CHAPTER 2

LITERATURE REVIEW

2.0 REVIEW OF LITERATURE

2.1. Fluorine and its Property

Fluorine is a naturally occurring member of the halogen family with atomic number 9 and atomic mass 19. Fluorine, at room temperature, is a pale yellow-green gas. It is most reactive of all chemical elements. Its elemental state as fluorine is thus not found in nature. The high reactivity of fluorine is basically due to its high electronegativity (Neumuller, 1981). Fluoride, an ionic form of fluoride, is characterized by small radius, great tendency to behave as ligand and easiness to form a great number of different organic and inorganic compounds in environment (Mirna Habuda-Stanić, 2014). Its great reactivity is in part attributable to the weakness of F-F bond in the fluorine molecule. An important feature in the formation of fluorides is that in reaction with fluorine, the elements usually give the highest known oxidation state (Bulusu *et al.,* 1979).

2.2. Source and Occurrence

Fluorine is reported to be the 13th (Smith. et. al., 1979) or 17th (Fleischer, 1953; Bell *et al.,* 1970; NAS, 1971) most abundant element in the earth's crust, occurring in igneous and sedimentary rocks at concentrations estimated to be between 0.06% and 0.09% by weight of the upper layers of the lithosphere (Koritnig, 1951). According to Fleischer (1953), fluorides account for 0.032% of the earth's crust. Thus with an average concentration of 625 mg/kg, fluoride is one of the more abundant trace elements in the Earth's crust (Edmunds and Smedley, 2005; Tavener and Clark, 2006, Ozsvath, 2009) however, its occurrence varies greatly from one rock type to another. Fluoride contents typically range from 100 mg/kg in ultramafic rocks and some limestones to 1,000 mg/kg in alkaline igneous rocks and 1,300 mg/kg in marine shales (Hem, 1985; Faure, 1991; IGRAC, 2003; Ozsvath, 2009).

The primary natural sources of fluoride into groundwater are fluoride-bearing minerals in the rocks, soil, and sediments (Handa, 1975; Saxena and Ahmed, 2001). The most common sources of fluoride bearing minerals in rocks are fluorspar, or calcium fluoride (CaF_2), the aluminium compound cryolite (Na_3AIF_6), apatite, a calcium phosphate complex ($3Ca_3(PO_4)_2.Ca(F,OH,Cl)_2$), Villiaumite, or sodium fluoride (NaF), but in most soils fluoride is associated with micas and other clay minerals (WHO, 1984; Hem, 1985; Apambire *et al.,* 1997; Cronin *et al.,* 2000; Saxena and Ahmed, 2003; Edmunds and

Smedley, 2005; Chae *et al.,* 2007). Majority Fluorspar is found in sedimentary rocks (limestone and sandstone) and as cryolite in igneous rocks (granite). In igneous rocks (including volcanic rocks), the fluorine is mostly bound in micas and amphiboles (up to 80%) and to a lesser extent in apatite (up to 20 %). However, in basalt all fluorine can be found bound in apatite.

In India, geological formation containing fluoride bearing minerals in majority of state is given in Table 1. Most common minerals in earth's crust of India are fluorspar (CaF_2), Apatite and rock phosphate and phosphorites. Fluorspar deposits are found in Gujarat, Rajasthan, Andhra Pradesh, Bihar, Himachal Pradesh, Jammu and Kashmir, Madhya Pradesh, West Bengal and Tamilnadu. Two major apatite deposit bearing states in India are Bihar and Andhra Pradesh while minor occurrences have been reported from Gujarat, Tamilnadu, Orissa, Rajasthan and West Bengal. The third major source of fluoride, phosphorites-the sedimentary phosphate deposits, occurs in abundance in two regions in India: North-West part of India comprising the States of Uttar Pradesh, Jammu and Kashmir, Rajasthan and Tamilnadu in Southern part of India (Patil and Ingole, 2012).

In general, geographical areas with groundwater fluoride contamination are mostly characterized by the presence of crystalline basement rocks and/or volcanic bedrocks, arid/semi-arid climatic conditions, Calcium deficient-Sodium bicarbonate type groundwater (Handa, 1975; Saxena and Ahmed, 2001; Edmunds and Smedley, 2005; Sreedevi *et al.,* 2006; Amini *et al.,* 2008) and long groundwater residence time and distance from the recharge area (Apambire *et al.,* 1997; Genxu and Guodong, 2001; Jacks *et al.,* 2005; Guo *et al.,* 2007; Shaji *et al.,* 2007).

Other than the natural sources anthropogenic activities like industrial processes contribute to fluoride addition in environment. The Emission and effluents from fertilizer industries (Arora and Chattopadhiya, 1974; Mourad *et al.,* 2009), glass and ceramic industries (Fan and Li, 2013; Ponsot *et al.,* 2013), metal industries (Sujana *et al.,* 1997; Shen *et al.,* 2003; Blagojevic *et al.,* 2002), electronic industries (Haung and Liu, 1999; Hu *et al.,* 2005; Drouiche *et al.,* 2009; Drouiche *et al.,* 2013), refineries and nuclear as well as thermal power plants (Paulson, 1977; Bhatnagar *et al.,* 2011) contribute significantly to fluoride addition to atmosphere and hydrosphere. In addition, incineration of municipal waste like fluorinated plastic, fluorinated textiles or waste sludge emits HF into the atmosphere (BAT, 2006).

Table 1: Lithology in different states of India

State	**Geological Formation**	**Reference**
Andhra Pradesh	Archean granite and gneissic complex	Rao and Devadas (2003)
Assam	Cretaceous sandstone	Chakraborti *et al.* (2000)
Bihar	Archean granite and gneissic complex	Ray *et al.* (2000)
Delhi	Amphibolites and quartzites	Susheela *et al.* (1996)
Gujarat	Basalt and quaternary sediments	Chinoy *et al.* (1992)
Haryana	Granite rocks	Garg *et al.* (2009)
Karnataka	Archean granite and gneissic complex	Wodeyar and Sreenivasan (1996)
Kerala	Archean granite and gneissic complex	Shaji *et al.* (2007)
Madhya Pradesh	Archean granite and gneissic complex	Chatterjee and Mohabey (1998)
Maharashtra	Archean granite and gneissic complex	Deshmukh and Chakravarti (1995)
Orissa	Archean granite and gneissic complex	Kundu *et al.* (2001)
Rajasthan	Archean granite and gneissic complex, Micaceous sands	Choubisa *et al.* (2001)
Tamil Nadu	Charnokite and gneissic complex	Handa, (1975)
Uttar Pradesh	Archean granite and gneissic complex	Raju *et al.* (2009)

2.3. Routes of Fluoride Uptake in Human

Water, air, food, drugs, and cosmetics are the main sources of fluoride for humans. The major sources of ingested fluoride are water and other dietary sources.

Water: Although there are several sources of fluoride intake, it is roughly estimated that 60% of the total intake is through drinking water. This is the most accessible form of fluoride and, hence, the most toxic. The details of fluoride-rich groundwater have been given in Table 2.

Air: Inhalation of air contaminated by volcanic gas emissions, and air-borne soil dust (Angelis and Legrand, 1994; Saether *et al.*, 1995; Tavener and Clark, 2006) and industrial emissions explained earlier.

Food: Almost all the food items contain at least traces of fluoride. The fluoride of food items depends upon the fluoride contents of the soil and water used for irrigation; therefore, the fluoride content of the food items may vary from place to place. The details of fluoride-rich food have been given in Table 3.

Cosmetics and drugs: Prolonged use of drugs utilized to treat skeletal problems like osteoporosis, rheumatism, arthritis and dental problems have been associated with fluorosis. Similarly, in the fluoridated brands for cosmetics, there is a deliberate addition of fluoride which may range from 1000 to 4000 mg/L.

Table 2: General range of fluoride concentration in groundwater

State, district/place (in aphabetical order)	Fluoride Concentration (mg/l)	Reference
Andhra Pradesh	Upto 21 mg/l	Rao *et al.* (1993), Rao (1997), Sujatha (2003), Rao (2003), Sreedevi *et al*. (2006), Mondal *et al.* (2009), Reddy *et al.* (2010a), Reddy *et al.* (2010b), Brindha *et al.* (2011)
Assam	Upto 20.6 mg/l	Chakraborti *et al.* (2000), Das *et al.* (2003)
Bihar	Upto 2.5 mg/l	Ray *et al.* (2000)
Delhi	Upto 32.4 mg/l	Datta *et al.* (1996), Susheela *et. al.* (1996)
Gujarat	Upto 40 mg/l	Chinoy *et al.* (1992), Gupta *et al.* (2005), Dhiman and Keshari (2006), Salve *et al.* (2008)
Haryana	Upto 86 mg/l	Garg *et al.* (2009)
Himachal Pradesh	Upto 6.5 mg/l	Sharma (2003)
Jammu and Kashmir	Upto 18 mg/l	Sharma (2003)
Karnataka	Upto 7.8 mg/l	Wodeyar and Sreenivasan (1996), Latha *et al.* (1999)
Kerala	Upto 5.75 mg/l	Shaji *et al.* (2007)
Madhya Pradesh	Upto 6.4 mg/l	Chatterjee and Mohabey (1998), Nawlakhe *et. al.* (1995)
Maharashtra	Upto 13.41 mg/l	Madhnure *et al.* (2007)
Orissa	Upto 16.4 mg/l	Das *et al.* (2000), Kundu *et al.* (2001)
Rajasthan	Upto 14 mg/l	Choubisa (1996), Muralidharan *et al.* (2002)
Tamil Nadu	Upto 8.2 mg/l	Handa (1975), Apparao and Karthikeyan (1986), Karthikeyan *et al.* (2010)
Uttar Pradesh	Upto 17.5 mg/l	Ray *et al.* (1983), Gupta *et al.* (1999), Misra *et al.* (2006), Sankararamakrishnan *et al.* (2008), Raju *et al.* (2009)
West Bengal	Upto 1.18 mg/l	Kundu and Mandal (2009)

*Source: Brindha and Elango, 2011 and Raju *et. al*., 2009

Table 3: Fluoride concentration in various food items

Food items	**Reported range of Fluoride in ppm**	**Food items**	**Reported range of Fluoride in ppm**
Cereals:		**Beverages**:	
Wheat*	1.0 - 3.0	Tea (Dry leaves)	39.8 - 112.0
Rice*	0.99 - 2.1	Aerated drinks	0.77 - 1.44
Bajra*	0.99 - 3.2	Coconut water	0.43 - 0.60
Maize	~5.6	**Spices and condiments:**	
Pulses and Legumes:		Cumin*	1.25 - 3.9
Bengal gram*	0.85 - 1.9	Coriander*	0.55 - 1.2
Green gram dal*	1.3 - 2.0	Garlic	~ 5.0
Mung bean*	0.66 - 1.4	Ginger	~ 2.0
Soyabean	~4.0	Turmeric	~ 3.3
Leafy Vegetables:		**Foods from animal Sources:**	
Spinach*	0.65 - 1.2	Mutton	3.0 - 3.5
Cabbage*	1.1 - 1.5	Pork	3.0 - 4.5
Amarath leaves	4.91 - 7.14	Beef	4.0 - 5.0
Chowli leaves	1.79 - 7.33	Fishes	1.0 - 6.5
Other Vegetables:		**Certain Other items:**	
Cucumber	0.77 - 1.6	Areca Nut (Supari)	3.8 - 12.0
Tomato*	0.45 - 1.7	Betal leaf	7.8 - 12.0
Brinjal	1.2 - 2.48	Tobacco	3.1 - 38.0
Ladies finger	1.74 - 4.00	**Nuts and Oil Seeds:**	
Snake Gourd	0.75 - 3.44	Almond	~ 4.0
Roots and Tubers:		Cashewnut	~ 4.1
Carrot*	1.4 - 3.3	Coconut	~ 4.4
Potato*	1.2 - 2.6	Mustard Seeds	~ 5.7
Onions*	1.00 - 3.7	Groundnut	~ 5.1
Fruits:			
Grapes	0.84 - 1.74	Apple	1.05 - 5.7
Mango	0.8 - 3.7	Guava	0.24 - 5.1

*Patel and Bhatt (2007), Gupta and Deshpande (1998)

2.4. Fluoride in drinking water and its permissible limit

Of the various sources of fluoride in the environment, drinking water is the primary source and thus poses the greatest harm to human health. Drinking water is derived from a variety of fresh water sources depending on local availability: surface water (lakes, rivers, reservoirs and ponds), groundwater and rain water. Of this groundwater is primarily used for drinking purpose. It is estimated that more than 90 % of India's rural population depends on groundwater for domestic purposes (Mittal and Kumar, 2014). High concentrations of fluoride in groundwater is now recognized most serious inorganic contaminant in drinking water worldwide. Fluorosis is a huge public health disaster in many developed as well as developing countries. Following the accumulation of evidence for the chronic toxic effects of fluoride in drinking water, recommended and regulatory limits had been set by many authorities worldwide.

Different countries have set different standards of fluoride content in drinking water. According to the last edition of the WHO (2004) guidelines international standards (allowable concentrations) for fluoride in drinking water is 1.5 mg/l. The Bureau of Indian Standards (BIS) also has notified a desirable level as 1 mg/l and permissible limit as 1.5 mg/l for fluoride in drinking water (BIS (2012) (Table 4).

Galagan and Vermillom (1957) reported that the amount of fluoride ingested due to water consumption is primarily influenced by atmospheric temperature. USPHS (United States Public Health Service) thus have set of Drinking Water Standards (USPHS, 1962) based on the temperature range for maximum allowable range of concentrations fluoride in drinking water for communities (Table 5).

2.5. Fluoride effects on humans

Fluorine is often called as two-edged sword. While inadequate intake of fluoride in drinking water is associated with dental caries (Shashi and Singla, 2013), prolonged ingestion through drinking water in excess of the daily requirement is associated with dental and skeletal Fluorosis (Mahapatra *et al.*, 2016).

Table 4: Drinking water standards

Agency/Sources	Desirable limit	Permissible limit
BIS (2012) IS:10500	1.0 mg/l	1.5 mg/l
WHO guidelines	---	1.5 mg/l

Table 5: Recommended fluoride concentration

Annual average of maximum daily air (ºC)	Recommended fluoride concentration (mg/L)			Maximum allowable fluoride (mg/L)
	Lower	Optimum	Upper	
10-12	0.9	1.2	1.7	2.4
12.1-14.6	0.8	1.1	1.5	2.2
14.7-17.7	0.8	1	1.3	2
17.8-21.4	0.7	0.9	1.2	1.8
21.5-26.2	0.7	0.8	1	1.6
26.3-32.5	0.6	0.7	0.8	1.4

Source: USPHS, 1962

Table 6: Physiological effects of fluoride on humans

Fluoride Concentration (ppm)	Impact on Human Health
1	Reduction in dental caries
2 or more	Mottled enamel
5 or more	Signs of osteosclerosis
8 or more	10% osteosclerosis
20 or more	Crippling effects
50 or more	Thyroid changes
100 or more	Growth retardation
125 or more	Kidney damage
More than 5 grams	Death

Source: Sinha, 1997

2.5.1. Beneficial effects

A preponderance of evidence indicates that moderate levels of fluoride ingestion can reduce the incidence of dental caries and under certain conditions promote the development of strong bones (Kaminsky *et al.,* 1990; Heller *et al.,* 1997; Yiming *et al.,* 2001; Rao, 2003; Harrison, 2005; Edmunds and Smedley, 2005; Doull *et al.,* 2006).

2.5.2. Adverse effects

Sinha (1997) showed (Table 6) other toxicity symptoms of large doses or a persistent intake of small amounts of fluoride over a number of years. Fluoride ingestion can have dental, skeletal and non-skeletal effects (Plate 2). The detail of this effects are as follow:

Dental manifestations

Dental fluorosis is characterized by a mottling of the enamel. Prolonged exposure to fluoride during developmental process causes a dose-related disruption of enamel mineralization resulting in anomalously large gaps in its crystalline structure, excessive retention of enamel proteins, and increased porosity (Aoba and Fejerskov, 2002), thus become hard and brittle, this is dental fluorosis. Initial stages or mild forms of dental fluorosis are evidenced by the appearance of white horizontal striations on the tooth surface or opaque patches of chalky white discolorations (WHO, 1996; Susheela, 2003; Rao, 2003). In moderate to severe forms of fluorosis, the opaque patches can become stained yellow to brown or even black, and eventually the increased tooth porosity leads to structural damages, such as pitting or chipping (Rao, 2003).

Skeletal manifestations

Skeletal fluorosis is generally observed in adults. It is characterized by increased bone mass and density, accompanied by a range in skeletal and joint symptoms. The mechanism(s) that leads to skeletal fluorosis are poorly understood; however, the stages of development are well-documented (Hileman 1988; WHO, 1996; Rao, 2003; Susheela, 2003; Edmunds and Smedley, 2005). Early stages of skeletal fluorosis start with pain in bones and joints, muscle weakness, stiffness of joints and chronic fatigue. Later stiffness increases with calcification of bones accompanied by increased bone density (osteosclerosis). Slowly every vertebrae in spine fuse to become one continuous column of bone, a condition referred as "poker back". In its most advanced stages, fluorosis produces neurological defects, muscle wasting, paralysis, crippling deformities of the bones and compression of the spinal cord (Reddy *et al.,* 1985).

Non-skeletal manifestations

Reproductive

Large number of *In-vitro* researches on animals are being carried out in order to explore relationship between fluoride ingestion and reproductive structure or function, but lack of human trial leads to an uncertain conclusion (Doull *et al.,* 2006). However these studies suggest that high fluoride ingestion might have various effects on males, including the morphology and mobility of sperm (Chinoy and Narayana, 1994), or the levels of testosterone, follicle-stimulating hormones and inhibin-B (Susheela and Jethanandani, 1996; Ortiz-Perez *et al.,* 2003).

Developmental

Many works evaluated direct correlation between fluoride concentrations in blood plasma to that of blood plasma in umbilical cord, which imply passive diffusion of fluoride from mother to foetus (Gupta *et al.,* 1993; Malhotra *et al.,* 1993). Another study carries out by Gupta *et al.* (1994) and Gupta *et al.,* (1995) raised the likelihood to unusually high incidence of spina bifida occulta in fluorosis-prone regions. In vitro studies on animals suggested intake of high fluoride concentration can lead to unfavourable developmental outcomes; but insufficient data due to lack of human trial make the result inconclusive (Doull *et al.,* 2006).

Renal

The renal system, removing toxic elements from the body, is assumed to be facing maximum contact period with fluoride during its expulsion. Thus people surviving in fluoride prone areas are at severe risk (Whitford, 1996). Singh *et al.* (2001) revealed that people living in a fluoride affected areas were 4.6 times more likely to develop kidney stones. However, because the subjects of this study were probably at greater risk of kidney stone formation because of malnutrition, it is difficult to draw firm conclusion

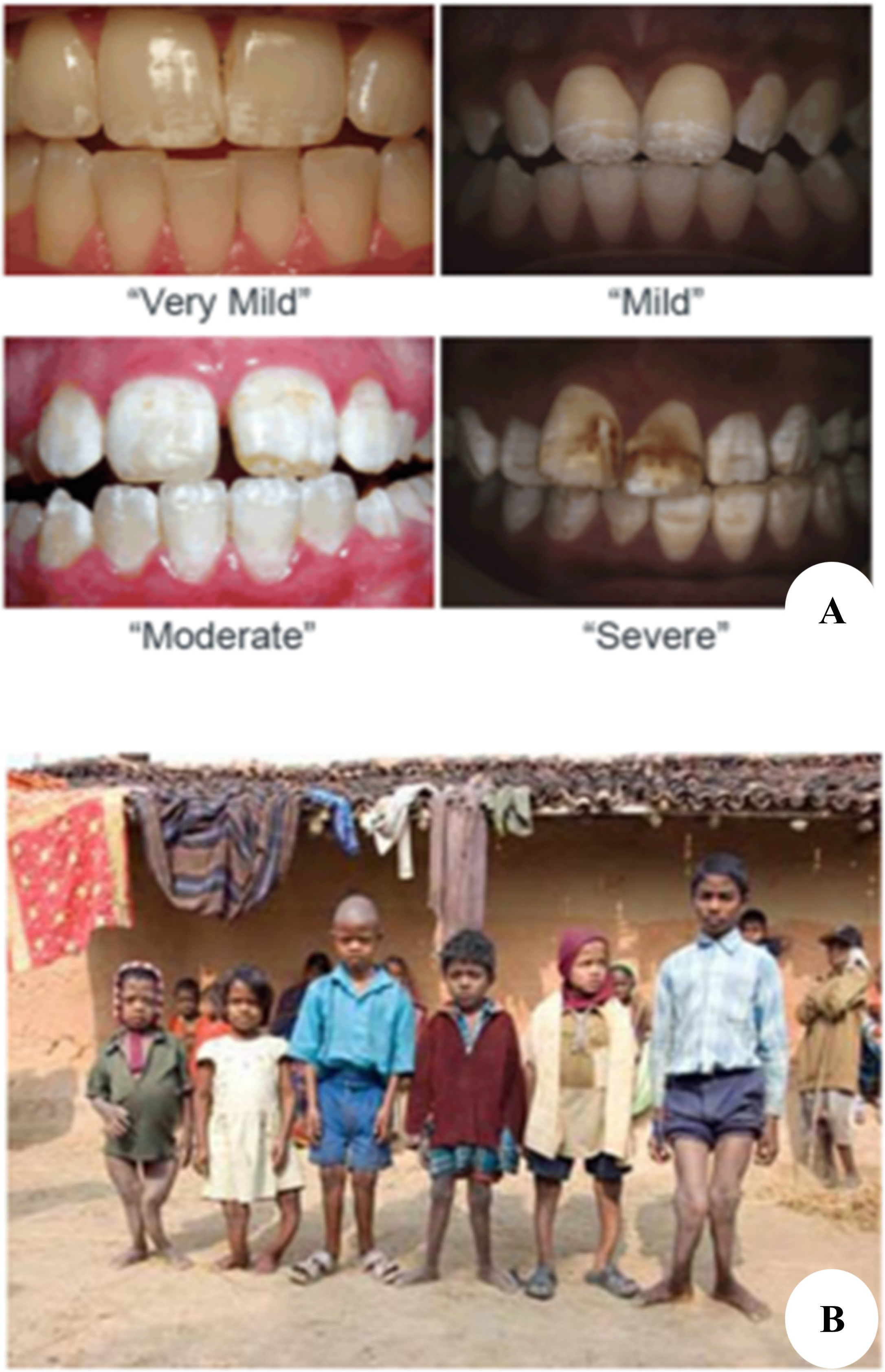

PLATE 1

PLATE 1

A: Dental fluorosis

B: Skeletal fluorosis

Neurological

Trivedi *et al.* (2007) revealed a statistically significant impact of fluoride on the intelligence quotient (IQ) of school-aged children. Based on a study, maximum threshold fluoride level required for a neurotoxicity response is between 2 and 4 mg/l. The reason for neurological manifestation has not been identified, but Spittle (1994) described several types of biochemical changes that fluoride might cause in proteins and enzymatic systems which could interfere with normal brain function and cause impaired cognition and memory. A study by Calderon *et al.* (2000) suggests that fluoride could affect reaction times and visuo-spatial abilities, which would then be manifest as lower IQ scores in time-sensitive tests.

Endocrine

Studies of laboratory animals and human populations indicate that fluoride can affect normal endocrine function and response, but there is considerable ambiguity involved in interpreting the results of this research. Doull *et al.* (2006) summarized this body of research and concluded that the primary effects of fluoride exposure on the endocrine system are decreased thyroid function, increased calcitonin activity, increased parathyroid activity, secondary hyperparathyroidism, and impaired glucose tolerance (Type II diabetes). However, these effects vary in degree and kind in different individuals, and many could be classified as subclinical, meaning that they are not considered adverse health effects.

Gastrointestinal

A variety of gastrointestinal effects, including nausea, vomiting, diarrhea, and abdominal pain, have been reported in cases of acute fluoride toxicity (Gessner *et al.,* 1994; Penman *et al.,* 1997; Sidhu and Kimmer, 2002). Animal studies reveal that fluoride can stimulate the secretion of stomach acid, reduce blood flow away from the stomach lining, and even cause the death of gastrointestinal tract epithelium cells (Doull *et al.,* 2006). The level of chronic fluoride ingestion required to cause these types of responses in humans is not established, and it is likely that this threshold varies with other factors.

2.6. Fluorosis in India

Endemic fluorosis remains a challenging and extensively studied national health problem in India. The case of endemic fluorosis was reported in Prakasam District of Andhra Pradesh (Shortt *et al.,* 1937), when the disease was prevalent in only four states, namely, Andhra Pradesh, Tamil Nadu, Punjab, and Uttar Pradesh. During the surveys between periods of 1960 to 1986, nine fluoride affected states were identified. In 1991, Mangla reported 13 fluoride affected states but this had risen to 17 by 1999 (UNICEF, 1999). The recent report by CGWB shows 19 states affected by fluoride. The most seriously affected areas are Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh (Kumaran, *et al.,* 1971; Teotia *et al.,* 1984). The highest concentration observed to date in India is 48 mg/L in Rewari District of Haryana (UNICEF, 1999). Susheela (1999) reported 197 districts belonging to 19 fluoride endemic states of India. This count increased to 224 districts in same 19 states at the end of 2010. From these areas many workers reported high fluoride in groundwater from all around India, some of this works are reported dental as well as skeletal fluorosis as shown below (Table 7, 8).

2.7. Fluorosis prevalence in Gujarat

The Gujarat Ecology Commission's draft Action Environmental Programme said in 1991 just 831 villages had fluoride levels in groundwater higher than permissible limit. In 1997, this figure reached 2,836. Now, the GWSSB survey says that the number of such villages have nearly doubled to 4,341 in 2010. In Gujarat, the prevalence of dental fluorosis was 36 per cent among children and adults, of 28,425 study population; and 4,590 (16 per cent) of the same population were afflicted by at least one of the six basic symptoms of fluorosis (Shah and Indu, 2004).

Ünver *et al.* (2012) showed that in Gujarat 18.2% of population showed the symptoms of backache, joint pain, and stiffness, 35.3 % dental fluorosis, 38.1 % 4pmm urinary fluoride level and 71% radiological changes in the area were fluoride level in drinking water was 0.5-4.0 ppm. The districts severely affected by fluoride contamination are Mehsana, Patan, and Sabarkantha. An epidemoiological survey for Mehsana district, where groundwater mining takes place unabated, presented occurrence of fluorosis in 236 out of 559 villages (Fawell *et al.,* 2006).

A defluoridation camp was organized in 1987 at Kheralu taluka after observing high amount of fluoride concentration in the groundwater of Mehsana district. After this there was no work done till date on Kheralu taluka.

Table 7: Dental fluorosis in India

State/Area	Age group	Prevalence	Author
Cuddalore, TN	5-12	31.4	Sarvanan et.al. (2008)
Alapuzzha, kerala	10-17	35.6	Gopalakrishnan et.al. (1999)
Vadodara, Gujarat	Adults	39.2 - 59.3	Kotecha *et al.* (2012)
Davangere, Karnataka	12-15	13-100	Chandrasekhar and Anuradha (2004)
Jhajjar, Haryana	7-15	30-94.9	Yadav *et al.* (2009)
Birbhum, West Bengal	Adults	61-66.7	Majumdhar (2011)
Punjab	5-60	91.1	Shashi and Bhardwaj (2011)
Nalgonda, A.P	12-15	71.5	Shekar *et al.* (2012)
Durg, Chattisgarh	Adults	8.2	Pandey (2010)
Dungarpur, Rajasthan	All ages	39.2-72.1	Choubisa *et al.* (2010)
Palamau, Jharkhand	children	83.2	Srikanth *et al.* (2008).
Assam	All ages	31.3	Chakraborti *et al.* (2000)
Uttar Pradesh	All ages	28.6	Srivastava *et al.* (2011)
Kareka, Shivpuri (MP)	13-50	86.8	Narwaria and Saksena (2013)
Raigad, Maharashtra	0-23	91.7	Bawaskar and Bawaskar (2006)
Nalgonda, A.P	Adults	30.6	Nirgude *et al.* (2010)

Table 8: Skeletal Fluorosis in India

State/Area	Age group	Prevalence	Author
Nalgonda, Andhra Pradesh	All ages	24.9	Nirgude *et al.* (2010)
Durg, Chattisgarh	Adults	6.3- 38.1	Pandey (2010)
Dungarpur, Rajasthan	All ages	12-27.6	Choubisa *et al.* (2010)
Bihar, India	1-5	20	Khandare *et al.* (2005)
Palamau, Jharkhand	Adults	47.4	Srikanth *et al.* (2008)
Assam	Adults	1.74	Chakraborti *et al.* (2000)
Uttar Pradesh	All ages	14.2	Srivastava *et al.* (2011)
Kareka, Shivpuri(Madhya Pradesh)	13-50	39.2	Narwaria and Saksena (2013)

2.8. Remedial Measures

A community with excessive fluoride in its water supply can address their problem in two ways:

1. By improving the nutritional status of population at risk.
2. Treatment of high fluoride groundwater

2.8.1. Better Nutrition

Numerous clinical researches have shown that dietary supplement with high calcium, rich vitamin C & high carbohydrate food, i.e. improved nutritional status of an affected population might be an effective supplement to the technical solutions of the problem (Dinesh, 1998).

2.8.2. Treatment techniques

2.8.2.1. In-situ treatment technique

Generally high fluoride content is observed in groundwater with high evopo-transiration. In-situ treatment includes various techniques involving dilution of contaminated water via artificial recharge with dam constructions or rainwater harvesting or diluting contaminated water with another source of fresh pure water.

2.8.2.2. Ex-situ treatment techniques

Ex-situ technique involves methods to defluorinating groundwater before utilizing. Defluorination can be done at local or community level. Many scientists have developed many methods to remove fluoride from groundwater. All of these can be categorized into 4 principle techniques viz: Precipitation-coagulation, Ion-exchange, Membrane based techniques and Adsorption.

Membrane technique

The membrane techniques involves various methods as Reverse Osmosis (RO), Nano-Filtration (NF), Dialysis or Electrodialysis (ED)

Reverse Osmosis: It is a physical process in which the contaminants are removed by applying pressure on the feedwater to direct it through a semipermeable membrane, which overcome the natural osmotic pressure. RO produces water of extremely high purity.

Nanofiltration: It is a pressure-driven membrane process wherein the feedwater is pressurized through filters having pore size in nanometers.

Dialysis: It separates solutes by transport of the solutes through membrane rather than using a membrane to retain the solutes while water passes through it as in reverse osmosis and nanofiltration. The membrane pores are much less restrictive than those for nanofiltration, and the solute can be driven through by either the Donnan effect (Donnan 1911) or an applied electric field.

Electro-Dialysis: Electro-dialysis is the removal of ionic components from aqueous solutions through ion exchange membranes under the driving force of an electric field.

Ion-exchange

In this method ions are exchanged from solution that are held electrostatically on the surface of a solid with ions of similar charge. The ion exchange medium is usually packed into a column. Fluoride contaminated water is passed through the columns and the contaminants are removed.

Precipitation and Coagulation

It is one of the cheapest techniques accepted worldwide (Ayoob *et al.*, 2008). In these processes dissolved contaminants are transformed into an insoluble solid by using chemicals. The solid is then removed from the liquid phase by clarification or filtration. Dissolved fluoride may also be adsorbed on the surface and co precipitated with other precipitating species.

Adsorption

This method concentrates solutes at the surface of an adsorbent, thereby reducing their concentration in the aqueous phase. Adsorption depends on ions (adsorbate) in fluid diffusing to the surface of a solid (adsorbent), where they bond with the solid surface or are held there by weak intermolecular forces.

Table 9: Merits and Demerits of defluorination techniques

Technology	Merit	Demerit
Coagulation or precipitation	High efficiency; commercially available chemical	Expensive, efficiency depends of pH and presence of co-ions in water, adjustment and readjustment of pH is required, formation of sludge with high amount of toxic fluoride complex and high amount of retained water (sludge dewatering is required prior disposal)
Membrane filtration	High efficiency; remove other contaminates	High capital high running and maintenance costs toxic waste water produced
Electrochemical treatments	High efficiency; high selectivity	High cost during installation and maintenance
Ion-exchange	High efficiency	Expensive, vulnerable to interfering ions (sulfate, phosphate, chloride, bicarbonate, etc.), replacement of media after multiple regenerations, used media present toxic solid waste, regeneration creates toxic liquid waste, efficiency highly pH-dependent
Adsorptive materials	Economical, simple operation, availability for wide range of adsorbents	High efficiency often demand adjustment and readjustment of pH, some common water ions can interfere fluoride adsorption

*Source: Habuda-Stanić *et al.* (2014)

2.9. Adsorption

Adsorption is found to be more appropriate, as it has a lower cost of design and operation, and it is simple to apply (Kumar *et al.,* 2009). The adsorption process has been previously applied for defluoridation using various adsorbents from geomaterials, industrial by-products, metal oxides, carbonaceous materials and biosorbents. (Bhatnagar, 2011; Habuda-Stanic, 2014).

The studies conducted by various scientist revealed that the process depends on many factors of which selectivity for metal ions, temperature, pH of solution, contact time, particle size and adsorbent dosage are the most important characteristics which determined adsorbent suitability for practical application. Among the above-listed characteristics and process parameters, adsorbent's selectivity for fluoride ions seem to be most important adsorbent characteristic since some of adsorbents showed high efficiency in test bench but, in the same time, fail under real conditions at water treatment plant due to reducing the effective adsorption capacity caused by adsorbents active sites occupation by other co-ions present in treated water (Habuda-Stanic, 2014).

Recently the interest is growing in fluoride removal by biomass based adsorbents due to their lower cost and easy availability. It has been reported that the presence of chemical functional groups such as hydroxyl, carbonyl, carboxyl, sulfhydryl, thio-ether, sulfonate, amine amide, imidazole, phosphonate, and phosphodiester on the biosorbent surface contribute to biosorption (Hunt, 1986; Greene *et al.,* 1987; Mann, 1990). However, challenges such as access to real low-cost adsorbents, simpler processes for development of efficient adsorbent at local levels, sufficient availability at or near to fluoride affected areas, and high fluoride removal efficiency on real groundwater conditions such as the existence of neutral pH are still prevailing. So, the main task of scientists and experts is to find or develop cheap, efficient and environment-friendly, but highly selective adsorbent with high effective adsorption capacity for rural areas in the developing, and undeveloped countries.

2.9.1. Mechanism of Adsorption

Theoretically, the adsorption of fluoride on to solid particles normally takes three essential steps (Fan *et al.,* 2003):

1. Transport of adsorbate from the bulk of the solution to the exterior film surrounding the adsorbent particle;
2. Adsorption of fluoride ions on to particle surfaces;
3. The adsorbed fluoride ions probably exchange with the structural elements inside adsorbent particles depending on the chemistry of solids, or the adsorbed fluoride ions are transferred to the internal surfaces of porous materials.

2.9.2. Types of Adsorption

2.9.2.1. Physical Adsorption

Physical adsorption is relatively non-specific due to the operation of weak forces of attraction of Vander Waals forces between molecules. Here, the adsorbed molecule is not affixed to a particular site on the solid surface, but it is free to move over the surface. In addition, the adsorbed material may condense and form several superimposed layers on the surface of the adsorbent. Physical adsorption is generally quite reversible, with a decrease in concentration; the material is desorbed to the same extent that it is originally adsorbed (Habuda-Stanić *et al.* (2014).

2.9.2.2. Chemical Adsorption

Chemical adsorption is the result of much stronger forces, comparable with those leading to the formation of chemical compounds. Normally the adsorbed material forms a layer over the surface, which is only one molecule thick, and the molecules are not considered free to move from one surface site to another. When the surface is covered by the monomolecular layer, the capacity of the adsorbent is essentially exhausted. Also, chemical adsorption is seldom reversible. The adsorbent must be generally heated to higher temperature to remove the adsorbed materials (Habuda-Stanić *et al.* (2014).

2.9.3. Biosorption

Biosoption offers advantages of high efficiency in dilute effluents (Habuda-Stanić *et al.*, 2014). Recently, trends are emerging on the application of biosorbent materials for removal of various pollutants. It provides a cost-effective solution for water purification. Various previous work are as given below:

Sinha *et al.* (2003) conducted experiment for fluoride removal from aqueous solution using activated carbon prepared from *Eichhornia crassipes*. The results showed adsorbent prepared at higher temperature (H-type activated at 600°C) showed 72–98% adsorption in compared to 51–93% adsorption by one temperature (L-type activated at 300°C) carbon. The adsorbent followed Langmuir isotherm with maximum sorption capacity for fluoride removal calculated to be 1.54 mg/g. Column studies were also performed with an initial concentration of 15 mg/L and the effluent volume at breakthrough was found to be 100 bed volumes, and the column capacity was calculated as 4.4 mg/g.

Sivabalan *et al.* (2002) studied adsorption of fluoride using activated carbon prepared from palm seed coat (PSCC) by dolomite process. Adsorption of fluoride was found to be pH dependent and higher removal efficiencies were observed in the pH range of 4–8. The pH, total alkalinity, total hardness, total dissolved solids of the treated water were not found to change appreciably.

Parmar *et al.* (2006) investigated adsorption of fluoride on untreated and aluminium chloride/calcium chloride treated corn cobs powder. Untreated powdered corn cobs did not show remarkable adsorption but aluminium treated corn cobs (Al-ccp) had good adsorption capacity. All the experiments were carried out at pH 6.5. The breakthrough fluoride capacity was found to be 18.9 mg/g and 15.12 mg/g for Ca-ccp with Al-ccp, respectively, at initial fluoride concentration of 12.60 mg/l. The fluoride was found to leach out up to 25% using 0.1 M NaOH. The experimental results revealed that leaching of Ca^{2+} and Al^{3+} was negligible.

Daifullah *et al.* (2007) investigated fluoride removal using activated carbon prepared by one-step steam pyrolysis of rice straw at 550, 650 and 750 °C and modified by liquid-phase oxidation using HNO_3, H_2O_2 and $KMnO_4$. Batch adsorption studies for effect of pH (2–10), adsorbate concentration (5–20 mg/l, adsorbent dosage (25–500 mg/L), contact time (1–24 h), temperature (25–55 °C), and co-ions (SO_4^{2-}, Cl^-, Br^-) were performed. The authors reported that the best results and 100% of fluoride removal was obtained with activated carbons oxidized with $KMnO_4$ at optimum pH 2.0. They emphasized that the solution pH was the most important parameter affecting adsorption. Sorption occurs better at lower temperatures and the presence of natural organic matter decreases fluoride adsorption.

Karthikeyan *et al.* (2007) undertook fluoride adsorption study using activated carbon obtained by burning and carbonization of the *Moringa indica* bark. The authors reported appreciable defluoridation efficiency of over 71% from neutral aqueous fluoride solution of 2 mg/L. Further increase of fluoride concentration resulted in decrease of adsorption capacity of tested activated carbon.

Sathish *et al.* (2007) investigated for fluoride removal from water by zirconium-impregnated coconut shell carbon (ZICSC). The fluoride adsorption by ZICSC was above 90% for the entire pH range of 2–9. The Langmuir maximum capacity of ZICSC for fluoride was 7.51 mg/g at pH 6.

Mohan *et al.* (2007) investigated defluoridation studies using *Spirogyra* IO2 as adsorbent. The results showed impact of pH on fluoride removal. Removal efficiency showed a marked decrease as the pH of the solution increased from 2.0 to 10.5. At acidic pH due to the protonated effect of surface functional groups such as amino, carboxyl, thiol, the algae imparts positive charge on the surface and encouraged the sorption of fluoride. Maximum adsorption efficiency and Langmuir adsorption capacity of 54% and 1.272 mg/g respectively were observed at pH 7. Desorption was found to be more evident in inorganic solution and distilled water which were supposed to be an indication of the combined effect of ion exchange and physical sorption phenomena for fluoride removal by *Spirogyra* IO2. The FTIR results of the fluoride sorbed *Spirogyra* IO2 exhibited the participation of surface functional groups associated with hydrogen atoms in the carboxylic groups in sorption interaction.

Same workers studied fluoride sorption potential of non-viable algal *Spirogyra* IO1. The Langmuir maximum sorption capacity of fluoride was 1.272 mg/g. Fluoride sorption was dependent on the aqueous phase pH and higher fluoride uptake was exhibited at lower pH and such behaviour was attributed to positively charged surface of adsorbent at lower pH which facilitated fluoride sorption, probably by the anionic exchange process.

Ramanaiah *et al.* (2007) carried out fluoride adsorptive studies using waste fungal biomass (*Pleurotus ostreatus* 1804) derived from laccase fermentation process. Fungal sorption system showed a marked decrease as the pH of the solution increased from 2.0 to 10.0. The fluoride sorption efficiency and Langmuir maximum sorption capacity at pH

7.0 was found to be 52% and 1.272mg/g. The fluoride sorption phenomenon on fungal biosorbent was attributed to the chemical type of interaction.

Sathish *et al.* (2008) investigated applicability of zirconium-impregnated coconut fiber carbon (ZICFC) as an adsorbent for fluoride removal from water. Maximum defluoridation was obtained at pH 4.0. The fluoride sorption capacity decreased at higher pH due to the competition of active sites on ZICFC surface between OH^- and F^-. Langmuir sorption capacity of 40.02 mg/g at pH 4 was reported for fluoride by ZICFC. A combination of chemisorption and physisorption processes with intraparticle diffusion, were accounted for the high defluoridation ability of ZICFC.

Emmanuel *et al.* (2008) studied removal of fluoride on commercially activated carbon and indigenously prepared activated carbons from *Pithecellobium dulce*, *Ipomoea batatas* and *Peltophorum ferrugineum*. The results of the experiments have shown that the percentage of fluoride removed increased with the increase of contact time (10–120 min) and dose of adsorbent (0.5–9 g/L). Conversely, the percentage of removal decreased with the increase in initial concentration of the standard fluoride solution (1–8 mg/L). The results suggest that intraparticle adsorption is very important in the adsorption process. The adsorption process is found to be of first order with the intra particle diffusion as one of the rate determining steps. Among the adsorbents under consideration, *Pithecellobium dulce* carbon possesses the highest or the maximum adsorption capacity. Hence it is the best and the most effective adsorbent in the removal of the fluoride content in water. The next in the order on the basis of its efficacy in removing the fatal content is *Ipomoea batatas* carbon and *Peltophorum ferrugineum* carbon. The adsorption capacity and efficacy in the removal of fluoride are far greater than commercial activated carbon.

Miretzky *et al.* (2008) conducted defluoridation study was using aquatic macrophyte biomass (*Eleocharis acicularis*) pre-treated with Ca^{2+}. The maximum fluoride adsorption capacity reported was 0.110 mmol/g with an efficiency of 64.5% (pH 6.0; 5.0 g/L Ca-pretreated biomass). The binding of Ca^{2+} to the biomass exhibited an increase in the removal efficiency over 100%.

Rao *et al.* (2009) carried out adsorption studies on the removal of fluoride from potable water using activated *Dolichos lablab* carbon under various experimental conditions. The results of experiments have shown that the percentage of fluoride removal has increased with the increase of contact time and dose of adsorbent. Among the four activated adsorbent samples prepared from activated *Dolichos lablab* carbon under consideration, HNO_3 activated carbon possesses the highest or maximum adsorption capacity. Hence it is the best and the most effective adsorbent sample in the removal of fluoride content in water.

Alagumuthu and Rajan (2010) investigated the potential of zirconium impregnated cashew nut shell carbon (ZICNSC) and compared its performance with that of cashew nut shell carbon for fluoride removal from aqueous solutions. The ZICNSC exhibited 80.33% fluoride removal when compared with cashew nut shell carbon (72.67%) in a contact time of 180 min. The CNSC with 53 m particle size registered high defluoridation efficiency due to larger specific surface area and were used for further experiments. The maximum percentage removal of fluoride by the samples was observed at pH 3 with the pHzpc for CNSC and ZICNSC being reported as 7.6 and 4.2. The presence of CO_3^{2-} resulted in the decrease of fluoride removal from 80.33% to 60.23% whereas Cl^-, SO_4^{2-} and NO_3^- showed no remarkable influence on fluoride removal. The enhanced removal of fluoride by ZICNSC was attributed to adsorption by physical forces and strong coordination between the fluoride ion (a Lewis base) and zirconium ions adsorbed on CNSC (which acted as Lewis acid sites).

Alagumuthu and Rajan (2010) evaluated fluoride removal by zirconium impregnated groundnut shell carbon. The sorption of fluoride ion on groundnut shell carbon and zirconium impregnated groundnut shell carbon has been investigated as a function of contact time in the range of 60–210 min with 3 mg/L as initial fluoride concentration and 2.0 mg of adsorbent at room temperature. The zirconium impregnated carbonized ground nut shell recorded a maximum percentage of fluoride removal, 83.77%, when compared with carbonized ground nut shell which showed fluoride removal of 63.67%. No significant influence on fluoride removal of the material was observed in the presence of Cl^- and SO_4^{2-}. However, in the presence of excess HCO_3^-, the defluoridation efficiency decreases from 83.77% to 74.6% in presence of about 500 mg/L of bicarbonate. It is observed that with increasing of pH of solution, the fluoride removal by these sorbents decreased. At pH = 3, the maximum percentage of fluoride removal by groundnut shell carbon and zirconium impregnated groundnut shell carbon was 84.67% and 94.33%, respectively.

Alagumuthu *et al.,* (2011) studies adsorption of fluoride on activated carbon prepared from *Cynodon dactylon* Fluorides have been removed by the level of 83.77% while keeping 3.0 mg/L fluoride concentration and 1.25 g dosage of adsorbent at neutral pH. However, the presence of bicarbonate ions interfere the effective removal of fluoride. The sorption of fluoride using this adsorbent followed Redlich–Peterson isotherm as well as Langmuir isotherms and was found to be spontaneous and endothermic in nature. The rate of sorption followed the pseudo-second-order kinetic model and occurred through intraparticle diffusion. The used adsorbents could be regenerated by 67.4% using of 2% sodium hydroxide. Based on the above said descriptions

Ganvir and Das (2011) investigated possibility of fluoride removal using rice husk ash which was coated with aluminium hydroxide. Rice husk ash was obtained by burning rice/paddy husk which is an abundantly available and is an inexpensive raw material. The adsorption experiments were conducted with initial fluoride concentrations in range of 10–60 mg/L and 0.1 g of adsorbent, while pH value of the initial fluoride solution was adjusted to about 7. All of the experiments were carried out at 27 °C during 1 h. Adsorption study indicates the adsorption capacity of modified rice husk ash to be 15.08 mg/g, while column studies show 9.5 mg/g capacity. Experiments show strong pH-dependence since the maximum fluoride removal was obtained when the pH was kept at 5.0.

Rao *et al.,* (2011) investigated batch adsorption dynamics and equilibrium studies for the removal of fluoride ions from aqueous solution using indigenously *Acacia farnesiana* carbon under various experimental conditions at room temperature. Results found that, initially, the percentage removal of fluoride ions increased with a decrease in initial concentration and increased with an increase in contact time and, after 40–45 min, the percentage removal is found to be almost constant. Adsorption is highly pH sensitive and the optimum pH range for maximum adsorption of fluoride ion is found to be 6.5–7.0, with maximum absorption around 6.9, after which it decrease with increasing pH. For the same pH, fluoride adsorption follows the Freundlich isotherm, indicating that the *Acacia farnesiana* carbon surface is highly heterogeneous. It is a widely used adsorbent in the treatment of wastewaters due to its exceptionally high surface areas (500 m^2/g to

1500 m^2/g), well-developed internal microporosity structure as well as the presence of a wide spectrum of surface functional groups (Yin *et al.,* 2007).

Veeraputhiran and Alagumuthu (2011) investigated the efficiency of activated carbon prepared from *Phyllanthus emblica* (Indian Gooseberry) for fluoride removal from groundwater. It was concluded that the rate of adsorption of fluoride was increased with increase in contact time. Also the adsorption capacity decreases with increase in concentration. The removal efficiency at 2 mg/L concentration was found to be 87.95% and at 10 mg/L it was found to decrease to 47.22%. It was concluded that the removal efficiency is highly dependent upon contact time, adsorption dose and concentration and fluoride could be successfully removed from groundwater using *Phyllanthus emblica* based activated carbon. Also the presence of bicarbonate ions interfere the defluoridating property of this adsorbent but this interference is insignificant for other co-anions.

Huang *et al.* (2011) investigated adsorption capacity for fluoride anion by using cheap garlic peel as the raw materials via simple saponification and Zr (IV)-loading treatment. This biosorbent may be applied to the purification of drinking groundwater in the countryside areas where fluoride pollution is severe. The pH value has strong effect on its adsorption behaviour, and pH 2.0−4.0 is suitable for adsorption of fluoride. The adsorption capacity of the Zr-loaded garlic peel is evaluated to be 0.89mmol/g and 1.10 mmol/g at equilibrium pH 6 and 2 respectively. The adsorption process fits the pseudo-second order kinetic model, and the corresponding adsorption rate constant is evaluated to be 3.25×10^{-3} g/mg·min.

Vardhan and Karthikeyan (2011) investigated fluoride sorption onto rice husk powder. Maximum sorption of 83% was accomplished with sorbent dosages of 6 g/l of rice husk and equilibrium time of 3 hours. pH does not have any significant impact in the range of 3-10, whereas pH of more than 10 resulted in a steep decrease in fluoride removal. The isotherm study shows rice husk follows Langmuir isotherm.

Paudyal *et al.* (2012) developed a metal loaded orange waste gel for the removal of trace concentration of fluoride from aqueous solution. Various metal loaded adsorbents were prepared from orange waste through chemical modification followed by loading with metal ions to systematically evaluate the adsorption behaviors. The association of various multi-valent metal ions such as Al_3^+, La_3^+, Ce_3^+, Ti_4^+, Sn_4^+ and V_4^+ with fluoride is high because of their high stability with fluoride ions.

Ghimire (2012) reported that cerium and lanthanum metal ion loaded phosphorylated orange juice residue gel is also highly effective for fluoride ion removal. Thus, the new material produced from orange juice waste can be used for the treatment of fluoride contaminated wastewater.

Hernández-Montoya *et al.* (2012) investigated the possibility to obtain low cost carbon selective for fluoride removal, and, therefore, they impregnated pecan nut shells with a calcium-rich solution extracted from egg shell using L_4 orthogonal array of the Taguchi method for optimization of the carbon synthesis. After synthesis, obtained low cost carbon was tested for fluoride removal from synthetic and real groundwater samples. The fluoride adsorption capacities of carbon were measured at 30 °C using an adsorbent/solution ratio of 8 g/L and a model solution with initial fluoride concentration of 20 mg/L, while used real groundwater had initial fluoride concentration of 14.10 mg/L. They observed that used synthesized low cost carbon had better adsorption performances when model solution was treated (84% of initial fluoride concentration was reduced), while only 20% of initial fluoride concentration was reduced from groundwater samples when the same low cost carbon was used.

Chakrabarty and Sarma, (2012) carried out research on adsorption capacity of neem charcoal from fluoride solutions. 94 % fluoride ions were removed from solution of 10 mg/L fluoride concentration and equilibrium was achieved in 180 min.

Bark of babool was used as an adsorbent by Mamilwar *et al.* (2012) and found that when bark of babool is used at an optimum dosage of 5 g/L, it had maximum capacity of 0.77 mg/g.

Merugu *et al.* (2012) investigated removal of fluoride by fungal biosorbent prepared from *Fusarium moniliforme.* Fluoride removal capacity was found to be 24% at pH = 5.0 and 11% at pH = 8.0. The capacity of fluoride removal decreased with increased bicarbonate concentration, but was independent of the presence of chloride and sulfate. The kinetics of fluoride removal exhibited a rapid phase of binding for a period of 1 h and a slower phase of binding during the subsequent period.

Pandey *et al.* (2012) utilized *Tinospora cordifolia* for fluoride biosorption experiment. The result indicated strong effect of pH on biosorption capacity. The biosorption was rapid and equilibrium was achieved within 120 min with uptake capacity of 25 mg fluoride per gram adsorbated at optimum pH 7. The results indicate that Langmuir and Freundlich sorption models were good agreement with the experimental results. Further, the biosorbents were characterized by FTIR spectral analyses. The biomass was found to be very efficient, instantaneous and economical for removing fluoride from drinking water. This biosorptive material is very useful to reduce fluoride within standard WHO permissible limit (1.5 mg/L) at neutral pH.

Singanan (2013) investigated adsorption capacity of *Tridax procumbens* from fluoride solutions. The biosorption process of fluoride ions on AMEBC technology is promising and is influenced by many experimental factors. Remarkably, fluoride removal is favoured at room temperature and slightly at basic pH. The result indicates that maximum removal (98%) of fluoride ion in synthetic sample was achieved in 180 minutes. The amount of biocarbon dose is 2.0 g. Removal of fluoride of concentration from 3.6 to 0.7 mg/L from the field water sample was achieved successfully. The removal process caused by electrostatic and hydrogen bond formed between fluoride ions and the adsorbent and also involves ion-exchange mechanism. The result was well fitted in both Langmuir and Freundlich isotherm models.

Suneetha *et al.* (2014) studied impact of activated carbon from stems of *Abutilon Indicum* plant on removal of fluoride from waters. The optimized result was obtained at neutral pH with dosage of 5 g/l adsorbent of 45µ micron particle size at the end of an hour. The adsorption process followed Langmuir isotherm. The adsorbate were adsorbed on monolayered adsorbent via physisorption.

Tomar *et al.* (2014) examined defluoridation by a suitable adsorbent obtained from treated *Citrus limonum* (lemon) leaf. Batch experiments were performed to study the influence of various experimental variables such as pH of aqueous solution (2–8), adsorbent dose (1–10 g/50 mL fluoride solution), contact time (5–145 min), initial fluoride concentration (2–15 mg/L) and the presence of few competing anions on the adsorption of fluoride on *C. limonum* (lemon) leaf adsorbent. The authors reported that maximum defluoridation capacity was achieved at pH 2. `The experimental data revealed that both the Langmuir and Freundlich isotherm models fitted with the fluoride sorption process but followed a Freundlich isotherm model very well.

***Tamarindus indica* as a biosorbent**

The tamarind (Tamarindus indica L.) is a tree-type of plant which belongs to the Leguminosae, caesalpiniaceae family. It is indigenous to tropical Africa but also cultivated in subtropical China, India, Pakistan, Philippines, Java and Spain. Recently *Tamarindus indica* is the most commonly used biosorbent for adsorption of many pollutants either dyes or metals.

Sivasankar *et al.* (2010) have presented the defluoridation capacities of activated tamarind fruit shell (ATFS) and MnO_2 coated tamarind fruit shell (MTFS), using batch and column sorption techniques. They found that sorption capacities of the ATFS and MTFS adsorbents were 0.2145 and 0.2178 mg/g, respectively, at pH of 6.5 with an initial fluoride concentration of 2 mg/L. The interference of bicarbonate ions was observed with a decreased defluoridation percentage of 63.5 and 98 for ATFS and MTFS, respectively. The diffusion-based models revealed that the fluoride sorption onto the above sorbents was governed by the combined effects of the surface and intraparticle diffusion processes. The Freundlich adsorption constant (K_F) of MTFS was found to be 1.58 times greater than that of ATFS. Chemosorption was justified by Temkin from the column experimental results, the fitness of the Thomson equation indicated that the increase in bed height caused an increase in the mass transport resistance and axial dispersion, which was confirmed from the k_T values.

Ramanjaneyulu *et al.* (2013) utilized waste material such as Ficus leaf powder and Tamarind fruit shell for the investigated of fluorine removal from drinking water. The adsorbents used are natural, economically cheap and eco-friendly. Tamarind fruit shell exhibited highest fluorine removal efficiency 85% at pH of 2, initial fluorine concentration of 3 mg/l, contact time of 90 min, adsorbent dosage of 2g/100ml and maintaining temperature of 307K. From the experimental data the Langmuir isotherm was best fit since the correlation coefficients for Langmuir isotherm was higher than the Freundlich isotherm. With the increase of adsorbent amount the percentage removal of fluoride increases but the adsorption capacity decreases because of availability of more unsaturated adsorption sites.

Kumar *et al.* (2012) investigated defluorination potential of tamarind fruit cover in its natural and acid treated forms. The maximum uptake of fluoride ions occurs at pH 6.0. The data obtained fit well to both the Langmuir and Freundlich isotherms. At room temperature maximum monolayer biosorption capacities of TNFC in both natural and acid treated forms was recorded to be 4.14 mg/g, 6.11 mg/g, respectively. The kinetic studies indicated that the sorption of fluoride on TNFC in both natural and acid treated forms followed pseudo-second-order kinetic model. Results of this investigation proved that TNFC in its virgin and acid treated forms is a suitable alternative for the removal of fluoride ions from aqueous media compare to other bioadsorbents.

Sivasankar *et al.* (2012) performed defluoridation experiment with carbonized T. indica fruit shell impregnated with ammonium carbonate solution. The adsorbate was studied for fluoride removal efficiency of ACA–TIFSC as a function of pH, initial fluoride concentration, sorbent dose and co-ionic interference. The experiment emphasized on influence of two agitation methods, shaking and stirring, on defluoridation. Results revealed that the stirring method appeared more efficient than the shaking method. The adsorbent follows Langmuir isotherm, thus monolayed adsorption, in both the studies. Stirring and shaking method showed greater influence on adsorption kinetics. Overall the adsorbent was efficient enough to defluorinated highly contaminated water. However, the chemosorption of the fluoride was hindered by bicarbonate ions a lot. Even bicarbonate-free groundwater increased the the fluoride scavenging capacity of ACA–TIFSC to a maximum of 8% and 11% during shaking and stirring sorption methods.

With this in perspective, current work was undertaken to explore the feasibility of fluoride adsorption from aqueous solutions and groundwater samples from Kheralu Taluka by *Tamarindus indica* seeds as adsorbents. This adsorbent is waste agricultural material easily available in almost all of the rural areas. The plant is proven to be beneficial in fluoride eradication from the body of rats. Also it has many other medicinal properties.