Chapter II

REVIEW OF LITERATURE

2.1. Introduction

Water is renewable natural resource of earth and is essential for all living organisms (animals, plants and human) for their existence and metabolic processes in the world. Major water sources on the earth are saline water (seas and oceans) which constitutes 99% of the total water available and remaining 1% of water sources include the fresh water bodies on the earth and the groundwater sources. The meager quantity about 45% of the groundwater is met for our country’s agriculture demand, domestic about 88% of rural areas in our country and industrial purposes (Bathusha and Saseetharan 2006).

2.2. Biggest challenges of 21st century

The biggest challenge is to make sure that hygiene and clean drinking water is the essence of health and environment. The widespread drinking water shortage, aggravated pollution and gradual deterioration in various parts of the world demand for incorporated management of water resources (Haron and Yunus 2001). The United Nations conducted World Water Assessment Programme stating that water availability will be reduced to one-third over next 20 years. World Health Organization (2008) gave a statistics of about 2.7 billion people will face water shortage problem by 2025.

The occurrence of fluoride and its concentration in surface water, water resource and groundwater is based on the criteria like geochemical composition of aquifers, alkalinity, hardness, total dissolved solids and pH (Stanic et al. 2014). The elevated concentrations of fluoride in many other countries are due to pollution from fluorine contaminated waste water discharges from glass and ceramic manufacturing processes, steel production factory, superphosphate fertilizer
industry, aluminium and zinc smelters, uranium enrichment facilities, beryllium extraction plants, coal fired power stations, oil refineries, silicon based high tech-semiconductors production, photovoltaic solar cells industry, municipal waste incineration plants through hydrogen fluoride (HF) emissions caused by incinerating of fluorinated plastic and fluorinated textiles or CaF$_2$ decomposition in waste sludge (Bhatnagar et al. 2011; Paudyal et al. 2012; Drouiche et al. 2009; Ponsot et al. 2013 and Fan and Li 2013).

2.3. Defluoridation techniques

The World Health Organization (WHO) has drawn a line of permissible range for fluoride in drinking water as 1.5 mg/L due to the pollution of fluoride and health problems that it causes for the mankind. Based on this, various technologies have been identified to remove fluoride from groundwater, they are: membrane process (Chakrabortty et al. 2013 and Ghosh et al. 2013), coagulation and precipitation (Gohary et al. 2010 and Gong et al. 2012), electrochemical treatments (Cui et al. 2012; Piddennavar 2013 and Un et al. 2013), ion-exchange process (Guo and Tian 2013 and Paudyal et al. 2013a) and adsorption method (Alagumuthu et al. 2010).

In the present defluoridation study, adsorption process was adopted though it has some disadvantages like readjustment of pH and interference of common water ions with fluoride adsorption but it has greater accessibility, simple operation, low cost and availability of wide variety of adsorbents.

2.3.1. Adsorption

Adsorption technology has been widely used in recent years for the high-valence metals to the functionalized sorbents and argues that the technique is highly economical, efficient and produces high quality water (Onyango et al. 2004). Adsorption of fluoride process on to the solid adsorbent involves transport of fluoride ions on to the outer surface of the adsorbent from the aqueous solution,
adsorption of fluoride on to the active sites of the adsorbent and the adsorbed fluoride ions exchange with the elements present in the adsorbent that depends on the chemistry of solids or intra particle diffusion (Fan et al. 2003 and Mohapatra et al. 2009).

Adsorption is based on the adsorbate in the solution that diffuses through the adsorbent and bond with weak intermolecular forces (Li et al. 2011). The characteristic of adsorbent are determined for its suitability based on the selectivity for fluoride ions, adsorption capacity like pH, initial fluoride concentration, temperature, contact time, adsorbent dosage, particle and pore size, compatibility, cost and regenerability (Tomar et al. 2014 and Knaebel 2014).

2.3.2. Adsorption isotherm

Brunauer et al. (1972) categorized the adsorption isotherm into monolayer and multilayer. Adsorption isotherm is defined as the relationship between the amount of adsorbate adsorbed on the surface of adsorbent and equilibrium concentration of the adsorbate at a certain temperature. Adsorption capacity was experimented with batch and column mode studies. An isotherm model is suitable tool to assess the adsorption capacities. In batch study, a fixed quantity of adsorbent was made to react with adsorbate in a rotary shaker as batch system whereas in column study adsorbent was packed in column and adsorbate was continuously passed through the adsorbent.

2.4 Adsorbents for defluoridation

2.4.1. Alumina and aluminum based adsorbents

2.4.1.1. Alumina

Activated alumina had been the better adsorbent with high surface area, activation process and crystalline nature. Stewart (2009) reported that the activated alumina exhibited a complex process in adsorbing the fluoride based on temperature, pH, initial fluoride concentration, common ions like bicarbonate and
sulfate interfered with fluoride and surface morphology for the removal of fluoride from groundwater. The optimum pH was found to be in the range of 4.0-6.0 which was due to the electrostatic interactions between the fluoride concentration and the active sites present on the surface of the activated alumina. The equilibrium second ordered kinetic model fitted well with adsorption data and the defluoridation capacity was found to be 1566 mg/kg.

Johnston and Heijnen (2002) compared with untreated hydrated alumina (UHA) and thermal treated hydrated alumina (THA). It was heated at 200°C, the pH 4-9 showed high efficiency, fitted well with Freundlich isotherm and regenerated with 4% sodium hydroxide. Tripathy et al. (2006) showed the efficacy of alum-impregnated activated alumina (A/AA) treated at pH 6.5, adsorbent dose of 8 g/L, fluoride concentration 25 mg/L for 3h of contact time. Defluoridation capacity was 92.6% and the EDAX analysis showed that the uptake of fluoride on surface of the adsorbent.

The defluoridation capacity was increased further by incorporating alumina polymeric composites onto the chitosan polymeric matrix in a form of candles, beads and membranes. The alumina/chitosan complex was not influenced by pH but interfered by the presence of bicarbonate ions. The adsorption capacity followed Freundlich isotherm and the reaction was endothermic, spontaneous and controlled by electrostatic adsorption and complexation mechanism with a maximum defluoridation capacity of 3809 mg/kg (Viswanathan and Meenakshi 2010).

2.4.1.2. Alumina plus manganese dioxide/magnesium oxide

Maliyekkal et al. (2006) reported with manganese oxide-coated alumina (MOCA) had the capacity of removing 2.85 mg/g of fluoride. Tripathy and Raichur (2008) improved the adsorbent with manganese dioxide-coated activated alumina. The experiment was carried out at pH 5.5 and fluoride concentration 10 mg/L which reduced to 0.2 mg/L of fluoride. Zeta potential, kinetics, isotherm modeling and EDAX showed the adsorption of fluoride on to the adsorbent. Teng et al. (2009)
synthesized hydrous manganese oxide-coated alumina (HMOCA). It was experimented in batch and column mode with the fluoride concentration 5 mg/L was reduced to 1 mg/L in the treated water.

Maliyekkal et al. (2008) continued with magnesia-amended activated alumina (MAAA) calcined at 450°C and studied at neutral pH, 10 mg/L of fluoride concentration and 3 h contact time. The percentage of removal was 95% with the maximum sorption capacity of 10.12 mg/g and had no interference of ions. Magnesium oxide or magnesia (MgO), a well known adsorbent was used along with chitosan as MgO/chitosan composite for the removal of fluoride. The defluoridation capacity was found to be 4440 mg/kg, not influenced by pH except for the interference of bicarbonate ion and the equilibrium data obeyed Freundlich isotherm (Sundaram et al. 2009).

### 2.4.1.3. Alumina plus iron oxide

According to Biswas et al. (2007) aluminium and iron (III) hydroxides was a good adsorbent when compared to aluminium hydroxide or iron (III) hydroxide. It was because of the bonding between Fe-O-Al bonds confirmed through Fourier transform infrared (FTIR) spectra. An irregular surface morphology was observed by scanning electron microscopy (SEM) that showed high surface area and high porosity. It obeyed Langmuir isotherm with the monolayer adsorption. Chubar et al. (2005) studied with aluminium and iron (III) chloride which showed defluoridation (88 mg/g of adsorbent) was effective at pH 4.

Dey et al. (2004) studied the interaction of fluoride solutions with hydrous iron oxides and hydrous ferric oxides as a scavenger of fluoride from contaminated water. Tang et al. (2009) learned with commercial granular ferric hydroxide to understand the parameters like pH, ionic strength and co-existing anions. Zhao et al. (2010) examined the synthesized Fe$_3$O$_4$-Al (OH)$_3$ magnetic nanoparticles towards fluoride removal from aqueous solution. Batch mode of study was carried...
out with pH varied from 5-9, temperature 25-50°C, initial fluoride concentration 0-110 mg/L, adsorption time 0-240 min and common ions. The adsorption capacity increased with increase in temperature and was found to be 88.48 mg/g at pH 6.5 which followed pseudo second order rate equation.

2.4.1.4. Alumina plus calcium minerals

Alumina plus calcium minerals reminded of the Nalgonda technique namely alum (aluminium sulphate or potassium aluminium sulphate) and lime (calcium oxide) are mixed with the fluoride contaminated water. The Nalgonda technique has been introduced in Kenya, Senegal, Tanzania and India. Apparao and Kartikeyan (1986) criticized the technique that 67-82% ionic fluorides are converted into Al\(^{3+}\)-F complex ions, a toxic compound which causes dementia, musculoskeletal, respiratory and cardiovascular systems (Nayak 2002). Meenakshi and Maheshwari (2006) have commented on the maintenance cost, a plant of 10,000 L per day capacity requires Rs. 3000 every month which are extremely high.

2.4.1.5. Aluminium hydroxide coated rice husk ash

The rice husk ash (RHA) reported to have high surface area 70-100 m\(^2\)/g with 85-95% silica, 4-12% carbon and 0.25-0.3 g/cm\(^3\) bulk density which made a good filter material fabricated with RHA, pebbles and ordinary Portland cement. A novel and inexpensive patented technique using aluminum hydroxide (AH) coating on the rice husk ash (RHA) surface was reported by Ganvir and Das (2011). The defluoridation process was based on the interaction between F\(^-\) and OH\(^-\) charges that ultimately forms fluoride aluminum hydroxide complex.

2.4.2. Calcium based sorbents

A widespread research had been done with calcium salts as calcium for the removal of fluoride as it was found with affinity towards fluoride ion (Bhatnagar et al. 2011). Turner et al. (2005) used crushed limestone to treat fluoride concentrations ranging from 3 to ~ 2100 mg/L and surface-sensitive techniques such as X-ray
photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and zeta potential. The surface techniques proved that the precipitation reactions and surface adsorption removed fluoride from aqueous solutions based on the calcite surface area. The AFM and Zeta potential technique showed that the adsorption process was instantaneous. The dissolution of Ca$^{2+}$ concentration in solution saturated with CaF$_2$, fluorite precipitation and replenishing dissolved Ca$^{2+}$ allowing further precipitation of CaF$_2$.

Islam and Patel (2011) worked with activated quick lime. The Langmuir isotherm was $16.67 \text{ mg/g}$ and the percentage of fluoride removal was $80.6\%$ for $50 \text{ mg/L}$ of fluoride concentration. Scanning electron microscopy (SEM) micrographs and X-ray diffraction (XRD) studies revealed that the defluoridation process was due to precipitation and chemisorptions. Jain and Jayaram (2009) treated fluoride with aluminium hydroxide impregnated limestone (A1LS). The adsorption capacity occurred due to physi-sorption and was found to be $84.03 \text{ mg/g}$.

2.4.3. Iron based sorbents

2.4.3.1. Schwermannite

Schwertmannite is a natural geomaterial, stability at low pH and has magnetic properties to attract fluoride ions from fluoride contaminated water. Schwertmannite was studied in a batch system with pH 3-11, adsorbent dosage 0.025-0.10 g/50 mL, adsorbate concentration 10-90 mg/L and co-existing ions such as chloride, nitrate, sulfate and phosphate. The adsorbent had the capacity to reduce the fluoride level to the acceptable value (1.5 mg/L) and was regenerated after the precipitation or coagulation process. The adsorption capacity was observed in acidic pH at 3.0 and the removal of fluoride increased with increase in pH but the adsorbent efficiency decreased sharply. The equilibrium adsorption data were obtained at 295.6, 303 and 313 K and are interpreted in terms of two-site Langmuir,

2.4.3.2. Iron-impregnated granular ceramics

Chen et al. (2010) used iron-impregnated mesoporous granular ceramics for fluoride removal from aqueous solution. Batch mode of studies were reported with pH ranging from 4.0-10 and co-ions interfered with fluoride sorption capacity in the presence of phosphate, sulfate and carbonate whereas the fluoride sorption increased with the presence of chloride and nitrate ions. The maximum adsorption capacity was found to be 2.16 mg/g at 30°C and fitted well with the Langmuir and Freundlich isotherm models and followed pseudo second order kinetic model. Desorption was carried out with 0.1 M HCl and exhibited as a promising material for the removal of fluoride from groundwater due to its granular structure, high surface area and good adsorption capacity.

Chen et al. (2011) extended the work with iron-impregnated granular ceramics mixed with Kanuma mud, zeolite, starch and FeSO₄·7H₂O/Fe₂O₃ (in the ratio of 4:3:2:1) which was efficient, novel and cost effective for the removal of fluoride from drinking water. The granular ceramics (GC) (FeSO₄·7H₂O) was more effective for fluoride removal than GC (Fe₂O₃) in adsorption capacity. The optimum pH for fluoride removal on GC (FeSO₄·7H₂O) and GC (Fe₂O₃) was 7.0 and 4.0 respectively. Maximum adsorption of fluoride on GC (FeSO₄·7H₂O) and GC (Fe₂O₃) were 94.23% and 60.48% respectively. The experimental data fitted with Langmuir and Freundlich isotherm models for these two adsorbents. The two adsorption process followed pseudo second order kinetics with intra-particle diffusion as the rate determining step. The thermodynamic parameters were favorable, spontaneous and endothermic in nature.
2.4.4. Metal oxides/hydroxides/oxyhydroxides, mixed metal oxides, metal impregnated oxides as sorbents

2.4.4.1. Bauxite

Das et al. (2005) used thermal activated titanium-rich bauxite (TRB) at temperature 300-450°C, pH 5.5-6.5 and equilibrium adsorption was reached within 90 min without interference of ions. Sajidu et al. (2008) studied with locally available bauxite which has the capacity to adsorb 93.8 % at a dose of 2.5g/200 mL of 8 mg/L F⁻ solution. X-ray diffraction characterization of the raw bauxite showed gibbsite (Al(OH)₃) and kaolinite (Al₂Si₂O₅(OH)₄) as the major components. It followed pseudo first order kinetics. Similar kind of experiments was done by Sujana and Anand (2011) in the groundwater samples of Orissa, India to investigate the probability of utilizing bauxite for fluoride removal.

Roberto et al. (2012) investigated potential adsorbent as high alumina content bauxite for the removal of fluoride from drinking water. Batch and column mode studies were conducted with an initial fluoride concentration of 5-50 mg/L and flow rate was experimented up to 2.5 mL/min until the breakthrough time was reached. From the column mode study, it was found that the adsorption capacity decreased with the increased bed height and fluoride concentration. The maximum capacity of the adsorbent was 3.125 mg/g and the equilibrium data followed Freundlich isotherm.

2.4.4.2. Red mud

The major components of red mud are aluminium and iron oxides and are highly alkaline (pH 10–12) (Mohan and Pittman 2007). The alkalinity was reduced by washing with seawater (Fuhrman et al. 2004). Red mud could remove 77% of 21 mg/L fluoride leaving 2.7 mg/L fluoride in solution which was still higher than the acceptable levels. It was further processed by Tor et al. (2009) as granular red mud (GRM). Granular red mud fitted well with isotherm and kinetic models. Regeneration of GRM-column was done by 0.2 M of NaOH.
2.4.4.3. Bimetal mixed oxide

Synthetic and hydrous oxides such as iron (III) oxide (Dey et al. 2004), iron (III)-zirconium (IV) hybrid oxide (Biswas et al. 2007) and iron (III)-aluminum (III) mixed oxide (Biswas et al. 2007) has been used for the fluoride removal studies.

Iron (III) oxide is a natural water purifier. But, the synthetic hydrous iron (III) oxide (Dey et al. 2004) showed low adsorption capacity towards fluoride. The adsorption capacity was increased by incorporating iron (III) oxide with tin (IV) (HITMO), a cation with positively charged material. The adsorbent HITMO characterized by Biswas et al. (2009) for FTIR, XRD and SEM image with irregular surface morphology. pH was constant at 5.0–7.5 and followed pseudo second order equation. The Langmuir capacity was approximately 10.50 mg/g and adsorption energy 9.05 kJ/mol. The co-ions had no effect on the sorption process except for the bicarbonate ion. Swain et al. (2013) reported a hybrid material (Fe/Zr)-alginate (FZCA) microparticles. The particle size was found to vary between 70.89 nm and 477.7 nm. The sorption followed pseudo-second order kinetics. The percentage of desorption was 89% at pH 12.

2.4.4.4. Trimetal mixed oxide

Rare earth metals oxide (La2O3) was successful in defluoridation process (Raichur and Basu 2001). Rare earth metals are present in the acidic range, expensive and was restricted for water treatment because of which the rare earth metals are mixed with cheaper metals like Al (III), Fe (III) and Zr (IV) or loading rare earth metals on support materials would be a cost-effective way to reduce the use of expensive rare earth metals and at the same time to keep high fluoride adsorption capacity (Luo and Inoue 2004). Zhang et al. (2003, 2005) developed Ce–Fe bimetal oxide with the optimum pH 3.0 for the removal of fluoride from aqueous solution.
Singh et al. (2012) gave an account of hydrous bismuth oxides for removing fluoride from water. Srivastav et al. (2013) projected those hydrous bismuth oxides (HBOs) as the potential adsorbent for fluoride removal from water. XRD pattern pointed out the crystalline structure, FTIR showed the presence of Bi-O bond and SEM image confirmed the porous and rough nature of the material.

2.4.4.5. Ternary mixed oxide

Biswa et al. (2010) reported the fluoride scavenging efficiency of synthetic hydrated iron(III)-aluminum(III)-chromium(III) trimetal mixed oxide (HIACMO) from the aqueous solution. Hydrated iron(III)-aluminum(III)-chromium(III) ternary mixed oxide (HIACMO) was synthesized and characterized. FTIR studies confirmed the presence of M-O-M1 type bond in HIACMO. The fluoride removal efficiency at varied conditions showed that the reaction was pH sensitive and the optimum pH (initial) was between 4.0 and 7.0. The time required to attain dynamic equilibrium was 1.5 h.

The pseudo-second order equation described all kinetic data very well. The rate of reaction was multistage diffusion phenomena. The Langmuir isotherm equation described the equilibrium well. Thermodynamic analyzes of equilibriums indicated that the adsorption reaction of fluoride with HIACMO from water was endothermic and spontaneous in nature. The equilibrium solution pH analyzes suggested ion or ligand exchange mechanism for fluoride adsorption. Regeneration was possible up to 90% with 0.5 M NaOH and 0.2 g of HIACMO reduced the fluoride level to the maximum permissible value (1.5 mg/L).

2.4.5. Carbon based sorbents

The recent research used various carbons prepared from different adsorbents for defluoridation process. The carbonaceous materials such as plant, animal or mineral origin with high concentration of carbon was changed into an activated carbon prepared with chemical or gas activation methods. The raw materials used for carbon preparation are charcoal, nut shells, wood, fruit pits, lignite, peat, brown
and bituminous coals, bone and paper mill waste (lignin) and synthetic polymers (PVC). Activated carbons are obtained by carbonization by slow substrate heating at 600°C in the absence of air (Stanic et al. 2014).

Activated carbon prepared from one-step steam pyrolysis of rice straw at 550, 650 and 750°C were activated with HNO₃, H₂O₂ and KMnO₄. Batch studies were carried out at pH 2-10, adsorbent dosage 25-500 mg/L, contact time 1-24 h, adsorbate concentration 5-20 mg/L and co-ions such as SO₄²⁻, Cl⁻ and Br⁻. The rice straw carbon showed 100% of fluoride removal with chemically activated KMnO₄ adsorbent based on the surface area, acidity, porosity, pH and alkalinity (Daifullah et al. 2007).

The adsorbent Acacia farnesiana was used for the removal of fluoride ions. The carbon prepared from Acacia farnesiana was studied at pH 6.5-7.0 and the adsorption capacity increased with decrease in fluoride concentration and increased contact time at 40-45 min. The adsorption followed Freundlich isotherm and the nature of adsorption was heterogeneous (Hanumantharao et al. 2011). Activated carbon of Acacia farnesiana was found with the surface area ranging from 500-1500 m²/g, micropore structured and with the presence of functional groups on the surface of the adsorbent (Yin et al. 2007).

Activated carbon prepared from Pithacelobium dulce, Peltophorum ferrugineum and Ipomoea batatas studied with the adsorbent dosage 0.5-9.0 g/L and contact time 10-120 min. The percentage of removal decreased with the increase in initial fluoride concentration 1-8 mg/L and the adsorption process followed first order with the intra particle diffusion. Among the three adsorbents, Pithacelobium dulce carbon showed the maximum adsorption capacity when compared with the Ipomoea batatas and Peltophorum ferrugineum (Emmanuel et al. 2008).

Graphene is a single flat atomic sheet of carbon with the atoms arranged in a two-dimensional (2D) honeycomb configuration. The adsorption capacity was evaluated with pH, temperature and contact time with an excellent fluoride
adsorption capacity of 17.65 mg/g at fluoride concentration of 25 mg/L and temperature of 25°C (Romero et al. 2009). Graphene exhibited as a promising adsorbent based on its unique electronic and mechanical properties, excellent mobility of charge carriers, high thermal conductivity and specific magnetism and also used in solar cells, sensors, field-effect transistors and heavy metal removal (Li et al. 2011).

Abe et al. (2004) ordered various carbon based adsorbents for fluoride removal as: bone char > coal charcoal > wood charcoal > carbon black > petroleum coke. Daifullah et al. (2007) used activated rice straw carbon at 750°C treated with nitric acid, hydrogen peroxide and potassium permanganate. The carbon activated with permanganate gave better result in fluoride adsorption and was highly porous in nature when compared to other acids. Gupta et al. (2007) applied waste carbon slurries from fuel-oil energy generators for defluoridation. It contained 92% carbon, 0.45% aluminium and 0.6% iron. Fluoride adsorption and regeneration was carried out at pH 7.6.

2.4.5.1. Alumina-impregnated carbon nanotubes

Li et al. (2001, 2003) investigated on alumina supported on carbon nanotubes prepared by pyrolysis of a propylene-hydrogen mixture with Ni particles as the catalyst. The product was ball-milled, stirred with aluminium nitrate solution and heated at 500°C under nitrogen for 2 h. After heating it was ground and sieved to appropriate particle size. Adsorbent dosage of 0.2 g/100 mL solution was shaken for 12 h with F⁻ solutions. The adsorption capacity of the Al₂O₃/carbon nanotubes was found to be 13.5 times higher than that of AIC-300 carbon, four times higher than that of γ-Al₂O₃ and also higher than that of IRA-410 polymeric resin.
2.4.6. Natural materials as sorbents

2.4.6.1. Lateritic ores

Sarkar et al. (2007) reported goethite for fluoride adsorption as it had high iron content. Generally, nickel laterites and chromite mine contain high content of iron and small amounts of chromium, alumina, cobalt, nickel and manganese. Sujana et al. (2009) have evaluated various goethite containing geo materials in India for fluoride adsorption.

Preliminary findings (Ayamsegna et al. 2008) on the fluoride removal capability of some Ghanaian geomaterials are easy to manage rural community based fluoride removal system. Batch experiments were performed on geomaterials (laterite and bauxite tailings) with raw fluoride-contaminated water (10.31 mg/L) from a borehole to determine their potentiality of removing excess fluoride from rural drinking water supplies. The raw bauxite tailings showed the higher removal capacity. Further experiments were conducted using heat-treated bauxite tailings. The results indicated that the optimum fluoride removal was attained when the bauxite was heated to 600°C but the removal capacity decreases with increase in heating temperature.

2.4.6.2. Clays and soils

There have been a large number of studies on minerals and soils like Illinois soils of USA (Omueti and Jones 1977), fly ash (Chaturvedi et al. 1990), clay pottery (Hauge et al. 1994), fired clay (Bardsen and Bjorvatn 1995), Ando soils of Kenya (Zevenbergen et al. 1996), Alberta soil (Luther et al. 1996), bentonite and kaolinite (Srimurali et al. 1998) and illite-goethite soils in China (Wang and Reardon 2001).

Wang and Reardon (2001) investigated with the heavily-weathered tertiary soil from Xinzhou, Shanxi, China for developing cost-effective fluoride sorbents. The soil is composed of feldspar, illite, quartz, goethite and iron oxide content of
6.75%. Batch mode studies were done with the temperature from 100-900°C and fluoride concentration between 0 - 60 mg/L.

Clays have attracted the interest in defluoridating process because of its availability, environmental stability, inexpensiveness, high surface area or sorption capacity and ion exchange properties. Guo and Tian (2013) studied the anionic clay, hydrocalumite for the adsorption of fluoride from water with the initial fluoride concentration of 0.3, 10 and 20 mmol/L and common ions such as HCO$_3^-$, Cl$^-$ and SO$_4^{2-}$. The adsorbent hydrocalumite involved the process of dissolution-reprecipitation and anion exchange. The fluorite precipitation was induced by the release of Ca$^{2+}$ due to the increased dissolution of the adsorbent with the increase in initial fluoride concentration and the maximum fluoride uptake capacity was found to be 71.91 mg/g.

Puka (2004) explained that the structure of the clay plays a key role in determining the charge on the clay surface and type of exchange that can occur with ions in solution. Agarwal et al. (2003) investigated the silty clay (C) in defluoridation process. It was amended with 50 mg/g each of Al (activated Al$_2$O$_3$), Fe (FeCl$_3$) and/or Ca (CaCO$_3$) at pH 6 that improved the F$^-$ sorption capacity. Equilibrium time reached within 5 min of shaking. Sanjay et al. (2009) incorporated metal oxide (lanthanum, magnesium and manganese) with bentonite clay. On comparison with Mn-bentonite, Mg-bentonite and bare bentonite clay, 10% La-bentonite was better for defluoridation process. Equilibrium time reached within 30 min. Carbonate and bicarbonate anions affected the defluoridation process. The equilibrium data fitted well with Langmuir and Freundlich isotherm models.

Puka (2004) reported with South African clays which was pre-treated with sodium carbonate solution followed by dilute hydrochloric acid and then stirred with 1 M solutions of aluminium or iron (III) salts. The effectiveness of the material was compared with coated and uncoated material. Tor (2006) used montmorillonite treated with hydrochloric acid for fluoride sorption with various parameters like pH,
initial fluoride concentration, contact time and adsorbent dosage. Meenakshi et al. (2008) showed that kaolinite clay rated low in adsorption. On mechanochemical activation, the increased surface area of the sorbent thus helped in increased sorption capacity.

Omueti and Jones (1977) well thought out on Illinois soil for the presence of amorphous aluminium hydroxides for fluoride sorption. It was analyzed by Langmuir and Freundlich isotherms. Bjorvatn et al. (1997) gave attention on the soil samples of Ethiopia. Five samples were collected from highland area from Addis Ababa which reduced the fluoride concentration from 15 to 1 mg/L. Zevenbergen et al. (1996) studied with Ando soil of Kenya and came into view that it is efficient and economical method for defluoridation process.

Wang and Reardon (2001) worked with heavily-weathered tertiary soil from Xinzhou, China. It was found that the FeOH group in the soil was responsible for $F^-$ sorption property. Equilibrium reached in 1.5 h. There are many soil sorbents tried by many researchers China clay (Yadava et al. 1991), zeolites (Mayadevi 1996), red mud (Cengeloglu et al. 2002), spent bleaching earth (Mahramanlioglu et al. 2002) and wallostonite and montmorillonites (Karthikeyan et al. 2005).

2.4.6.3. Zeolites

Zeolites are the natural materials which are effectively used as adsorbents with the cation exchange properties for the removal of fluoride whereas Samatya et al. (2007) emphasized the partial range of zeolite with negative charges on the surface of the adsorbent at all pH. The presence of negative charges on Zeolite attracted the positively charged ions (cations) and result in multi-valent metallic cations that increased the adsorption capacity of the adsorbent. Gomez et al. (2013) used naturally occurring zeolite in Ethiopia (Tigrae region) for removing fluoride from drinking water. Batch study was used with different fluoride concentrations ranging from 20-200 mg/L which showed good adsorption capacity with the adsorbent dosage of 200 g/L, initial fluoride concentration 18.3 mg/L and 90%
fluoride removal (0.47 mg/g) was obtained. Regeneration of the adsorbent was carried out with NaOH which showed 87% of desorption of fluoride ions from the adsorbent.

Onyango et al. (2004) prepared zeolite loaded with sodium ion and then immersed in Al\(^{3+}\) or La\(^{3+}\) solutions to form trivalent ions. It was inferred that fluoride adsorption on Al\(^{3+}\) exchanged zeolite was by ion exchange and La\(^{3+}\) exchanged zeolite was by electrostatic attraction. Later, Onyango et al. (2005, 2006) focused on Al\(^{3+}\) loaded with low-silica zeolites towards fluoride removal which showed the highest adsorption at pH from 4-8.

2.4.7. Biosorbents

Biosorption is the promising technique for water treatment working with various biomaterials like chitin and chitosan with the unique characteristics of biocompatibility, biodegradability, physical and mechanical properties, chemical reactive groups (acetamido, hydroxyl or amino groups) and low cost (Yao et al. 2009). Ilhami et al. (2005) defined that biosorbents bind to metals or organic pollutants with minimized sludge, high efficiency, low-cost, no nutrient requirements, environmental friendly and economically viable. Srimurali et al. (1998) put forth many biosorbents used for fluoride removal like nirmali seeds and lignite (6-8%), kaolinite (18.2%), charfines and bentonite (38 and 46%). Many investigators reported activated carbon minerals (Raichur et al. 2001), fish bone charcoal, coconut shell carbon and rice husk carbon with different degrees of success (Mohan and Pittman 2007).

2.4.7.1. Algal biomass

Algal biomasses are cost-effective (Volesky and Holan 1995), ubiquitous in distribution and has high carbon content (Bhatnagar 2002). Mohan and Pittman (2007) worked with *Spirogyra* IO2 for the removal of fluoride. The adsorption capacity decreased with increase in pH from 2.0-10.5. It was due to the protonation at acidic pH that imparts positive charge on the surface of the functional groups such as
amino, carboxyl and thiol and encouraged the adsorption at pH 7.0 with 54% fluoride removal. The Langmuir capacity was 1.272 mg/g. The FTIR results showed that the functional groups were linked to hydrogen atoms in the carboxylic groups.

Sinha et al. (2003) used aquatic macrophyte biomass (*Eleocharis acicularis*) pretreated with Ca$^{2+}$ for the removal of fluoride from aqueous solution. The highest efficiency was 64.5% at pH 6.0 with 5.0 g/L Ca-pretreated biomass. Water hyacinth (*Eichhornia crassipes*) was experimented for fluoride removal process. It was activated at 600°C and was found to be 72-98% for H-type carbon and 51-93% was obtained for L-type carbon. The higher efficiency of F$^-$ removal was found with non-carbonised plant. The Langmuir isotherm was found to be 1.54 mg/g. Column mode studies were carried out with an initial fluoride concentration of 15 mg/L, breakthrough curve was 100 bed volumes and the column capacity was found to be 4.4 mg/g.

### 2.4.7.2. Bone char

Mjengera et al. (2003), Fawell et al. (2006) and Ayoob et al. (2008) considered bone char (prepared at 500°C for 4 h) as a potent adsorbent for removal of fluoride from drinking water. Bone char was activated based on the temperature, beyond 600°C, it reduced the fluoride adsorption. It had its own disadvantages such as: obnoxious smell, distasteful and imparted yellow color in the treated water. Abe et al. (2004) had also studied with bone char that involved physicochemical interaction.

Ramos et al. (2010) interpreted the fluoride sorption on bone char using diffusional and kinetic models. He explained the diffusional model through intraparticle diffusion, external mass transfer and adsorption on active site. The effective pore volume diffusivity varied from $2.73 \times 10^{-6}$ to $3.71 \times 10^{-6}$ cm$^2$/s. The first, second and $n^{th}$ order kinetic models were fitted to the experimental data. The findings concluded that the diffusional model was superior to the kinetic model.
2.4.7.3. Neodymium-modified chitosan

Chitosan is a natural polymer and its distinctive properties are: biocompatibility, biodegradability, meticulous physical and mechanical properties with chemical groups like hydroxyl, acetamido or amino functions and it is cost-effective (Yao et al. 2008). In general, polysaccharides have the capacity to attract fluoride ions by physical and chemical interactions. Ma et al. (2007) worked with magnetic-chitosan for the sorption of fluoride ions with the effect of temperature and kinetics that described the sorption capacity.

Chitin-Chitosan was derived from shellfish processing waste which played a key role in ecological engineering to suit biological, domestic and environmental conditions. It was modified by lanthanum nitrate and studied various parameters like initial fluoride concentration, adsorbent dosage, co-anions and pH for the sorption of fluoride (Kamble et al. 2006). Yao et al. (2009) applied neodymium modified chitosan to remove excess fluoride ions from water. In batch process, effect of pH (5-9), temperature (283-323 K), adsorbent dosage (0.2-2.0 g/L), particle size (0.10-0.50 mm) and the presence of co-anions (NO$_3^-$, Cl$^-$ and SO$_4^{2-}$) were optimized. The maximum Langmuir sorption was 11.411-22.380 mg/g. It fitted well with the pseudo second order kinetics and the exhausted adsorbent was regenerated with 4 g/L of sodium hydroxide for 24 h.

2.4.7.4. Plant biomass

Mwakabona et al. (2014) compared with sisal leaf biomass with other plant biomasses like maize leaf (ML), goose grass (GG), banana false stem (BFS), Aloe vera (AV), untreated sisal fibre (USF) and sisal pith (SP). Adsorbent dosage of 0.5 g of each biomass was mixed with 10 mg/L of F$^-$ concentration. The fluoride removal capacity was found to be 4.1 (ML), 4.6 (GG), 7.1 (BFS), 26.6 (AV), 29.4 (USF) and 47.3% (SP) respectively which was confirmed that, stereochemistry and solubility of the active compounds played a vital role in defluoridation process.
Misl and Gurani (2014) studied with *Phoenix dactylifera* (date palm) seeds which were chemically activated with NaCl. Batch experiments revealed that the optimum contact time for NaCl activated carbon of impregnated ratio 0.25, 0.50 and 0.75 are 55, 50, 45 min with removal efficiency of 76, 80 and 85% respectively. Optimum adsorbent dosage was 200, 180 and 160 mg with removal efficiency 78.5, 85.2 and 87.0% for the above listed impregnation ratio at pH 7.0.

Shyam and Kalwania (2014) tried a different mechanism through fluoride precipitation and adsorption by *Aloe vera* and calcium chloride. The optimum fluoride removal was found to be 88% at pH 7.4 with adsorbent dosage of 40 g of *Aloe vera* and 3 g of calcium chloride for 1000 mL of fluoride solution with a contact time of 40 min. Equilibrium data obeyed Langmuir and Freundlich isotherm which had concluded that the force responsible for adsorption and precipitation of fluoride with *Aloe vera* and calcium chloride was dependent on the columbic force between positively charged calcium ions and negatively charged fluoride ions.

**2.4.8. Layered double hydroxides/hydrotalcite like compounds/apatite and hydroxyapatite as sorbents**

Layered double hydroxides (LDH) are extensively used as a trapper to trap anionic pollutants and thus act as a good adsorbent for environmental contaminants (Chitrakar et al. 2008). Carlino (1997), Khan and Hare 2002) showed that it is a good anion exchanger. LDH have the capacity to trap radioactive 131I (Fetter et al. 1997; Kang et al. 1999), chromate, and selenate or selenite (You et al. 2001), nitrate (Tezuka et al. 2004) and phenols (Yapar and Yilmar 2004).

Benito et al. (2006) explained that LDH are hydrotalcite-like compounds, brucite like structure, positively charged anions trapped in the interlamellar region to balance the net charge, has high specific area on heating at 500°C. Das et al. (2003) and Pavan et al. (2000) prepared layered double hydroxides from low-cost precursors to treat fluoride. Later, Lv et al. (2006a,b) started to study the calcination
temperature varied from 200°C, 400°C, 500°C, 600°C and 800°C. At 500°C, fluoride sorption was high beyond which it decreased. The experiment conditions were maintained at pH 6.0 and adsorbent dosage 2.1 g/L which removed 80 mg fluoride per 1 g solid from 100 mg/L fluoride over 6 h at 30°C. The X-ray diffraction, FTIR and TG-MS proved the reconstruction of initial layered structure (Lv et al. 2007).

The adsorption behavior of calcined Zn/Al hydrotalcite-like compound was studied by Das et al. (2003). Experimental parameter such as temperature, adsorbent dosage, adsorbate concentrations and pH were analyzed. It was found to be efficient at pH 4-6 and the adsorbent was characterized by XRD and FTIR. Diluted alkali solution was used for regenerating the exhausted adsorbent. Mandal and Mayadevi (2008) tried with cellulose-supported uncalcined layered double hydroxides (CSLDHs). The adsorption capacity was better when compared to carbon nanotubes and activated alumina.

Chang et al. (2011) prepared Mg-Al layered double hydroxides (magnetic composite) by ultrasound-assisted co-precipitation method followed by calcination treatment. A hydrotalcite-like phase was obtained through ultrasound process which increased the surface area and the adsorption capacity was found to be 47.7 mg/g. Kinetic studies revealed that the magnetic composite was involved in renovation of the layered structure in the composite. It can be separated by applying magnetic field and regenerated by using desorbing agent.

Mandal et al. (2013) synthesized Mg-Cr-Cl layered double hydroxide for defluoridation. The material was characterized with scanning electron microscope, X-ray powder diffraction, Fourier transform infrared, thermogravimetric analysis and differential thermal analysis. The percentage of fluoride removal was 88.5% at pH 7, adsorbent dose of 0.6 g/100 mL solution for the initial fluoride concentration of 10 mg/L and 100 mg/L. It fitted well with the Langmuir isotherm ($R^2 = 0.9924$). Regeneration was not applicable for this material.
2.4.8.1. Polymeric composites

Kim et al. (2006) used an advanced material called alumina as it possesses excellent physical and textural properties. Alumina has high affinity towards fluoride, cheaper in rate and can be easily regenerated and has been frequently used polymeric material. Synthetic polymers are biodegradable and biocompatible than natural polymers like cellulose, lignin, starch, chitin and chitosan. Muzzarelli (1988) suggested chitosan and chitin for its excellent properties such as non-toxic, better adsorption properties, biocompatible and biodegradable.

Polymeric composites had attracted the attention of researchers to prepare both organic-inorganic hybrid composites and easy to handle (Habraken et al. 2007). Sundaram et al. (2008, 2009) and Liu et al. (2010) gave an idea that with polymeric composites, it can be made into membranes, beads and candles for the purpose to be fulfilled. Viswanathan and Meenakshi (2008) had worked with chitosan varieties like carboxylated chitosan beads, lanthanum incorporated chitosan beads and raw chitosan. It was found to possess 1.385, 4.711 and 0.052 mg/g respectively of defluoridation capacity.

Viswanathan and Meenakshi (2010) amalgamated alumina/chitosan (AlCs) composite by dissolving the alumina particles in the chitosan polymeric matrix to remove fluoride from aqueous solution. AlCs composite possessed higher defluoridation capacity than alumina and chitosan. The presence of bicarbonate ions disturbed the defluoridation capacity and was not affected by the pH. The composite followed Freundlich isotherm. Defluoridation was controlled by electrostatic adsorption, complexation mechanism and the nature of the reaction was spontaneous and endothermic.

Karthikeyan et al. (2009) investigated with polyaniline/chitosan (PANi/Ch) and polypyrrole/chitosan (PPy/Ch) in defluoridation. The amounts of fluoride ions adsorbed per unit mass of the adsorbents were found to be 5.9 mg/g for PANi/Chand 6.7 mg/g for PPy/Ch, at 50°C for the initial fluoride concentration 10
mg/L. The experimental data fitted well to the Langmuir and Freundlich isotherms and was an endothermic process. Polymer composites were characterized (before and after treatment) with FTIR, X-ray, SEM and EDAX confirmed that the defluoridation occurred through dopant-exchange process. There are other polymers developed like zirconium (IV) tungstophosphate (ZrWP) into the chitosan biopolymeric matrix (Viswanathan and Meenakshi (2010), combined use of cake alum and a polymeric anionic flocculent (PAF).

2.4.8.2. Hydroxyapatite

Hydroxyapatite, a high solubility product but was not an efficient adsorbent for removing fluoride (Choi and Chen 1979). Later many researchers studied hydroxyapatite in the form of hydrotalcite-like compounds and calcined materials, co-ions and fluoride concentration (Hammari et al. 2004), pH (Almaraz et al. 2007), sorbent dosage (Sundaram et al. 2008), contact time (Gao et al. 2009) and particle size (Gao et al. 2009).

Sundaram et al. (2009) synthesized nano-hydroxyapatite/chitin composite to study pH, co-ions, contact time and initial fluoride concentration. A similar kind of study was carried out by Reyes and Rios (2010) but with hydroxyapatite as a sorbent. The maximum sorption was between pH 5 and 7.3, adsorbent dosage 0.01 g for 25 mL of fluoride solution and contact time 16 h. The equilibrium data obeyed pseudo second order and Freundlich isotherm. The results pointed out the fluoride sorption exhibited chemisorptions process in a heterogenous manner. Desorption was carried out with alkaline solution.

2.4.9. Building materials as sorbents

2.4.9.1. Plaster of paris

Elango and Gopal (2007) explored with plaster of Paris as an adsorbent was to remove fluoride ions from aqueous solutions. Batch processes are involved with fluoride concentration, agitation time, pH, co-ions, adsorbent dosage and
temperature. Wide range of pH and low temperature was suitable for the sorption process. The data obtained from batch process portray plaster of paris as a potential adsorbent for fluoride removal from aqueous solutions.

The experiment followed Freundlich and Langmuir isotherms. Thermodynamic studies were carried out to understand the parameters such as $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ and was concluded that the adsorption process was exothermic and spontaneous. Kinetic studies revealed that the adsorption process obeyed first order. The mechanism involved with adsorption process was intraparticle diffusion, external surface adsorption and equilibrium. XRD studies confirmed the mechanism process. In batch adsorption studies, data showed that plaster of Paris has considerable potential for the removal of fluoride ions from aqueous solutions. Wide range of pH and low temperature ranges were found as the optimum conditions for maximum fluoride adsorption by the adsorbent.

### 2.4.9.2. Fly ash

Goswami and Das (2006) reported that fly ashes are the by-product and major solid waste from coal-fired power plants. It is carried by the flue gases in a fine residue form with a uniform particle size ranging from 1 to 100 μm. Fly ash consists of alumina, iron oxides, silica, calcium oxide and residual carbon. It possesses higher surface area 1 to 6 m$^2$/g and thus made available as a good adsorbent for fluoride removal.

Column study was performed by packing the fly ash with 450 g bed volume at 20°C. The column was allowed to run with the fluoride concentration varying from 1, 5, 10, 20, 50, and 100 mg F/L. The flow rate was fixed at $\leq$ 2 mL/h. When the lowest F$^-$ concentration (1 mg/L) was passed through fly ash bed, the effluent solution contained fluoride at the initial collection, and then gradually decreased down to 0 mg/L after 120 h. As the concentration of fluoride increased in the feed solution, the fluoride in the effluent solution decreased to 0 mg/L after 120 -168 h
and concluded that coal fly ash was an effective sorbent for F ions, especially at high concentrations in water.

2.4.9.3. Hydrated cement

Kagne et al. (2008) found a low cost material called Portland cement from a building material. It consists of dicalcium silicate, tricalcium aluminate, tricalcium silicate and tetracalcium aluminoferrite. Portland cement was mixed with to get hydrated cement (HC). Various parameters like effect of initial fluoride concentration, pH, co-ions, adsorbent dosage and contact time were evaluated. It was observed that over a wide range of pH, fluoride sorption exhibited significant fluoride removal. Interfering ions like carbonate and bicarbonate affected the fluoride sorption. The equilibrium data fitted well with Freundlich and Langmuir isotherm. A comparative study was done between simulated and field water, fluoride sorption was effective with simulated water. This findings concluded that hydrated cement (HC) was efficient, did not produce sludge, easily available, low cost and highly economical.

2.4.10. Agricultural wastes as sorbents

2.4.10.1. Neem and Kikar leaves

Kumar et al. (2007) stated that adsorption processes are simple, cheap, easily available and accessible in developing country like India. Adsorbents like coconut shell carbon (Arulanantham et al. 1992), activated alumina (Li et al. 2001) and activated carbon (Mariappan et al. 2002 and Sivabalan et al. 2002) has been extensively used for defluoridation.

Kumar et al. (2008) reported on neem and kikar activated leaves for fluoride removal. The leaves were activated at 400°C in electric furnace and then sieved to get 0.3 mm and 1.0 mm particle size. Initial fluoride concentration 5 mg/L was used in batch process to study pH, adsorbent dosage and contact time. The optimum dosage was found to be 0.5g/100 mL for ANC (activated neem leaves carbon) and
0.7g/100 ml for AKC (activated kikar leaves carbon) at pH 6.0 for 1 h. It was found that 0.3 mm was better than 1.0 mm particle size. The experimental parameters obeyed Freundlich isotherm and first order kinetics and indicated intraparticle diffusion process for defluoridation. Similarly, Tembhurkar and Dongre (2006) developed *Azadirachta Indica* (Neem) and *Ficus Religiosa* (Pipal) to remove fluoride from water. The leaves of both the plants has high fiber content making it suitable to be converted into biosorbents and are abundantly available in India, known for their medicinal and other purposes.

### 2.4.10.2. *Morrninga indica*

*Morrninga indica* bark, an agricultural waste was charred and carbonized by the method of pyrolysis and activation (Chang 2003) for fluoride removal. Activated carbon possessed diverse pore structure, surface area and has noticeable defluoridation efficiency. Malik et al. (2010) stated that crystalline structure, fracture, surface edges, nature and distribution of pores also regulate the adsorption efficiency. Batch mode of study was conducted with adsorbent dosage at 3 mg/L, pH 2-12, co-ions like nitrate, sulfate, chloride, bicarbonate (anions), calcium and magnesium (cations) and temperature ranging from 30-50°C. The adsorption capacity followed Langmuir isotherm, Freundlich isotherm and pseudo first order kinetic model. The thermodynamic studies revealed that the adsorbent *Morrninga indica* was an endothermic process at higher temperature with a negative value of delta G°. SEM and XRD studies were carried out to understand the surface morphological behavior of the adsorbent and the binding of fluoride was observed on the surface of the adsorbent (Karthikeyan and Ilango 2007).

### 2.4.10.3. Tamarind seed

Some of the biosorbents which were used as defluoridating agents are: serpentine (Maruthamuthu and Venkatanarayana 1987), Tamarind gel (Maruthamuthu and Venkatanarayana 1987), Duck weed *Spirodelapolyrrhiza* (Shirke & Chandra 1991), *Hydrilla Verticillata* (L.f) Royale plants (Sinha et al.
2000) and *Aloe vera* (Murugan and Subramanian 2002). Much work was not done in the above listed sorbents that was the reason for Murugan and Subramanian (2006) to perform with Tamarind seed (plant material).

Murugan and Subramanian (2006) obtained tamarind seed from the kitchen waste after removing the pulp and used as cattle feed. The objective of the author was to develop a cheap and viable defluoridation method for village communities and urban dwellers. Batch process parameters like agitation time, pH, initial fluoride concentration, particle size and sorbent dosage were carried out. The maximum sorption capacity was at pH 7.0. The fluoride uptake decreased with increase in temperature and particle size and followed Langmuir and first order kinetics. Desorption was successful with 0.1 N HCl (90%). The reason behind the process was coulombic interaction which was characterized with FTIR and SEM.

### 2.4.10.4. Corn cobs

Corn cob (cellulose based) are quite common, cheap and easily available product. It was powdered and used for fluoride adsorption. The limitation that was found with the corn cob powder was, it was not the apt substrate for adsorption instead it was modified with metal ions of aluminium chloride and calcium chloride. Corn cob was put in water, it obtained negative charge which was not conducive for fluoride sorption. Experimental parameters were optimized with concentration, contact time, temperature and pH. Neutral pH and contact time between 90-120 min was found to be suitable for defluoridation. The reaction was exothermic and followed Freundlich isotherm (Parmer et al. 2006).

### 2.4.10.5. Gulmohar fruit shell

Shashikant and Mise (2009a) prepared activated carbon from gulmohar fruit shell to determine the effects of dosages and pH accordingly to equilibrium and kinetics. The removal of fluoride by adsorption was studied on two types of carbon: physically activated and chemically activated with impregnation ratio of 0.25, 0.50 and 0.75. It was observed that as dosage increases the adsorption increased along
with the increase in impregnation ratio (I.R). It was also noted that as I.R increases the surface area of the activated carbon also increased. The maximum removal of fluoride was obtained at pH 7±0.20.

2.4.10.6. Plant waste as an adsorbent

Jamode et al. (2004); Tembhurkar and Dongre (2006); Mohan et al. (2007b) and Deng et al. (2011) used activated charcoal, Mn-Ce oxide, rice husk, leaf biomass, algal biomass and bio-char as an adsorbent (low cost and easily available) for the removal of fluoride. Mann (1990) explained that the functional groups such as carbonyl, amine amide, phosphonate, hydroxyl, carboxyl, sulfhydryl, theioether, sulfonate, imidazole and phosphodiester contribute to biosorption.

Activated carbon developed (Sivabalan et al. 2003) from palm seed coat (PSCC) by dolomite process was found to be efficient at pH from 4-8. When treated with field water, it did not affect the pH, total alkalinity, total hardness and total dissolved solids. Low cost adsorbents from agricultural waste materials like rice husk, coconut shell fibers and coconut shell was developed by Mohan et al. (2008). The order of removal was coconut shell fiber carbon (ATFAC), coconut shell carbon (ATSAC) and rice husk carbon (ATRHC) at 40°C.

An investigation was done with zirconium-impregnated coconut shell carbon (ZICSC) for fluoride removal (Sathish et al. 2007). The adsorption capacity was above 90% for the pH from 2-9. The Langmuir isotherm was 7.51 mg/g at pH 6.0. The work was expanded with zirconium-impregnated coconut fiber carbon (ZICFC) (Sathish et al. 2008) which stated that fluoride uptake decreased with increase in pH. The interaction was between the OH− and F− charges on the active sites of ZICFC. The Langmuir value was 40.016 mg/g at pH 4. The finding stated that physisorption and chemisorption along with intraparticle diffusion accounted for defluoridation process.
Paudyal et al. (2011) attempted with dried orange juice residue (DOJR) which contains 12% pectin (methyl ester of pectic acid). It was saponified with calcium hydroxide (a good cation exchanger) that removed fluoride in a powerful manner. The same work was carried out by Paudyal et al. (2013b) used DOJR incorporated with Zr (IV), Ce (IV) and Al (III). The amount of Zr (IV), Ce (IV) and Al (III) loaded on the DOJR were evaluated as 0.90, 0.85 and 0.97 mmol/g, respectively. The maximum adsorption capacity of fluoride on the Zr (IV), Ce (IV) and Al (III) loaded DOJR were evaluated as 1.43, 1.22 and 0.67 mmol/g, respectively which was confirmed with Energy dispersive X-ray (EDX) and Infra red (FTIR) spectroscopic analysis.

Yadav et al. (2013) explored with wheat straw raw (WSR), sawdust raw (SDR), sugarcane activated bagasse carbon (ABC) and activated carbon (CAC) based adsorbents. The CAC, ABC, SDR, and WSR removed 57.6, 56.4, 49.8 and 40.2% respectively for 5 mg/L fluoride at pH 6.0, contact time 60 min and adsorbent dose of 4 g/L. Equilibrium data followed Freundlich, pseudo first order, pseudo second order and intraparticle diffusion models.

2.4.11. Miscellaneous adsorbents

There are quite a lot of other supplementary adsorbents such as lignite, kaolinite, bentonite, charfines and nirmali seeds for defluoridation process (Srimurali et al. 1998). Wasay et al. (1996) developed lanthanum-impregnated silica gel and were found to be a good adsorbent for removing fluoride (>99.9%) at pH 6 which was due to the interaction between lanthanum and silica gel. The co-ions such as Br\(^-\), NO\(^3-\), I\(^-\), Cl\(^-\) and SO\(_4^{2-}\) did not affect the adsorption process. Column mode study was done at a fixed flow rate of 0.5 mL/min at pH 7.0 that resulted in 99.9% of fluoride removal at pH 8.5.

An ion exchange fiber, polyacrylonitrile fiber (PANF) was created (Ruixia et al. 2002) by cross linking PANF with hydrazine hydrate. The percentage of fluoride removal in batch process was 90.4% at pH 3.0. In column experiment,
adsorption capacity was 45.0 mg/g and regenerated with 5mL of 0.50 mol/L NaOH at elution rate of 1mL/min. Kagne et al. (2009) evaluated the potential of bleaching powder (disinfectant agent) to remove fluoride. SEM image confirmed that chemisorption process was involved in the form of calcium fluoride. Optimum dosage was 50 g/L at pH 6-10 and there was interference of co-ions was observed in removing fluoride. The Langmuir maximum sorption capacity of bleaching powder for fluoride was reported to be 0.1308 mg/g.

Karthikeyan et al. (2009) performed with polypyrrole to remove fluoride from aqueous solution. The fluoride ion uptake decreased with increase in pH. On doping with chloride, the sorption capacity increased at pH <7. The presence of nitrogen in the polymer helped in adsorption. Xu et al. (2011) prepared a novel adsorbent, magnesia-loaded fly ash cenospheres (MLC) by wet impregnation of fly ash cenospheres with magnesium chloride solution. The optimum condition was: pH 3.0, adsorbent dosage (2.5 mg/L) and contact time (60 min). The co-ions interfered the sorption process in the order of phosphate>nitrate>sulphate. The sorption capacity was 6.0 mg/g for 100 mg/L of fluoride concentration at pH 3.0 at 318 K.

Chen et al. (2011) synthesized porous granular ceramic by dispersing aluminium and iron oxides followed by precipitation at 600°C. It was able to remove 1.79 mg/g of fluoride at pH 6.0. Gourouza et al. (2014) worked with calcined cattle bone which consists of hydroxyapatite and calcite. It was found that the fluoride uptake was depended on adsorbent dosage, fluoride concentration and contact time. Equilibrium data obeyed Freundlich isotherm and pseudo second order kinetics and the reaction was spontaneous. The adsorption mechanism was based on the precursor material present in the beef calcined bone that enabled as a potential material for defluoridation.