N}_2$ ), nitrous oxide ( $\text{N}_2\text{O}$ ), nitric oxide ( $\text{NO}$  and  $\text{NO}_2$ ),

and ammonia ( $\text{NH}_3$ ) [80]. Nitrate contamination poses a significant threat to the quality of groundwater resources worldwide. Unlike many other contaminants, its high solubility allows it to readily infiltrate the ground and pollute aquifers [78]. This contamination is particularly concerning due to its potential detrimental health effects. Raised nitrate concentrations in drinking water pose a serious risk for human health, particularly for infants. One of the most concerning health effects is methemoglobinemia, a condition that impairs the blood's oxygen-carrying capacity [81][82]. High nitrate intake has also been associated with an elevated risk of developing abdominal and intestinal cancers, highlighting the long-term health concerns associated with this contaminant. Understanding the sources of nitrate contamination is essential for designing and implementing effective mitigation strategies. Agricultural practices are a primary culprit, with the extensive use of fertilizers significantly contributing to nitrate leaching into groundwater [83]. Additional sources include animal farming operations, septic tank systems, atmospheric deposition, and industrial and municipal wastewater discharges [78]. Agricultural practices are widely recognized as a primary driver of nitrate contamination in groundwater resources [84]. Fertilizer application is a major culprit, with excess nitrate leaching from agricultural lands and infiltrating groundwater systems via runoff. This phenomenon is particularly prevalent in regions with intensive agriculture, where widespread use of fertilizers and animal manure significantly contributes to elevated nitrate levels in groundwater. While agricultural practices are a significant contributor, nitrate contamination can arise from various sources. Leakage from sewage systems, wastewater treatment processes without effective denitrification mechanisms, inadequate treatment and disposal of wastewater effluents, and the overuse of both fertilizers and animal waste all contribute to the problem [85]. These activities can contaminate many aquifers, particularly in areas where groundwater recharge is directly linked to surface water sources.

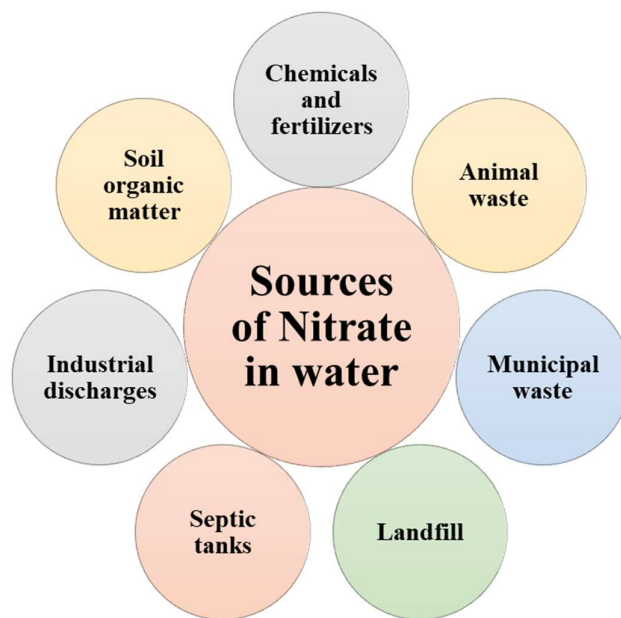
The persistence of nitrate contamination in groundwater necessitates a focus on preventive strategies. Due to the difficulty and cost associated with remediation efforts, prioritizing practices that minimize nitrate leaching from agricultural lands and other sources is crucial for ensuring the long-term viability and preservation of groundwater resources [85]. Nitrate contamination in aquatic systems poses a significant environmental threat by contributing to two major problems: eutrophication of surface waters and contamination of groundwater resources [86]. However, the detrimental effects extend beyond the environment, impacting human and animal health. Studies have also suggested associations between high nitrate intake and miscarriages, as well as non-Hodgkin's lymphoma [86]. Within the biological realm, nitrate undergoes a transformation through bacterial action. These bacteria convert nitrate ions ( $\text{NO}_3^-$ ) into nitrite ions ( $\text{NO}_2^-$ ), which can have detrimental consequences for animal health. One mechanism involves the combination of nitrite ions with blood pigments, forming methemoglobin, rendering the blood incapable of transporting oxygen. This can lead to acute poisoning within a short timeframe (30 minutes to 4 hours) in cattle that ingest plants or water high in nitrate [87]. Severe nitrate poisoning can even be fatal for livestock [88]. The persistence of nitrate contamination presents a significant challenge. Once nitrate infiltrates and reaches aquifers, it can remain a pollutant for decades, even with the implementation of effective measures to reduce future leaching [41]. This highlights the urgency of addressing current contamination and prioritizing preventative strategies.

### **1.3.2.1 Sources of nitrate contamination in groundwater**

Elevated nitrate levels in groundwater stem from various anthropogenic activities, posing a significant environmental and health threat. Agricultural practices are a primary contributor, with the overuse of fertilizers significantly increasing nitrate leaching into groundwater

[89,90]. However, agricultural sources are not the only culprits. Multiple other sources contribute nitrate into water bodies like (Fig. 1.4):

- i. **Agricultural Practices:** Excessive use of nitrogen fertilizers is a major driver of nitrate contamination, particularly in regions with intensive agriculture.
- ii. **Animal and Human Waste:** Nitrate contamination can also arise from improper management of animal waste and human sewage, especially in areas lacking proper sanitation infrastructure [91].
- iii. **Waste Disposal Practices:** Uncontrolled discharges of municipal and industrial wastewater, septic tank leakage, and landfill leachate can all contribute to nitrate pollution [90].
- iv. **Soil Organic Matter:** Decomposition of soil organic matter can also contribute to nitrate levels in groundwater [91].
- v. **Dietary Nitrate from Vegetables:** While not a direct source of groundwater contamination, Chung (2011) highlights the potential health risks associated with vegetable-borne nitrate and nitrite, particularly for infants under three months old [92]. High nitrate concentrations in vegetables can be a concern in some regions [93].



**Fig. 1.4 Different sources of nitrate in water**

### **1.3.2.2 Global and Indian scenario of nitrate contamination in water**

#### **1.3.2.2.1 International status of nitrate contamination in water**

Nitrate pollution in groundwater resources is a widespread environmental concern with significant public health implications. This issue transcends national borders, affecting countries across all continents [94].

Many European nations, including Great Britain, France, Germany, and Switzerland, grapple with nitrate contamination exceeding the WHO recommended limit of 50 mg/L for drinking water. In fact, a staggering 22 % of cultivated land in Europe exceeds this safety threshold [41]. Similar concerning levels have been documented in the United States and China [95,96]. Jalali (2005) found nitrate exceeding 50 mg/L in 37 % of wells in Hamadan, highlighting the problem in regions dependent on groundwater for drinking [97]. Sönmez et al. (2007) reported that 45 % of wells exceeded safe thresholds, signifying widespread contamination [98]. Fenton et al. (2011) documented the spatial and temporal variation of nitrate in shallow groundwater,

emphasizing the need for region-specific management strategies [99]. Beyond Europe, North America, and Asia: Countries like Israel, Spain (Mesa et al., 2002) [100], Bulgaria (Gatseva & Argirova, 2008) [101], Senegal (Sall & Vanclooster, 2009) [102], and Italy (Ghiglieri et al., 2009) [103] all report instances of nitrate contamination. A survey in Bulgaria identified excessive nitrate concentrations as the most prevalent issue in their drinking water [101]. Similarly, research in Pakistan by Kazmi and Khan (2005), Naeem et al. (2007), Farooqi et al. (2007), and Tahir and Rasheed (2008) documented widespread nitrate contamination in major cities [104–107].

#### **1.3.2.2.2 Indian status of nitrate contamination of groundwater**

India faces a significant challenge with nitrate contamination in groundwater resources, particularly within the Indo-Gangetic plain [108]. This geological region presents a heightened risk due to its specific physiographic characteristics. Studies have documented elevated nitrate levels in various locations across the country. For instance, Agrawal (2012) reported high nitrate concentrations in groundwater samples from Gangapur city in Rajasthan [109].

##### **➤ Data from Central Ground Water Board (CGWB)**

The Central Ground Water Board (CGWB), a government agency under the Ministry of Water Resources, regularly monitors nitrate levels in Indian groundwater. Tables 1.3 summarize their data on nitrate concentrations. These tables will provide valuable insights into the extent and spatial distribution of nitrate contamination in India.

**Table 1.3 Nitrate in water incidences in Indian districts (CGWB 2022)**

State	Cities [Nitrate (above 45 mg/l)]
Andhra Pradesh	Adilabad, Anantpur, Chittoor, Cuddapah, East Godavari, Guntur, Hyderabad, Karimnagar, Khammam, Krishna, Kurnool, Mahabubnagar, Medak, Nalgonda, Nellore, Nizamabad, Prakasam, Ranga Reddy, Srikakulam, Visakhapatnam, Vizianagaram, Warangal, West Godavari
Assam	-
Bihar	Aurangabad, Banka, Bhagalpur, Bhojpur, Darbhanga, Kaimur(Bha bua), Patna, Rohtas, Saran, Siwan
Chattisgarh	Bastar, Bilaspur, Dantewada, Dhamtari, Jashpur, Kanker, Kawardha, Korba, Mahasamund, Raigarh, Raipur, Rajnandgaon
Delhi	East Delhi, Central Delhi, New Delhi, North Delhi, North West Delhi, South Delhi, South West Delhi
Gujarat	Ahmedabad, Amreli, Anand, Banaskantha, Bharuch, Bhavnagar, Dahod, Jamnagar, Junagadh, Kachchh, Kheda, Mehesana, Narmada, Navsari, Panchmahals, Patan, Porbandar, Rajkot, Sabarkantha, Surat, Surendranagar, Vadodara
Haryana	Ambala, Bhiwani, Faridabad, Fatehabad, Gurgaon, Hissar, Jhajjar, Jind, Kaithal, Karnal, Kurukshetra, Mahendargarh, Panchkula, Panipat, Rewari, Rohtak, Sirsa, Sonapat, Yamuna Nagar
Himachal Pradesh	Una, Solan, Hamirpur, Kangra, Mandi, Kullu
Jammu & Kashmir	Jammu, Kathua, Anantnag, Kupwara
Jharkhand	Chatra, Garhwa, Godda, Gumla, Lohardaga, Pakur, Palamu, Paschimi Singhbhum, Purbi Singhbhum, Ranchi, Sahibganj
Karnataka	Bagalkot, , Bangalore, Belgaum, Bellary, Bidar, Bijapur, Chamrajnagar, Chikmagalur, Chitradurga, Davanagere, Dharwad, Gadag, Gulburga, Hassan, Haveri, Kodagu, Kolar, Koppal, Koorg, Mandya, Mysore, Raichur. Shimoga, Tumkur, Udupi, Uttar Kannada
Madhya Pradesh	Alirajpur, Anuppur, Ashok Nagar, Balaghat, Barwani, Betul, Bhind, Bhopal, Burhanpur, Chhatarpur, Chhindwara, Damoh, Datia, Dewas, Dhar, , Dindori, Guna, Gwalior, Harda, Hoshangabad, Indore, Jabalpur, Jhabua, Katni, Khandwa, Khargon, Katni, Mandla, Mandsaur, Morena, Narsimhapur, Neemuch, Panna, Raisen, Rajgarh, Ratlam, Rewa, Sagar, Satna, Sehore,

State	Cities [Nitrate (above 45 mg/l)]
	Seoni, Shahdol, Shajapur, Sheopur, Shivpuri, Sidhi, Singrauli, Tikamgarh, Ujjain, Umaria, Vidisha
Maharashtra	Ahmednagar, Akola, Amravati, Auragabad, Beed, Bhandara, Buldana, Chandrapur, Dhule, Gadchiroli, Gondia, Hingoli, Jalgaon, Jalna, Kolhapur, Latur, Mumbai, Nagpur, Nanded, Nandurbar, Nasik, Osmanabad, Parbhani, Pune, Sangli, Satara, Solapur, Wardha, Washim, Yavatmal
Odisha	Angul, Balasore, Bargarh, Bhadrak, Bolangir, Baudh, Cuttack, Deogarh, Dhenkanal, Gajapati, Ganjam, J.Singhpur, Jajpur, Jharsuguda, Kalahandi, Kendrapara, Keonjhar, Khurda, Koraput, Malkangiri, Mayurbhanj, Nawapada, Nayagarh, Phulbani, Puri, Sambalpur, Sundergarh, Sonpur
Punjab	Amritsar, Barnala, Bhatinda, Faridkot, Fatehgarh Sahib, Firozpur, Gurdaspur, Hoshiarpur, Jalandhar, Kapurthala, Ludhiana, Mansa, Moga, Muktsar, Nawan Shahr, Patiala, Ropar, Rupnagar, Sangrur, Tarn-Taran
Rajasthan	Ajmer, Alwar, Banswara, Baran, Barmer, Bundi, Bharatpur, Bhilwara, Bikaner, Chittaurgarh, Churu, Dausa, Dhaulpur, Dungarpur, Ganganagar, Hanumangarh, Jaipur, Jaisalmer, Jalore, Jhalawar, Jhunjhunu, Jodhpur, Karauli, Kota, Nagaur, Pali, Partapgarh, Rajasamand, Sirohi, Sikar, Swai Madhopur, Tonk, Udaipur
Tamil Nadu	Chennai, Coimbatore, Cuddalore, Dharmapuri, Dindigul, Erode, Kancheepuram, Kanyakumari, Karur, Madurai, Namakkal, Nilgiris, Perambalur, Pudukotai, Ramanathanpuram, Salem, Sivagangai, Theni, Thiruvannamalai, Thanjavur, Tirunelveli, Thiruvallur, Trichy, Tuticorin, Vellore, Villupuram, Virudhunagar
Uttar Pradesh	Agra, Aligarh, Allahabad, Ambedkar Nagar, Auraiya, Azamgarh, Badaun, Baghpat, Balrampur, Banda, Barabanki, Bareilly, Basti, Bijnor, Bulandsahr, Chitrakoot, Etah, Etawah, Fatehpur, Firozabad, GB Nagar, Ghaziabad, Ghazipur, Hamirpur, Hardoi, Hathras, Jaunpur, Jhansi, Kannauj, Kanpur Dehat, Lakhimpur, Mahoba, Mathura, Meerut, Mau, Moradabad, Muzaffarnagar, Mirzapur, Raebarelli, Rampur, Sant Ravidas Nagar, Shajahanpur, Sitapur, Sonbhadra, Sultanpur, Shravasti, Siddarth Nagar, Unnao
Uttarakhand	Dehradun, Haridwar, Udhamasinghnagar
West Bengal	Bankura, Bardhaman

### 1.3.2.3 Human health risks from nitrate contamination in drinking water

Nitrate contamination in drinking water poses a significant public health threat due to its potential to cause various adverse health effects [41,110]. These effects can be categorized into three primary mechanisms:

- i. **Primary Toxicity:** Direct effects of nitrate ingestion include abdominal pain, diarrhea, vomiting, and methemoglobinemia, particularly in infants under six months old [111]. Methemoglobinemia, also known as "blue baby syndrome," decreases the blood's capacity to carry oxygen, leading to symptoms like shortness of breath and bluish skin discoloration [111].
- ii. **Secondary Toxicity:** Microbial conversion of nitrate to nitrite in the gut can contribute to methemoglobinemia, especially in infants. Nitrite readily binds to haemoglobin, forming methemoglobin, hindering oxygen transport [111].
- iii. **Tertiary Toxicity:** The interaction between secondary or tertiary amines and nitrite in the stomach can form N-nitroso compounds. Some N-nitroso compounds are carcinogenic, teratogenic (causing birth defects), and mutagenic (causing genetic mutations) [111].

Studies suggest possible links between chronic exposure to high nitrate levels and several health problems, including:

- **Gastrointestinal Cancers:** Research by Seyyedsalehi et al. (2023) indicates a potential exposure to nitrates is associated with increased risk of stomach and prostate cancer [112].
- **Other Cancers:** Studies like those by Inoue-Choi et al. (2015) suggest a potential link between nitrate intake and cancers of the bladder and ovary [113].

- **Thyroid Issues:** Nitrate may impede the thyroid gland's ability to absorb iodine, potentially leading to goiter [114].
- **Respiratory Tract Infections:** Some studies suggest a possible correlation between high nitrate intake and increased risk of respiratory infections in children [115].
- **Diabetes:** A potential link between nitrate exposure and type 2 diabetes has been suggested [116].

#### 1.4 TECHNIQUES FOR ERADICATING IONIC IMPURITIES FROM WATER

The presence of ionic contaminants in water poses a significant threat to human health and environmental well-being. Consequently, efficient removal of these impurities is paramount. A diverse array of established methods has been developed to address this challenge, each offering unique advantages and considerations [117,118]. This section explores some of the most prevalent techniques employed for the elimination of ionic impurities from water supplies.

- i. **Ion Exchange:** Ion exchange utilizes synthetic resins containing charged functional groups that exhibit high selectivity towards specific ionic species. These resins operate based on the principles of ion recognition and exchange. The charged functional groups on the resin surface act as ligands, forming reversible electrostatic interactions with target ions in the contaminated water as it traverses a designated column or bed. Concurrently, the resin releases innocuous ions that were previously bound to its functional groups, maintaining electrical neutrality within the resin matrix [119,120].

**Pros:** Ion exchange is a highly effective method for the targeted removal of specific ionic contaminants, including nitrates, heavy metals, and fluorides. Furthermore, many resins possess regeneration capabilities, allowing them to be reused after reaching

saturation with captured contaminants. This regeneration process extends the operational lifespan of the resin and reduces waste generation.

**Cons:** Selecting the appropriate resin for a specific application is crucial. Improper operation or resin exhaustion can lead to contaminant leakage, compromising water quality. The regeneration process itself generates wastewater that necessitates proper treatment and disposal to safeguard the environment.

- ii. **Membrane Filtration:** Membrane filtration utilizes semi-permeable membranes that act as selective barriers based on the size and charge properties of dissolved species in water. These membranes are typically composed of synthetic polymers with a network of microscopic pores. The pore size and the chemical properties of the membrane material determine its selectivity. For ionic contaminants, the membrane can discriminate based on size exclusion and electrostatic interactions. Smaller ions, along with water molecules, can pass through the pores due to their smaller size. Conversely, larger ions are often repelled by the membrane's surface charge, preventing their passage. This selective transport process allows for the purification of water by retaining the unwanted ionic impurities while permitting the permeation of the purified water [7,121].

**Pros:** Reverse osmosis (RO) is a widely used and highly effective membrane filtration technique for desalination and the removal of various ionic impurities from water. Other membrane filtration technologies, such as nanofiltration and electrodialysis, offer varying degrees of selectivity and can be chosen based on the specific water treatment needs.

**Cons:** The effectiveness and economic feasibility of membrane filtration can be influenced by several factors, including the type of membrane employed, pore size, and operating pressure. Pretreatment of the water source may be required to prevent membrane fouling and ensure optimal performance.

- iii. **Chemical Precipitation:** Chemical precipitation involves the introduction of specific chemicals, known as precipitating agents, into the water. These precipitating agents react with dissolved ions in a controlled chemical reaction, transforming them into insoluble precipitates. The selection of precipitating agents is crucial and depends on the target contaminant. Once formed, these insoluble precipitates can then be effortlessly removed from the water through sedimentation or filtration techniques, significantly reducing the concentration of the targeted ionic impurities [122,123].

**Pros:** Chemical precipitation offers a targeted approach for removing specific metals by converting them into insoluble compounds. This method can be particularly effective for large-scale treatment applications.

**Cons:** Careful selection of precipitating agents is essential to ensure they target the desired ions and minimize the formation of unwanted byproducts. The process can generate significant amounts of sludge that require proper disposal, adding to the overall treatment costs.

- iv. **Coagulation and Flocculation:** Coagulation and flocculation are often employed in tandem to remove suspended particles and some ionic contaminants from water. Coagulants destabilize suspended particles, causing them to aggregate and form larger clusters. Flocculants then bridge these clusters, creating even larger flocs that settle more readily or are more easily eliminated through filtration [124].

**Pros:** Coagulation and flocculation are effective methods for removing turbidity and suspended solids from water. These processes can also be beneficial for removing some ionic impurities that are associated with the particles being coagulated. Additionally, they are relatively simple and cost-effective to implement.

**Cons:** The selection of coagulants and flocculants needs to be optimized for the specific water characteristics and target contaminants. Improper dosing can lead to ineffective floc formation or the generation of excessive sludge, increasing disposal costs.

- v. **Electrochemical treatment:** Electrochemical treatment is a promising technique for the removal of ionic contaminants, including nitrate and fluoride, from water. This method utilizes an electric current to drive the reduction or oxidation of the target ions, effectively removing them from the water. The process involves the application of an electric potential across the water, which induces the ions to migrate towards the respective electrodes, where they can be removed or transformed into less harmful substances. Electrochemical treatment has the potential to be a highly efficient and versatile approach for the purification of water, as it can be tailored to target specific ionic contaminants based on their electrochemical properties [125,126].

**Pros:** Electrochemical treatment offers advantages such as high efficiency, the potential for in-situ generation of disinfectants, and the ability to operate at ambient temperatures.

**Cons:** Disadvantage of electrochemical treatment include the potential for the generation of hazardous byproducts and the need for ongoing electrical input, which can increase operational costs (Zhang et al., 2019) (nageeb, 2013)

- vi. **Biological Denitrification:** Biological denitrification is a process in which nitrate is converted to nitrogen gas through the metabolic activities of microorganisms. It plays a crucial role in the nitrogen cycle by converting nitrate into harmless nitrogen gas ( $N_2$ ) that is released back into the atmosphere. The process involves the use of denitrifying bacteria, which utilize nitrate as an electron acceptor during their respiration, converting it to harmless nitrogen gas. Denitrifying bacteria use organic matter in the water as fuel and create an oxygen-free environment (anoxic) by consuming dissolved oxygen. In this anoxic environment, they employ nitrate as an alternative electron acceptor for respiration. Through a series of enzymatic reactions, nitrate is sequentially reduced to nitrite, nitric oxide, nitrous oxide, and ultimately, nitrogen gas, which is then released back into the atmosphere [86,127].

**Pros:** This method offers the advantage of being a selective and efficient approach for the removal of nitrate from water, without generating concentrated waste streams. It relies on naturally-occurring bacteria, which reduces the need for chemical additives, making it a more sustainable approach. Biological denitrification can be a cost-effective option when the water source has enough organic carbon to sustain the necessary microbial activity.

**Cons:** The process may require extensive post-treatment to ensure the removal of any residual microbial contaminants and byproducts, as the introduction of live bacteria into the water supply raises concerns about potential health and environmental impacts. Creating and sustaining anoxic conditions can be difficult in some treatment systems. Biological denitrification can also lead to the unintended production of nitrous oxide ( $N_2O$ ) if the process is not carefully managed.

#### 1.4.1 Advantages of Adsorption for Fluoride and Nitrate Removal:

- i. **High Efficiency:** Adsorption offers excellent removal efficiency for both fluoride and nitrate. The large surface area of adsorbent materials facilitates the capture of a significant amount of contaminant ions.
- ii. **Wide Applicability:** The adsorption process can be effectively implemented for a broad range of water sources, including groundwater and surface water with varying levels of contamination.
- iii. **Regeneration Potential:** Certain adsorbent materials can be regenerated, allowing for their reuse after reaching saturation with contaminants. This reduces waste generation and extends the lifespan of the treatment system.
- iv. **Simplicity and Scalability:** Adsorption systems are generally less complex to operate compared to some alternative methods. They can be readily scaled to accommodate varying treatment capacities, making them suitable for both small-scale and large-scale applications.
- v. **Environmentally Friendly:** This method utilizes readily available adsorbent materials and often avoids the use of harsh chemicals. The regeneration process, if employed, can be designed to minimize environmental impact.

1.4.2 Adsorbents used in fluoride and nitrate remediation

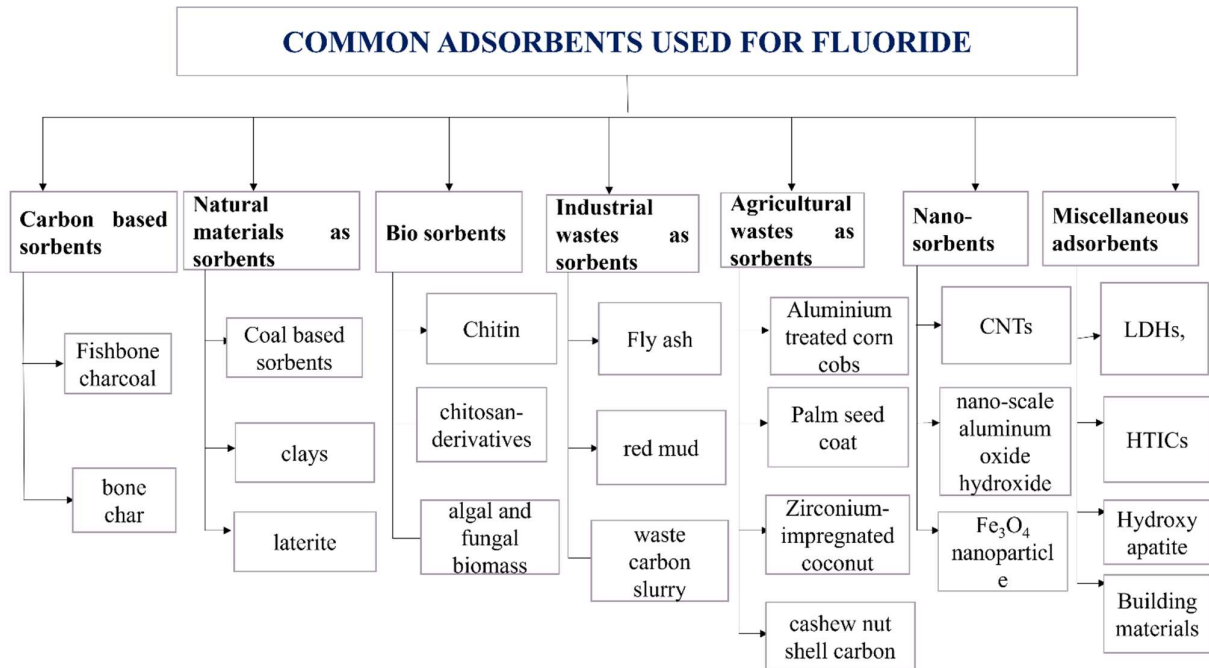


Fig. 1.5 Some common adsorbents used for fluoride removal from water

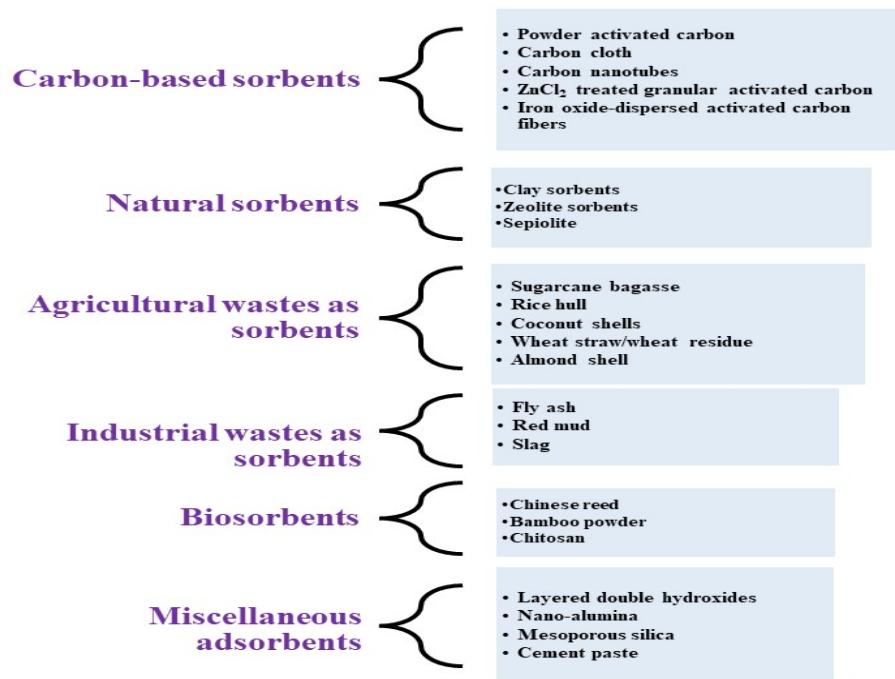


Fig. 1.6 Some common adsorbents used for fluoride removal from water

## 1.5 BIOCHAR

A carbon-rich, porous solid known as "biochar" is produced when biomass is thermally disintegrated at 350–700 °C in a reactor with little to no ambient air [128]. Using several techniques, the physicochemical characterization of biochar reveals that its surface area and porosity are less. However, it is rich in surface functional groups (hydroxyl, ketone, carbonyl, carboxyl, etc.) and minerals like NPK [129]. That is why it is used as a catalyst in the reaction, as a supporting base for catalysts and as an adsorbent for various pollutants [130,131]. Notably, biochar is an attractive substrate for synthesizing various valuable materials, given its easily tunable surface functionality and porosity [132]. Since anthropogenic carbon dioxide emissions can be reduced by transforming waste biomass or feedstock into biochar, the extensive usage of biochar-modified materials is considered a sustainable approach [128,133]. Due to its inexpensive cost and abundant availability, biochar is frequently employed as an adsorbent for removing fluoride. Teff (*Eragrostis tef*) straws were used to develop activated biochar having a surface area equal to 627.7 m<sup>2</sup>/g and hydro char. These adsorbents show high fluoride loading capacities of 212 mg/g and 88.7 mg/g, respectively [134]. Although pristine biochar has an excellent capacity for adsorbing organic chemicals, heavy metals etc., it has a significantly lower capacity for adsorbing anionic contaminants like phosphate and fluoride [135,136]. Biochar has been modified for fluoride adsorption to overcome raw biochar's limited adsorption ability. Raw biochar is functionalized in many ways, such as via co-precipitation, impregnation or chemical coating of different metals, oxides, hydroxides, non-metals, acids, etc. [137,138].

### 1.5.1 Production of Biochar

Pyrolysis is the thermal disintegration of lignocellulosic products in an oxygen-deficient environment. The word is derived from two Greek words: "lysis," which denotes disintegration into constituent elements, and "pyro," which signifies fire. In the Middle East and Southern

Europe, 5500 years ago, pyrolysis was first utilised to prepare charcoal [139]. Based on the difference in heating rate, pyrolysis may be broadly divided into fast and slow pyrolysis. The thermal breakdown of biomass having calorific values of  $11 \text{ MJ kg}^{-1}$  at medium temperatures (i.e., 400–600 °C) with a heating rate of more than 300 °C/min and a short vapour residence time is known as fast pyrolysis. The products of this process are biochar, syngas, and bio-oil [132]. The combustion of biomass over a broader range of temperatures (300-800 °C), with a slow heating rate (5-7 °C/min) and an extended vapour residence time, is referred to as "slow pyrolysis." Biochar is the result of this procedure [132]. Table 1.4 provides an overview of the traits of several pyrolysis processes and their usual biochar yields [140,141].

Many centuries have passed since biomass was first pyrolysed to create biochar [142]. Various pyrolysis methods can be used to synthesize biochar, such as flash pyrolysis, fast pyrolysis, slow pyrolysis, and pyrolytic gasification. Since pyrolysis produces substantial amounts of renewable bioenergy, such as bio-oil and gas, in addition to biochar, producing biomass from biomass is economical and environmentally sustainable. The concurrent reduction in greenhouse gas emissions is an added benefit [140].

If the biomass had a high moisture content (between 42 % and 62 %), It was noted that biochar yield could be improved by applying high pressures [143]. Numerous recent investigations have verified this [144–146]. The biomass's intrinsic composition, such as cellulose, hemicelluloses, lignin, and inorganic species, also plays a vital role in biochar production. Alkali or alkali earth metal complexes have an inherent catalytic activity that decomposes biomass and results in char formation [147].

*Slow pyrolysis* is a conventional method used for producing biochar that is still frequently employed. However, due to some drawbacks, such as energy inefficiency and time requirements, it is questionable that it remain the "technology of choice" for manufacturing biochar in the future. However, if the coproducts like bio-oil and syngas can be used in

appropriate applications, they will undoubtedly be more economical and environmentally sustainable. To overcome drawbacks of slow pyrolysis- fast pyrolysis, flash pyrolysis, and pyrolytic gasification are some efficient alternatives. These technologies produce a lower biochar yield than slow pyrolysis. However, their energy efficiency is much higher, and the emissions of pollutants are dramatically decreased, making them more economical and sustainable [132]. Different methods employed for synthesising biochar and its modification are depicted in Fig. 1.5

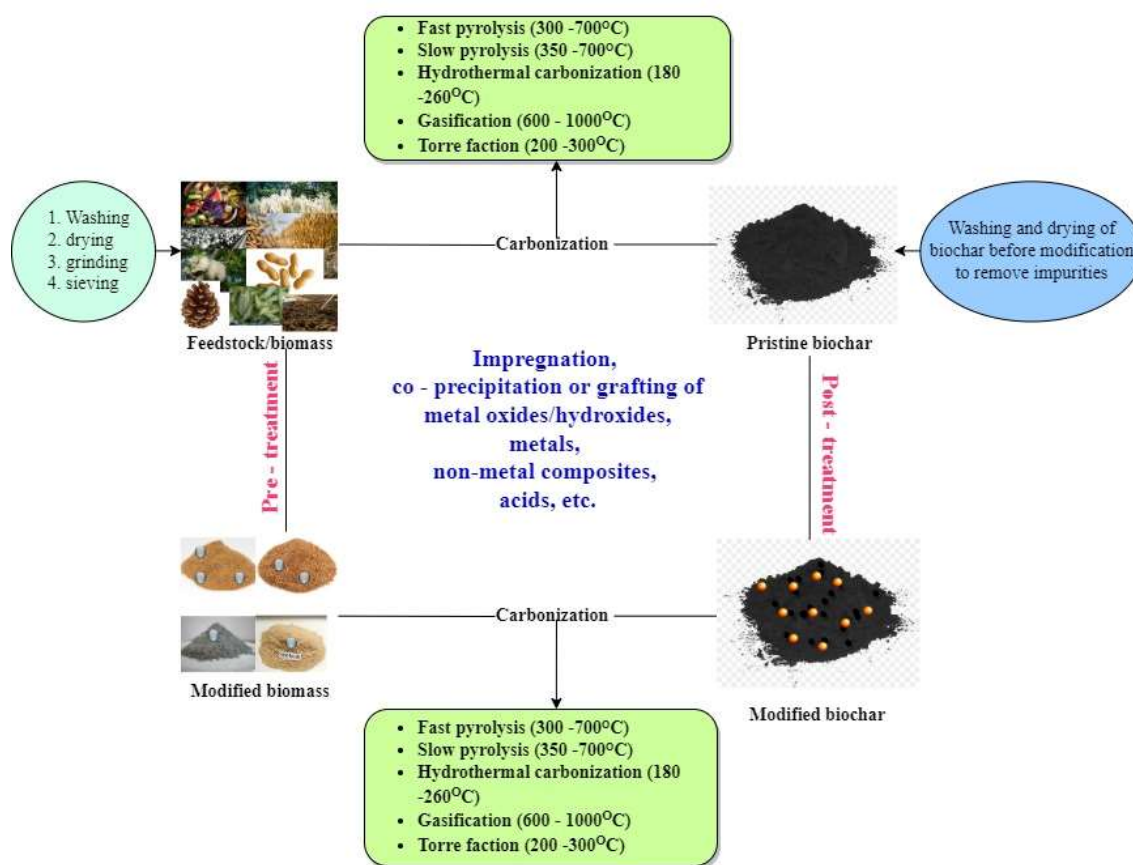


Fig. 1.5 Synthesis and modification of biochar.

**Table. 1.4 Different traits of pyrolysis processes and their biochar yield**

		<b>slow pyrolysis</b>	<b>fast pyrolysis</b>	<b>flash pyrolysis</b>	<b>pyrolytic gasification</b>
<b>Heating (°C/Min)</b>	<b>Rate</b>	5–7	300–800	~1000	–
<b>Temperature (°C)</b>		300–800	400–600	400–1000	750–1000
<b>Vapour time</b>	<b>residence</b>	More than 1 h	0.5–10 s	Less than 2 s	10–20 s
<b>End product</b>		biochar	bio-oil	gas	gas
<b>Biochar yield (%)</b>	<b>(Wt.)</b>	35–50	15–35	10–20	10–20