

# Chapter 1

## Introduction



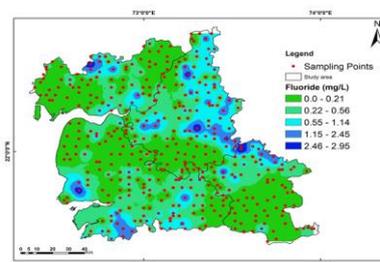
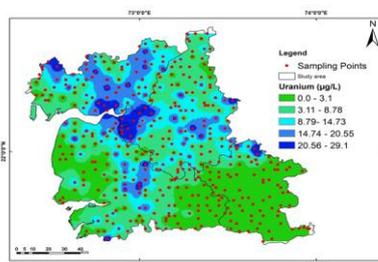
Samples collection



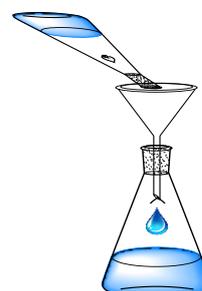
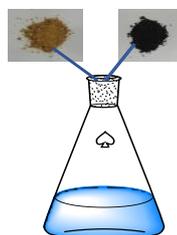
Analysis on field



Laboratory analysis



Groundwater monitoring and analysis



Remediation of uranium and fluoride

## 1.1.General

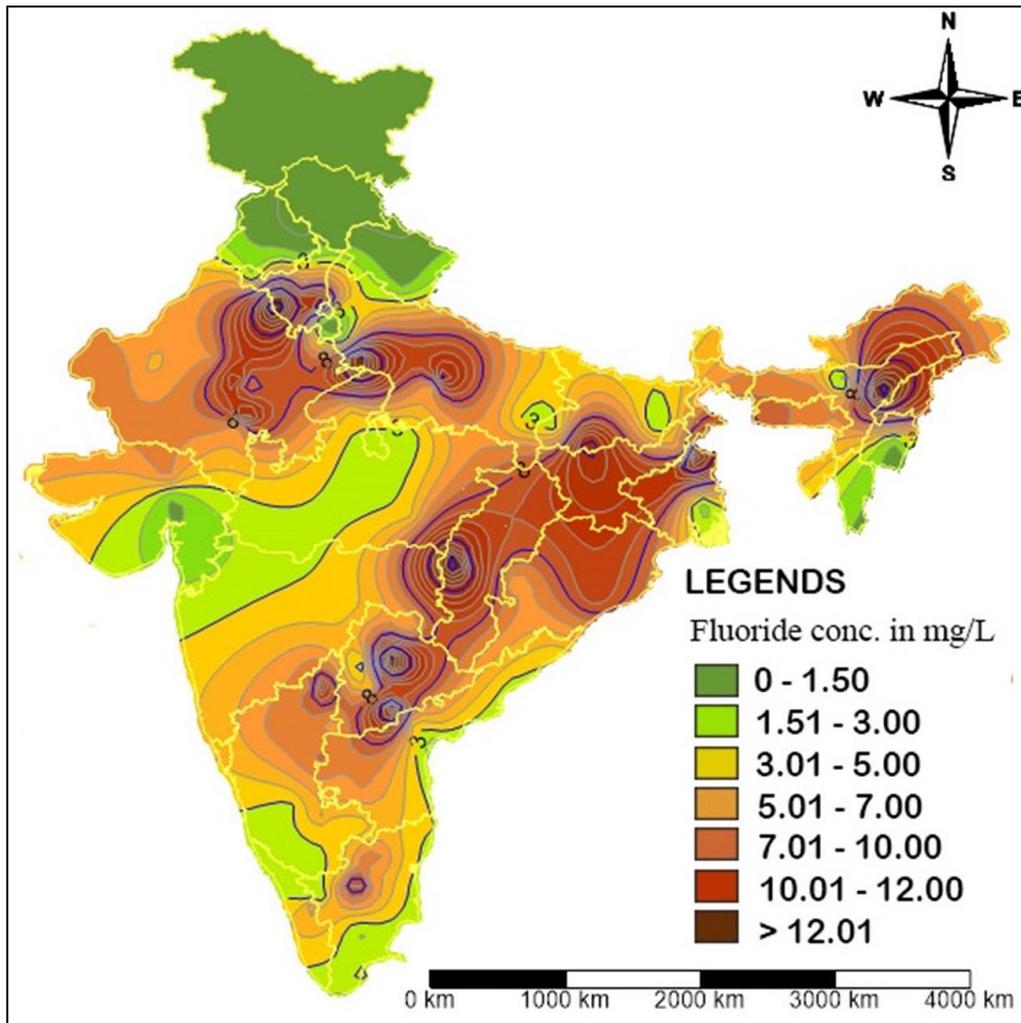
Groundwater is a vital natural resource for all aspects of our lives and environment. About two-thirds of the global population rely on groundwater resources (Katsanou and Karapanagioti, 2019). Globally, groundwater systems are under increased threat of contamination and exploitation due to the rapid growth of the population. Globally, numerous studies have reported dropping groundwater tables, diminishing groundwater reserves, and deteriorating groundwater quality (Verma, 2019; Zhu et al., 2015). In India, groundwater is the most dependable source of clean and fresh water. However, water quality problems have been noted in several areas of the country (Kumar et al., 2021; Trivedi et al., 2012). Higher levels of Arsenic, Uranium, Fluoride, Iron, and natural geological phenomena determine the salinity of groundwater, but day-to-day human activities accelerate the concentration of these contaminants in groundwater. Water pollution from human activities like mining and the disposal of industrial waste also results in nitrate and other heavy metal contamination.

## 1.2.Fluoride

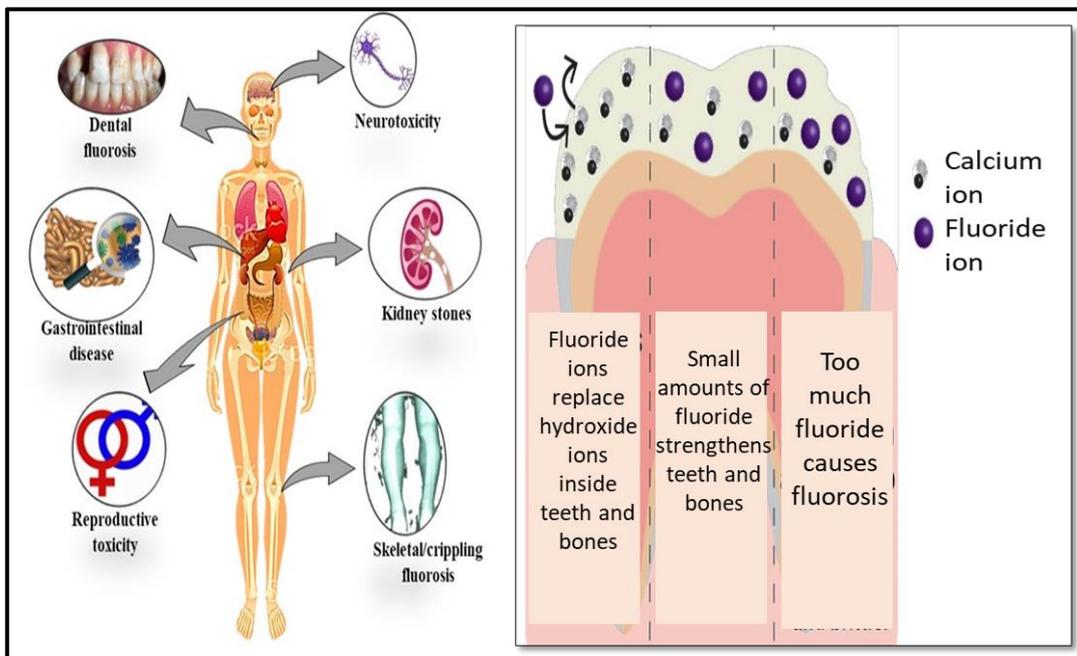
As the thirteenth most prevalent element in the earth's crust, fluoride is the ionic form of fluorine. The main dietary source of fluoride is water. It has gained the serious attention of many researchers due to its dual property. Fluoride is beneficial for human beings (beneficial effect on teeth and bones) when it is present up to a certain concentration in drinking water, but excess amount (above 1.5ppm of WHO limit) of fluoride in drinking water poses several adverse health effects like fluorosis, skeleton fluorosis, hypertension, and nervous system damage, etc.

In the semiarid regions of India, excessive fluoride levels pose a natural problem with groundwater quality (Mukherjee and Singh 2018; Mishra et al., 2017). Fluoride is one of the geogenic contaminants occurring in groundwater in various places of India, including Gujarat (Nizam et al., 2022), and has gained the serious attention of many researchers. **Figure 1.1** shows that almost every Indian state—including Rajasthan, Telangana, Tamil Nadu, Gujarat, West Bengal, Uttar Pradesh, Madhya Pradesh, Karnataka, Assam, Bihar, Chhattisgarh, Jharkhand, Orissa, Haryana, Manipur, and Punjab has high groundwater fluoride concentrations (Ali et al., 2019; DNA, 2012).

Small levels of fluoride (0.5 to 1 mg/L) are known to be advantageous for human health in the formation and maintenance of healthy teeth and bones. It supports enamel hardening and reduces the occurrence of tooth decay.



**Fig.1.1.** Indian scenario: spatial distribution of fluoride (Mukherjee and Singh, 2018)



**Fig.1.2.** Health hazards of fluoride exposure route and dental fluorosis.

Hence, a lack or excess of fluoride in our diet endangers human health. Consumption of less fluoride than advised produces detrimental health effects such as dental cavities, insufficiency of enamel production, and deficit of bone mineralization, particularly in youngsters. However, excess exposure ( $>1.5\text{mg/L}$ ) of fluoride causes calcium ions in teeth and bones to be replaced by fluoride due to its electronegative property, causing pathological changes in teeth and bones resulting in dental and skeletal fluorosis (**Figure 1.2**) (Ali et al., 2019).

### 1.3.Uranium

Uranium is a radioactive element that is found in nature and has an atomic number of 92 that is found in low concentrations in the earth's crust ( $2.8\ \mu\text{g/g}$ ) since its origin (CGWB, 2020). Intrusive igneous rocks such as alaskite, granite, pegmatite, monazite, and silicate-rich rocks are some of the rocks that are reported to contain uranium (Gronowski, 2013).

#### 1.3.1.Speciation and transportation of uranium in groundwater:

Uranium concentration in groundwater is affected by a variety of physical and chemical factors that regulate the interactions between rock and water as well as surface water and groundwater. The key mechanisms governing uranium mobility and speciation in groundwater are adsorption of organic and oxyhydroxides, dissolution/precipitation processes, pH, and redox properties of water (Smedley and Kinniburgh, 2023).

However, the concentration of uranium in groundwater is on the rise due to human activities such as the use of phosphate fertiliser, fly ash, emissions from the nuclear sector, and mill tailings. Uranium exists in nature as  $^{235}\text{U}$  and  $^{238}\text{U}$ , each of which has a distinct radioactive property. Nonetheless, because the molecular behaviour of these two isotopes is the same, any one of them would impact individuals in the same manner.

Hexavalent uranium can be found as stable uranyl hydroxide or carbonate complexes ( $\text{UO}_2(\text{CO}_3)_2^{2-}$ ) in an aqueous solution with a pH greater than 7 (Byrne et al., 2021). Uranium in its tetravalent form is comparatively insoluble and is present in ores and minerals primarily. Although with time, weathering and chemical transformation causes a change in uranium's oxidation state from tetravalent U(IV) to hexavalent U(VI) dissolving or mobilizing uranium in groundwater (Liesch et al., 2015). The permissible limit guidelines of uranium in drinking water in various countries are listed in **Table 1.1**.

Uranium is mainly used in the nuclear industry as fuel in nuclear power plants to produce energy, and also in nuclear weapons and glass production (Awan and Khan, 2015). Further, human activities like mining, mineral exploration, industry's use of fossil fuels and the

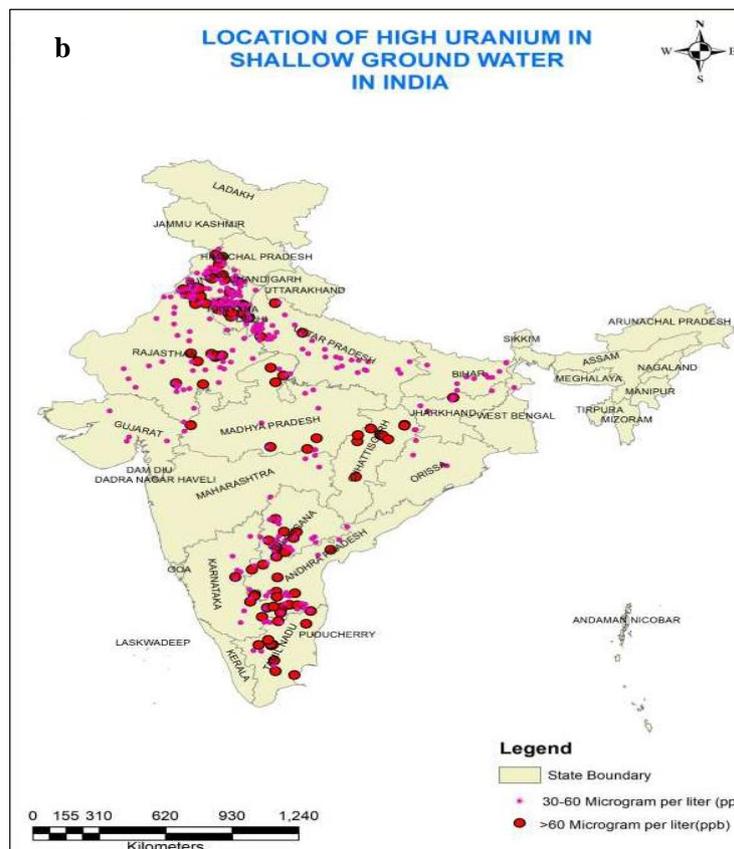
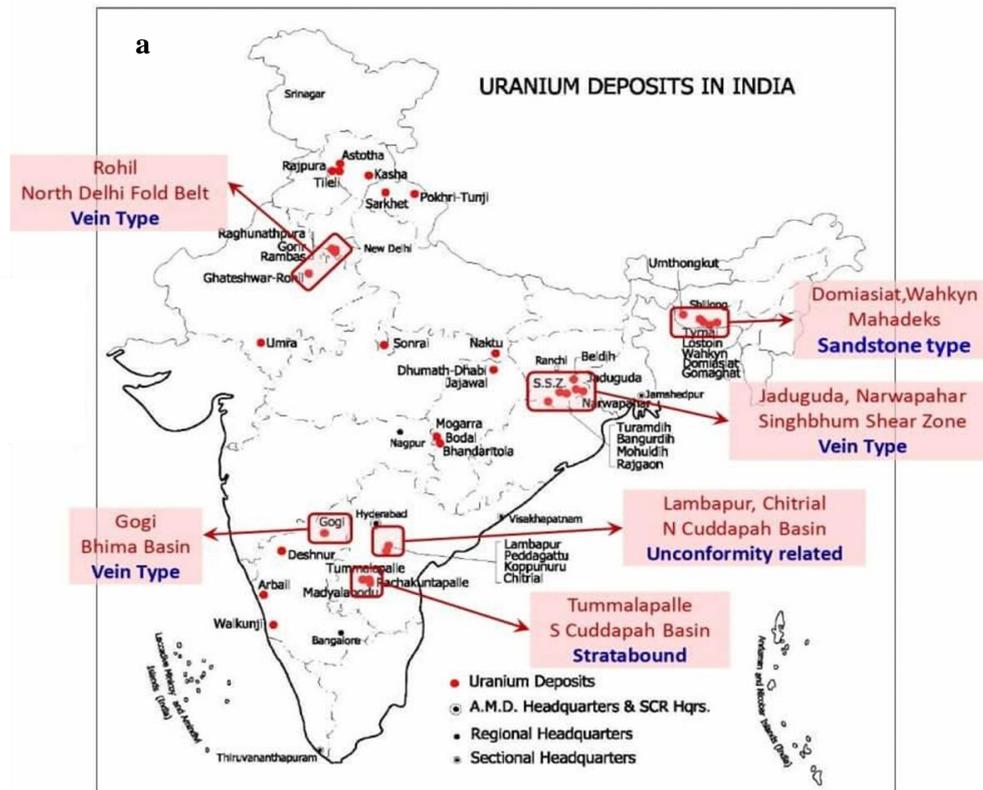
disposal of municipal waste, could raise the amounts in the environment (Balaram et al., 2022). Uranium is an emerging pollutant being reported globally (CGWB, 2020).

**Table 1.1.** Guideline values of uranium (Sahoo et al., 2020)

Sr. No.	Country/ agency/ Body	Limits/ guideline values (ppb)
1.	India (AERB*)	60
2.	Australia	17
3.	Bulgaria	60
4.	Canada	20
5.	Czech Republic	964
6.	Finland	100
7.	Germany	10
8.	Russian Federation	15
9.	Slovenia	6.8
10.	Slovakia	346
11.	Sweden	15
12.	Switzerland	30
13.	USA	30
14.	WHO	30

\*AERB – Atomic Energy Regulatory Board

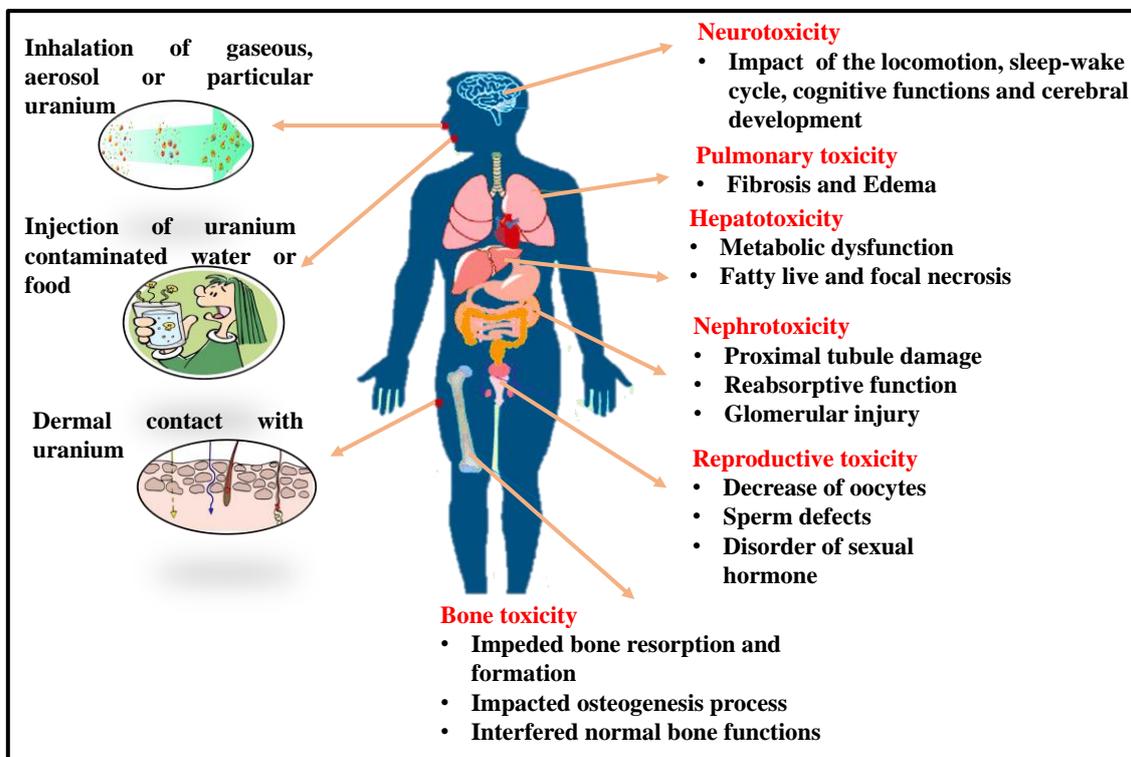
Numerous deposits of uranium have been discovered in some regions of India, including Jharkhand, Meghalaya, Telangana, Karnataka, Andhra Pradesh, and Rajasthan, as depicted in **(Figure 3(a))**, wherein Jharkhand has the largest uranium mineral reserves (Sarangi, 2022). However, as can be seen in **(Figure 3(b))**, shallow groundwater uranium is spread in many parts of India beyond permissible limits due to various geogenic and anthropogenic activities (such as the use of nitrate and phosphate-based fertilizers in agricultural fields, and industrialization) and decline in water tables as a result of overexploitation.



**Fig. 3. (a)** Major uranium deposits across India (Gupta and Sarangi, 2005) and **(b)** uranium distribution beyond permissible limits in shallow groundwater across India (CGWB, 2020)

### 1.3.2. Possible health hazards due to uranium:

Uranium, when it accumulates in our body, causes chemical and radiological effects that ultimately leads to various human health hazards affecting kidney, bone, liver, the reproductive system, lungs, and the nervous systems (Mahfoudhi and Boufi, 2020) (**Figure 1.4**). There are various compounds made from uranium, including uranyl nitrate, uranyl fluoride, and uranium tetra chloride that are soluble or moderately soluble in water. These compounds through ingestion enter the kidney and ultimately cause chemical toxicity. Continuous exposure to insoluble compounds of uranium, such as uranium dioxide, uranium peroxide, and uranium trioxide, increases the chance of lung carcinoma in human beings (ATSDR, 2013). High Uranium dosages can result in tissue damage in the kidneys subsequently followed by failure of the kidney and ultimately death.



**Fig.1.4.** The primary exposure route and possible health risks of uranium in human body

## 1.4. Physico-chemical parameters

Physico-chemical parameters are essential aspects for maintaining and determining groundwater's quality and safety for drinking, so, it is necessary to determine its pH, TDS, electrical conductivity (EC), as well as the presence of anions and cations. Physico-chemical parameters also help in modeling the speciation of metal and additional components that are

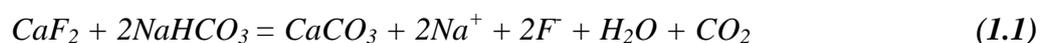
present in aquatic environments due to natural and anthropogenic activities (Khurelbaatar et al., 2022). **Table 1.2** lists the guidelines for various parameters of drinking water.

**Table 1.2.** Drinking water guidelines

Sr.No.	Parameters	BIS 2012/(WHO, 2011) limits	
		Acceptable limit	Permissible limit
1	pH	6.5 – 8.5	No relaxation
2	TDS (mg/L)	600	1000
3	EC (µS/cm)	-	1500
4	F <sup>-</sup> (mg/L)	1	1.5
5	Cl <sup>-</sup> (mg/L)	250	1000
6	NO <sub>3</sub> <sup>-</sup> (mg/L)	45	-
7	SO <sub>4</sub> <sup>2-</sup> (mg/L)	150	400
8	*TH (mg/L)	300	600
9	Ca <sup>2+</sup> (mg/L)	75	200
10	Mg <sup>2+</sup> (mg/L)	50	150
11	HCO <sub>3</sub> <sup>-</sup> (mg/L)	-	300

\*TH= Total Hardness

Seasonal variation also changes the intensity of different hydro-chemical processes such as oxidation-reduction potential or evaporation which can increase or decrease the rate at which minerals dissolve in the groundwater (Aladejana et al., 2020). Uranium mobility and speciation are also affected by associated physico-chemical parameters in aquifers (Eróss et al., 2018). U(IV) and U(VI) species are predominant in groundwater. Under reducing conditions U(IV) is strongly insoluble and tends to precipitate whereas in oxidizing conditions U(VI) in the form of uranyl nitrate is highly mobile. Some water parameters such as carbonate, phosphate, hydroxides, etc. enhance the mobility of uranium (Eróss et al., 2018). The most favourable circumstances for fluoride desorption from fluoride-containing minerals were found in alkaline water. Thus, fluoride concentration and mobility in aquifers can be enhanced by groundwater alkalinity (Mukherjee and Singh, 2018). In addition, as **Equation 1.1** illustrates, a high level of NaHCO<sub>3</sub> in groundwater accelerates the rate at which fluoride is soluble from fluorite (CaF<sub>2</sub>) minerals in groundwater as a result of the interaction between water and minerals (Mukherjee and Singh, 2018).



## 1.5. Studies on Groundwater Quality in India

In many regions of the world, groundwater contaminated with fluoride, arsenic, nitrate, chromium, cadmium, mercury, high water hardness, or other pollutants when consumed tends to cause a serious health risk (Li et al., 2021). It is widely accepted that the majority of India depends on the use of groundwater for domestic purposes either directly or indirectly as well as for agriculture and industrial processes. Arsenic pollution has a significant negative impact on the quality of the groundwater including in West Bengal, certain areas of Uttar Pradesh, Bihar, Jharkhand, Assam, Chhattisgarh, and Punjab (Shaji et al., 2021).

According to a study done on the groundwater quality in Ghaziabad, Uttar Pradesh, urban areas had somewhat greater levels of heavy metal pollution than peri-urban areas due to industrialization (Chabukdhara et al., 2017). However, Varanasi's water quality index (WQI) was poor despite its limited industrial activities. The deterioration was attributed to overexploitation, anthropogenic activities such as industrialization and urbanization, and agricultural practices (Singh et al., 2015).

In the semi-arid region of Siddipeta-Vagu, Telangana, India, the nitrate content of the groundwater samples ranged from 9 to 348 mg/L wherein 61% of the samples surpassed the 45 mg/L maximum permissible level in drinking water. On the other hand, 51% of the samples were reported to exceed the 1.5 mg/L threshold of fluoride concentration (Adimalla and Wu, 2019).

Humbarde et al. undertook a hydrogeochemical investigation of basaltic terrain in Beed, Maharashtra, India. Samples of groundwater obtained from bore and dug wells were analyzed in the pre-monsoon (PRM) and post-monsoon (POM) seasons. The outcomes were compared with the requirements for the quality of drinking water. Research has demonstrated that the higher concentrations of TDS,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$  may be related to industrial or human activity, landfill ash deposits, and basaltic rock weathering (Humbarde et al., 2014).

The suitability of groundwater in the Ariyalur district of Tamil Nadu, India, for agriculture and drinking was investigated by Devaraj et al. (2016). On comparing the geochemical parameters with those recommended by WHO, the majority of the samples were deemed unfit for human consumption but appropriate for irrigation, according to the classification of the samples using criteria such as sodium adsorption ratio (SAR) and residual sodium carbonate (RSC), TH, Base Exchange Index, and EC. The geochemical aspects of the groundwater have been examined using Piper plots and Gibbs plots, which demonstrated that

anthropogenic activities, ion exchange, and weathering controlled the region's groundwater chemistry (Devaraj et al., 2016).

In 2010, Dar et al. evaluated the nitrate concentration of the groundwater in Sopore Town of Kashmir, India. Approximately 85% of samples collected during PRM and 67% of samples collected during POM season had elevated nitrate concentrations which was attributed to the use of extensive nitrogenous fertilizers (Dar et al., 2010).

The groundwater in the Gorakhpur district of Uttar Pradesh, India, had an average uranium content of  $2.78\mu\text{g/L}$  and a maximum of  $21.60\mu\text{g/L}$ . In the aquifers of this area,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  were the predominant ionic species. Furthermore, the presence of bicarbonate complexes at neutral pH and oxidizing conditions in groundwater were found to be the determining factors in the dissolution and mobilization of uranium in groundwater (Yadav et al., 2020).

Within the northeastern state of Bihar, Uranium content was observed to be greater than the WHO safe limit of  $30\mu\text{g/L}$  in 7% of the 273 collected groundwater samples. High uranium content was generally observed in oxidizing conditions with a strong correlation between uranium and  $\text{HCO}_3^-$  as well as  $\text{NO}_3^-$  (Richards et al., 2020).

In the Kanker area of the Indian state of Chhattisgarh, the seasonal change of the uranium distribution was investigated. In the winter and summer seasons, uranium content ranged from  $0.5$  to  $69.9\mu\text{g/L}$  and  $0.5$  to  $87.9\mu\text{g/L}$ , respectively. The higher uranium content during summer was attributed to declining groundwater levels. Uranium concentration displayed a low value in winter after groundwater dilution resulting from rainwater input during the rainy season (Sahu et al., 2020).

A study on uranium sources and potential health risks was conducted by Pandit et al. for groundwater in the northern Gujarat and western Rajasthan regions wherein 30% of the samples out of 265 samples collected exceeded the WHO limit of  $30\mu\text{g/L}$ , with a mean value of  $24\mu\text{g/L}$  and the uranium concentration ranging from  $0.6$  to  $260\mu\text{g/L}$ . Detailed speciation analysis revealed that the enrichment was controlled by the dissolution of the primary uranium mineral carnotite [ $\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$ ]. High TDS and Na–Cl hydrogeochemical facies were characteristics of groundwater zones with elevated uranium content. The major hydrogeochemical processes governing uranium mineralization were determined to be water-rock contact and evaporation (Pandit et al., 2022).

Sharma et al. investigated the seasonal variation of uranium distribution and physicochemical parameters in groundwater samples from the districts of Kapurthala (45), Jalandhar (70), and Hoshiarpur (70) in northern Punjab, India along with associated health risks. The districts of Kapurthala, Jalandhar, and Hoshiarpur had an average uranium content of 12.7µg/L, 18.8µg/L, and 7.0µg/L in the pre-monsoon and 8.0µg/L, 17.3µg/L, and 5.6µg/L in the post-monsoon, respectively. More than 90% of groundwater samples in both seasons had uranium concentrations within the permissible limits of WHO standards. It was found that uranium exhibited a positive correlation primarily with TDS, EC, and total alkalinity. Principal component analysis revealed that some anthropogenic activities, such as the excessive use of pesticides and fertilizers and the disposal of household waste that seeps into the groundwater table, in addition to the dissolution of rocks and minerals contributed to the mineralization of associated aquifers (Sharma et al., 2022).

To determine the groundwater's quality and the possible hazards of fluoride exposure to human health, Adimalla and colleagues collected 170 samples of groundwater from the Shasler Vagu watershed in the Nalgonda district of Telangana state. They found that  $\text{HCO}_3^-$  -  $\text{Ca}^{2+}$  -  $\text{Mg}^{2+}$  and  $\text{Na}^+$  -  $\text{HCO}_3^-$  water type and rock weathering were the primary factors influencing groundwater chemistry. In accordance with the Ground Water Quality Index, 76% groundwater sources of the study area were found to be not fit for drinking. The fluoride concentration ranged from 1.4 to 5.9 mg/L, a value far higher than the recommended limit of 1.5 mg/L due to which a large percentage of the adult and children's populations in the study area, were at a risk of chronic toxicity from excessive fluoride ingestion (Adimalla et al., 2020).

Nawale et al. collected 93 groundwater samples from the Wardha sub-basin in Central India in May to evaluate its geochemical makeup as well as pollution status of groundwater. High concentrations of  $\text{NO}_3^-$  and  $\text{F}^-$  were found in 54.8% and 18.5% of the samples, respectively with  $\text{HQ} > 1$ . Several geogenic processes, including calcite precipitation, ion exchange, and the weathering of silicate, dolomite, halite, and carbonate, were important governing factors in the evolution and regulation of groundwater chemistry (Nawale et al., 2021).

## 1.6. Studies on Groundwater Quality in Gujarat

To ascertain the groundwater status in various regions of Gujarat, Patel and group carried out a study on the groundwater quality in Southern and Central Gujarat in which 45 soil and groundwater samples were collected for three seasons by random sampling. The monsoon

samples were observed to be of Ca-Cl type of groundwater. About 46% of the water samples were deemed inappropriate for irrigation during the PRM season based on Residual Sodium Carbonate (RSC) values. Furthermore, during the POM season there was a rise in moderate to poor-quality water samples due to enrichment of sodium and EC. They additionally found that human activity and geology had an impact on the groundwater quality in the districts of Tapi, Bharuch, and Vadodara. On the other hand, groundwater in Dang district was less affected as it was mainly dominated by hills and forest with limited industrialization (Patel et al., 2020).

Khatri et al. analyzed and evaluated the quality of the groundwater in Satlasana Taluka, Mehsana district, Gujarat. For this purpose, 50 groundwater samples collected from various sources in nine villages were tested for pH, turbidity, alkalinity,  $\text{Cl}^-$ , TDS, TH,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and DO. They used the Water Quality Indices, Weighted Arithmetic Water Quality Index (WAWQI) and Canadian Council of Ministers of Environment Water Quality Index (CCMEWQI) methodologies for assessing the groundwater quality. In Satlasna, 46% of the groundwater quality was rated as good by WAWQI, compared to 54% of the groundwater quality being rated as marginal by CCMEWQI (Khatri et al., 2020).

A team of researchers collected 162 samples from Vadodara and Chhota Udaipur districts during 2016 and 2017 in an effort to evaluate the groundwater quality of these areas and determine whether it is appropriate for consumption by humans. The study's findings indicated that while the region's groundwater quality was generally considered to be rather excellent, several of the samples had excessive nitrate levels, which raised concerns and required taking all reasonable steps to restore the groundwater's quality wherever it had deteriorated (Patel et al., 2021).

Prajapati et al. evaluated the quality of groundwater in rural Surat belt of Gujarat with a focus on fluoride pollution. They concluded that anthropogenic inputs had an impact on the hydro-geochemical composition of groundwater in the study area in addition to geogenic processes based on multivariate analysis. Out of 82 samples collected 35.3% of samples had more than 1.0 mg/L of fluoride concentration (Prajapati et al., 2020).

In order to evaluate potential chronic health hazards due to the elevated fluoride concentrations Senthilkumar et. al. undertook a study in Gujarat, India. A decadal assessment of groundwater was attempted in this study. 6407 samples have been collected for that purpose during ten years (2009-2018) from 641 representative locations distributed evenly

within the state. The analytical findings revealed that fluoride content ranged from 0.1-9.6 mg/L. It was observed that 42% of the collected samples had fluoride concentrations significantly below the desired limit while 19% of the water samples exceeded the acceptable limit due to which children of that region were more likely to suffer from dental morbidities (Senthilkumar et al., 2021).

With Uranium emerging as a global groundwater contaminant, Coyte et al. collected data on uranium content in groundwater from 324 wells of 16 states of India including Gujarat and Rajasthan and demonstrated an elevated level of uranium concentration beyond the WHO threshold of 30µg/L. Using geochemical and uranium isotope data, they concluded that uranium concentrations in rocks, aquifers, and groundwater chemistry that encourage the formation of soluble uranyl carbonate complexes could be the contributing factors to high uranium concentrations in groundwater. It was concluded that while geogenic factors were the main sources of uranium, human activities including groundwater table decline and nitrate pollution can significantly increase uranium mobility. Based on the study's findings, they recommended revisions to India's present water quality monitoring programme (Coyte et al., 2018).

## 1.7. Remediation Techniques

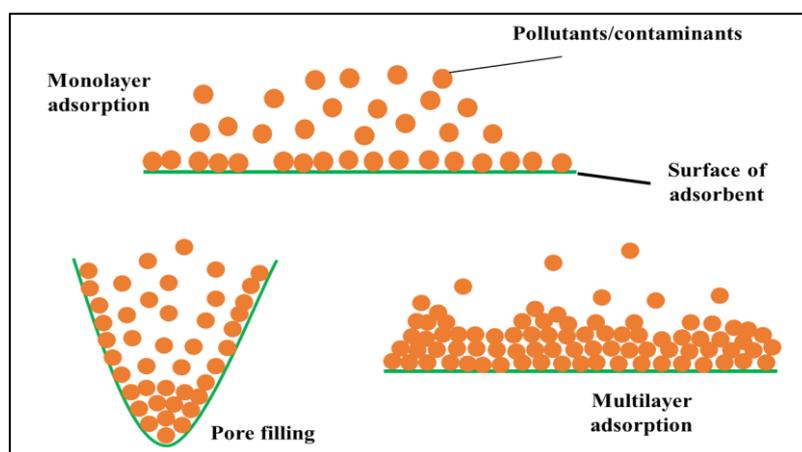
Numerous efficient ways have been identified to treat water contaminants till date. A variety of techniques, including membrane filtration, coagulation/filtration, photodegradation, ion exchange, dechlorination, activated alumina, phytoremediation, bioaugmentation, and lime softening, have been documented by different researchers for treating water (Dhanasekaran and Sahu, 2021; Ebrahimzadeh et al., 2021; Hansima et al., 2021; Tang et al., 2021). Yet due to their high technical requirements, majority of these technologies are not widely used. Due to their affordability, the most often used effective approaches include those based on oxidation, co-precipitation, and adsorption. Amongst these, adsorption has become the most practical and economical option because of its simplicity of usage, flexibility in design, simplicity, and lack of potential for secondary harmful product release.

## 1.8. Adsorption

Adsorption is a mechanism where molecules (pollutants called adsorbate) get adsorbed over the adsorbent in contact and get attached to the surface of the adsorbent through physical or chemical bonding (**Figure 1.5**) (Ugwu et al., 2020). Low-cost adsorbents can be synthesized

using readily accessible materials such as natural materials (clay, zeolites, etc.), agricultural wastes and byproducts, and industrial wastes. Extensive research has been directed toward remediation of pollutants by adsorption. However, the focus of our study is going to be uranium and fluoride.

**1.8.1. Biosorbents and other low-cost agro-based derived adsorbents:** There is a considerable body of literature on the performance of various biosorbents for the removal of various types of water contaminants, such as fluoride and uranium, under a variety of experimental conditions (Banerjee et al., 2022; Gebremariam et al., 2022). Some common bio-based adsorbents are listed in (Figure 1.6).



**Fig.1.5.** Simplified illustration of adsorption mechanisms.

**1.8.2. Raw and neat agriculture byproducts:** Peels of some fruits and vegetables as well as other agricultural byproducts such as rice husks, peanut husks, etc. have been shown to exhibit remarkable potential as adsorbents for different types of organic and inorganic pollutants in the aqueous solution because of specific area, pore size and other adsorbing properties (Aryee et al., 2021; Muzammal et al., 2023). The adsorption capacity of several inexpensive adsorbents, such as powdered pineapple, orange, horse gram, and ragi seeds, has been investigated by Gandhi et al. (2012). After 24 hours of contact time with an initial fluoride concentration of 12 mg/L the adsorption capacities of the adsorbents under study were observed to be: pineapple peel powder (86%), orange peel powder (79%), horse gram seed powder (75%), and ragi seed powder (65%) (Gandhi et al., 2012).



**Fig.1.6.** List of some explored agricultural by-products as biosorbents

Sabanovic and colleagues investigated citrus lemon peels as adsorbent for uranium from aqueous solution. They observed that chemically altered peels (24.39 mg/g) exhibited four times better adsorption potential for uranium than virgin citrus lemon peel (Šabanović et al., 2019). Furthermore, numerous investigators examined biobased adsorbents to adsorb contaminants such as heavy metals or dyes from aqueous solutions (Samet and Valiyaveetil, 2018). To improve the adsorption capabilities of these biobased byproducts, additional modifications such as thermal, chemical, or metal impregnation were attempted.

**1.8.3. Chitosan derivatives:** Chitin is one of the most abundant natural polysaccharides (Huang et al., 2023). Crustaceans, mollusks, squids, cephalopod beaks, fish scales, and lissamphibians are the most common hosts of chitin. In fungi, it's the main component of cell walls, while in arthropod exoskeletons, it's the main component of exoskeletons. Chitin offers several benefits, including non-toxicity, renewability, and biodegradability, making it a green and sustainable alternative to synthetic polymers. Chitosan is a derivative produced by deacetylation of chitin with improved properties.

For the adsorption of fluoride from aqueous solution, Kusrini et al. impregnated Praseodymium onto chitosan (Chi-Pr). Chi-Pr was found to have a maximum adsorption capacity of 15.87 mg/g (Kusrini et al., 2015). Vijaya and Abburi applied chitosan-coated silica for defluoridation and was found to have a maximum adsorption capacity of 44.4 mg/g at pH 4 (Vijaya and Abburi, 2009). Chitosan derivatives have also been used to remove uranium from aqueous solutions. Phosphorylated chitosan was synthesized and successfully evaluated for the removal of uranium from liquid waste of a uranium purification plant, with 95 percent uranium eliminated from 10mg/L uranium containing solution (Morsy, 2015).

Elsayed et al developed and analysed in detail an amidoxime-modified chitosan-based ion-imprinted polymer with maximum capacity for adsorption of 332 mg/g for uranium adsorption from water (Elsayed et al., 2021). Repo et al. synthesised Diethylene Triamine Pentaacetic Acid (DTPA) and Ethylene Diamine Tetraacetic Acid (EDTA) modified chitosan for the adsorption of Co (II) and Ni (II). The adsorption capacity of EDTA-modified chitosan was reported to be 63.0 mg/g and 71.0 mg/g for Co (II) and Ni (II), respectively, while that of DTPA-modified chitosan was 49.1 mg/g and 53.1 mg/g respectively (Repo et al., 2010).

To remove Pb (II) ions from aqueous solution, Khawar et al. modified chitosan with EDTA and Diammonium Phosphate (DAP). The Langmuir isotherm model demonstrated a maximum sorption capacity of 137 mg/g for the DAP/EDTA-modified chitosan (Khawar et al., 2018). Huang et al. immobilised DTPA-modified chitosan micro-gels into the alginate matrix to form Ca-DTCS/ALG bead composite that exhibited maximum adsorption capacity of 107.5 mg/g at pH 7 towards copper (Huang et al., 2018).

By binding EDTA dianhydride onto magnetic chitosan, Yuan et al. fabricated  $\text{Fe}_3\text{O}_4@CH\text{-EDTA}$  with potential as an adsorbent to remove Co (II) from aqueous solution. At pH 5, the  $q_{\text{max}}$  was determined to be 48.78 mg/g and the material was reusable for up to 4 cycles (Yuan et al., 2021a).

The difficulty of removing heavy metals is increased when commonly used chelating agents, such as Ethylene Diamine Tetraacetic Acid (EDTA), are found in aqueous solutions. To overcome this issue, Wang et al. synthesised magnetic silica ( $\text{Fe}_3\text{O}_4@SiO_2/Cs\text{-DTPA}$ ) functionalized with chitosan for the elimination of Cr (III) and Cr (III)-EDTA.  $\text{Fe}_3\text{O}_4@SiO_2/Cs\text{-DTPA}$  having superparamagnetic characteristics, and a core-shell structure was synthesised. Cr(III) and Cr(III)-EDTA chelates had maximal adsorption capacities of 39.27 and 22.24 mg/g respectively at pH 4 (Wang et al., 2020).

To separate and simultaneously remove Pb (II) and Zn (II) ions from aqueous solutions Panahandeh et al. synthesised  $\gamma\text{-MnO}_2/\text{chitosan}/\text{Fe}_3\text{O}_4$  nanocomposite, which was further modified using EDTA. The maximum adsorption values for Pb (II) and Zn (II) in their investigation were 310.4 and 136 mg/g, respectively (Panahandeh et al., 2021).

To remove Cr (VI) from aqueous solutions, Liu et al. synthesised diethylenetriaminepentaacetic acid-thiourea-modified magnetic chitosan (DTCS- $\text{Fe}_3\text{O}_4$ ). At pH 3, DTCS- $\text{Fe}_3\text{O}_4$  exhibited an adsorption capacity of  $321.3 \pm 6.0$  mg/g (Liu et al., 2021b). Verma et al. developed a polymer composite (CS-EDTA) by immobilizing EDTA onto chitosan by cross-linking for adsorptive elimination of numerous heavy metals from industrial effluent. The maximal adsorption capabilities for Pb (II), Cd (II), and Cu (II) were

reported as 370.37, 343.90, and 227.27 mg/g respectively (Verma et al., 2022). However, such Amino polycarboxylic acids modified chitosan derivatives have not been studied for uranium remediation.

**1.8.4. Other natural polymers:** Apart from chitosan, cellulose fibers derived mostly from abundant natural sources including wood, hemp, and cotton, natural polymers such as alginate (Shehzad et al., 2019), starch (Chauhan et al., 2016), guar gum (Saya et al., 2021), gelatine (Rigueto et al., 2021) etc. were commonly used as adsorbents for a range of metals and organic contaminants (Varghese et al., 2022). Alkaline-treated cellulose fibers were developed by Zhu et al. for uranium adsorption. Following the application of  $\text{NaClO}_2$  and  $\text{NaOH}$  to wood pulp, the majority of lignin and hemicelluloses were eliminated, resulting in the formation of cellulose fibres with a structure that resembles a web (Zhu et al., 2016). Further, functional groups were also modified with the addition of  $\text{CH}_3\text{COOH}$ , resulting in an abundance of active sites that are advantageous for uranium adsorption. An equilibrium process was achieved for the uranium adsorption by the alkaline-treated cellulose fibres in two hours, suggesting ion exchange as the chemical adsorption process. The results of the adsorption revealed that the process was dependent on pH levels, with maximal adsorption occurring at pH values between 4.0 and 5.5. Moreover, adding humic acid enhanced uranium adsorption at low pH values while reducing uranium adsorption at high pH values due to electrostatic attractions.

Guar gum/bentonite was synthesised by Ahmad et al. for the removal of  $\text{Pb (II)}$  and crystal violet dye, with maximum adsorption capacities of 187.084 and 167.93 mg/g, respectively (Ahmad and Mirza, 2018).

Shehzad et al. prepared amino-carbamate moiety grafted calcium alginate hydrogel beads (CA-1) by treating sodium alginate with 4-phenyl semi-carbazide and then ionotropically crosslinking with  $\text{Ca (II)}$  ions, as an adsorbent to remove uranium from aqueous solutions with maximum adsorption capacity of 233.2 mg/g (Shehzad et al., 2019). Wu et al. used ordered mesoporous carbon, magnetic nanoparticles, glass fiber carpet, and polydopamine (PDA) to prepare PDA-modified adsorbent for uranium remediation (Wu et al., 2017). Mahfoudhi and Boufi fabricated porous cellulose aerogel from commercially bleached eucalyptus pulp impregnated with aluminium hydroxide to adsorb fluoride from an aqueous solution (Mahfoudhi and Boufi, 2020).

**1.8.5. Agro-based Biochar:** Biochar is a byproduct during pyrolytic processing of biomass to biofuel under controlled thermal techniques, including gasification. The biochars exhibited potential as an adsorbent for the removal of micropollutants due to their highly condensed aromatic structure and enhanced surface density of functional groups. These qualities depend on the kind of feedstock, activation, and pyrolysis conditions (temperature and residence time). Biochar pyrolyzed at higher temperatures primarily consisted of polyaromatic carbons with a higher microporosity, whereas biochar pyrolyzed at lower temperatures possessed higher amounts of aliphatic carbons and functional groups. Using biochar derived from Macauba endocarps, uranium removal from wastewater and aqueous solution was investigated (Guilhen et al., 2021).

According to recent research, watermelon rind biochar prepared by different methodologies had an adsorption capability of 138.86 and 9.5 mg/g, respectively, for removing fluoride and uranium from aqueous solutions (Lingamdinne et al., 2022; Sadhu et al., 2021). Das et al. reviewed the use of biochar for removing hazardous contaminants from the environment, and the drawbacks of biochar. They concluded that employing biochar for hazardous pollution remediation and environmental management was a practical solution that may lessen a variety of farm wastes and ultimately move towards a greener and cleaner world (Das et al., 2020).

**1.8.6. Metal-impregnated biochar:** Impregnation with metals was reported to considerably improve biochar's adsorption efficiency. For the removal of water contaminants like uranium and fluoride, numerous industrial and agricultural wastes, including rice straw, bamboo, coconut shells, and others like fertiliser waste, algae, etc. have been employed as sustainable precursors for metal-modified biochar (Guilhen et al., 2021; Philippou et al., 2019; Thakur et al., 2022; Wang et al., 2021; Zhou et al., 2021). **Table 1.3** summarizes some reported metals impregnated biochars for removing fluoride and uranium. Reed biochar beads were synthesized by Wei et al. and cross-linked with cerium alginate using the gelation, spheroidization, and carbonization technique to function as an effective fluoride adsorbent (Wei et al., 2022). Ahmed and his colleagues successfully synthesised a hydroxyapatite (HAP) biochar nanocomposite (BR/HAP) from rice straw biochar (BR). According to batch study results, modified BR/HAP exhibited a notably improved adsorption capability over raw BR (Ahmed et al., 2021b).

**Table 1.3.** Some representative metal-impregnated biochars for fluoride and uranium removal

Biochar	Impregnated metals	Pollutants	References
Kenaf biochar (Al-KNF-BC)	Al	F <sup>-</sup>	(Choi et al., 2022)
Rice straw biochar (La/Fe/Al-RSBC)	La/Fe/Al	F <sup>-</sup>	(Zhou et al., 2021)
Zirconium ion-impregnated macadamia nutshell biochar (ZMNB)	Zr	F <sup>-</sup>	(Yegon et al., 2022)
Aluminium/lanthanum-loaded wheat straw biochar (Al-La-WSB)	Al/La	F <sup>-</sup>	(Yan et al., 2022)
Anchoring Al- and/or Mg-oxides to magnetic biochars	Al/Mg	F <sup>-</sup> and arsenate	(Shen et al., 2021)
Peanut shell biochar supported magnesium oxide	Mg	F <sup>-</sup>	(Shunli et al., 2019)
Calcium Pretreated Pinus Roxburghii Wood Biochar	Ca	F <sup>-</sup>	(Yadav et al., 2022)
Calcium-modified dairy manure - derived biochar	Ca	F <sup>-</sup>	(Wallace et al., 2020)
Waste generated bio-char supported co-nanoparticles of nickel and cobalt oxides	Ni and Co	U	(El Naggar et al., 2019)
MnO <sub>2</sub> -modified bamboo-derived biochar composites (MnO <sub>2</sub> @BBC)	Mn	U	(Chen et al., 2022)
Tea waste derived-biochar-supported-iron-manganese oxide composite	Mn/Fe	U	(Liu et al., 2021a)
Bi <sub>2</sub> O <sub>3</sub> doped horse manure-derived biochar	Bi	U	(Liao et al., 2022)
Ficus macrocarpa ( <i>banyan tree</i> ) aerial roots biochar (M-BC)	Mn	U	(Liu et al., 2023)

**1.8.7. Magnetic Biochar:** The conversion of biochar into magnetic biochar was reported to enhance the adsorption capacity due to improved surface area, pore size, surface morphology, functional groups, and stability of adsorbents (Gu et al., 2021) as well as facilitate separation without the need for filtration. Philippou and group synthesized magnetic biochar and magnetic oxidized biochar from pine needles in order to remove uranium from aqueous solutions. The biochar's magnetization of oxidized biochar resulted in improved uranium adsorption capabilities throughout a wide range of pH values (Philippou et al., 2019). Ahmed et al. synthesised biochar from *Citrullus lanatus L.* (watermelon) seeds and used spinel MnFe<sub>2</sub>O<sub>4</sub> to modify the biochar via the co-precipitation method in order to remove U(VI) from wastewater. The biochar with magnetic properties was shown to have a mesoporous structure, higher stability, enhanced adsorption capacity of 27.61 mg/g, in contrast to pristine biochar, which had an adsorption capacity of 21.24 mg/g (Ahmed et al., 2021a).  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> were effectively used by Dewage et al. to magnetize Douglas fir biochar to remove fluoride and nitrate from water. The researchers observed that over a pH range of 2 to 10,

both fluoride and nitrate adsorption on the adsorbent remained high with a maximum adsorption capacity of 15 mg/g and 9 mg/g, respectively (Bombuwala Dewage et al., 2018).

**1.8.8. Synthetic sorbents:** Among various adsorbents, synthetic adsorbents with distinctive properties have been demonstrated as potential adsorbents for the removal of various water pollutants such as uranium, fluoride, arsenic, dyes, organic pollutants, etc. in recent years. The properties include small size, high surface area, easy separation, and numerous active sites for adsorption (Tolkou and Zouboulis, 2023).

**1.8.9. Zirconium-based adsorbents:** Zirconium is not a particularly plentiful element, but its mineral, zircon, is resistant to weathering and is modestly mobile in the environment. Zirconium is 10 times more prevalent than lead and more than twice as abundant as copper and zinc (Ghosh et al., 1992). Various zirconium-based adsorbents for the removal of water contaminants, including fluoride, have been developed to date (Yuan et al., 2021b; Zhang et al., 2017b). Cai et al. loaded Al/Zr onto carboxymethyl starch sodium to produce CMS-ZR or CMS-Al-Zr for defluoridation applications (Cai et al., 2015). Zr-impregnated graphene oxide-coated sand (ZIGCS) was developed by Prathibha et al. with a defluoridation capacity of 6.12 mg/g (Prathibha et al., 2020).

**1.8.10. Lanthanum-based adsorbents:** In previous investigations, La a rare earth metal, demonstrated high affinity for fluoride and certain other water contaminants, including phosphate and chromium (Elkhilfi et al., 2022; Tolkou et al., 2022; Wang et al., 2018; Zhang et al., 2021). Lanthanum's use is however limited by its high cost. It might be cost-effective to load lanthanum onto low-cost materials in order to lower the amount of lanthanum while maintaining good adsorption capacity. For the elimination of fluoride and other contaminants, a variety of support materials that have been loaded with La have recently been developed such as La-modified activated carbon, and Al/La-modified natural magnetite adsorbents (Cheng et al., 2014; Gai and Deng, 2021; Wang et al., 2018). For instance, the removal of fluoride from water using colloidal lanthanum was observed to be effective, but its implementation in water treatment systems is highly difficult due to the difficulty of recovering after fluoride adsorption at the end of treatment (Vences et al., 2015). Sadhu and colleagues synthesised lanthanum-cholate (LaC) by treating bile salt sodium cholate with lanthanum with a defluoridation capacity of 9.26 mg/g (Sadhu and P, 2023).

**1.8.11. Metal oxide and hydroxide adsorbents:** Numerous benefits come with this class of adsorbents, including a high capacity for defluoridation, ease of manufacture, excellent selectivity, quick adsorption rate, etc. (Gai and Deng, 2021). Because of its strong affinity for fluoride, ease of operation, low cost, and simple preparation, activated alumina is a widely investigated and utilised adsorbent for fluoride removal. Through the use of ethanol treatment and a simple wet-chemical precipitation process, Zhang et al. synthesized a novel iron oxide adsorbent with a high fluoride removal capability of 60.8 mg/g in about 2 minutes (Zhang et al., 2017a). Dong and collaborators synthesized an effective Mg-Fe-Ce complex metal oxide adsorbent with Langmuir's maximum adsorption capacity of 204 mg/g for the removal of fluoride from aqueous solutions (Dong et al., 2021).

**1.8.12. Soil and minerals:** Clays, zeolites, sediment, soil, and ore materials fall in this category. They have been materials of choice as adsorbents of study for removal of fluoride, uranium, arsenic, and other heavy metals as well as organic contaminants due to their natural abundance, high specific surface area, and chemical stability (De Gisi et al., 2016). Sepiolite is an inexpensive, readily available natural clay mineral that is rich in Mg and Ca components. Lee's group investigated the adsorption capacity of thermally activated sepiolite for fluoride from aqueous solutions. At 950 °C, fluoride had a maximum Langmuir adsorption capacity of 169.95 mg/g and a fluoride removal efficiency of more than 98.5% in a continuous flow system (Lee et al., 2020). A review of zeolite-based adsorbents such as clinoptilolite, montmorillonite, and zeolitic tuff, among others, for the treatment of radioactive waste including cobalt, uranium, and cesium was provided by Jiménez-Reyes et al. (Jiménez-Reyes et al., 2021).

### *Aim*

The aim of this research was to systematically monitor and assess groundwater in the Anand, Vadodara, Bharuch, and Narmada districts of Gujarat with emphasis on uranium and fluoride as well as fabricate low-cost, non-toxic, sustainable, and eco-friendly adsorbents for uranium and fluoride remediation.

In-depth reviews of the literature showed that the districts of Anand, Vadodara, Bharuch, and Narmada did not have enough sampling populations. Uranium baseline data were not recorded in Anand, Vadodara, Bharuch, or Narmada districts. Additionally, the systematic grid sampling method was not used in these areas for groundwater sample collection and

monitoring. The remediation efficiency of geogenic fluoride and uranium by adsorbents has been less studied. It has also been observed that pristine biochar from agro-waste has been less explored for removal of uranium and fluoride. Further about 117 million tons of watermelon rind is produced worldwide, making it a plentiful fruit waste product. Moreover, literature studies revealed the efficacy of lanthanum and zirconium-doped adsorbents for removal of fluoride. Our research group have used water melon rind biochar and Lanthanum cholate for removal of fluoride (Sadhu et al., 2021; Sadhu and P, 2023). Research has also been directed towards the use of chitosan-based derivatives such as DTPA for the removal of chromium (Bhatt et al., 2015). Encouraged by the results it was felt that it would be worthwhile to explore the potential of water melon rind biochar and chitosan modified DTPA for removal of uranium and Lanthanum doped biochar as well as zirconium cholate for removal of fluoride. To the best of our knowledge, there are no reports till date on the synthesis and use of zirconium cholate as an adsorbent for the removal of fluoride. Diethylenetriamine pentaacetic acid (DTPA) is a good complexing agent for uranium, DTPA-modified adsorbents, however, have not yet been investigated for the removal of uranium from aqueous solution. Objectives of this research were designed with the above-indicated observations.

**The main objectives of this research:**

- Monitor and assess the groundwater composition in Anand, Bharuch, Narmada, and Vadodara districts of Gujarat with statistical validation
- Study the potential of DTPA-modified chitosan and watermelon rind biochar for the removal of uranium.
- Investigate Lanthanum loaded watermelon rind biochar and zirconium cholate as adsorbents for fluoride remediation

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