Review on the Effect of Fluoride Contamination and Methods for Fluoride Removal
With an Emphasis on Adsorption Using Low Cost Adsorbents

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Abstract: Fluoride contamination in groundwater and surface water due to geological and anthropogenic causes is a major problem in many parts of the world. Fluoride is an important trace element in human, animal and plants, its excess concentration may cause some adverse effects in terms of health in human and animals and in terms of productivity in plant species. Hence there is an eminent amount of research is dedicated on fluoride removal from ground water and waste water. Many methods are in use for the fluoride removal such as precipitation/coagulation, ion-exchange, membrane processes, reverse osmosis, adsorption, etc. Each of these processes has its own advantages and disadvantages but it is proven that adsorption is the best method available in terms of both economy and efficiency. In this review, fluoride effects on human, animals and plants are presented. The adsorption capacities of many types of adsorbents for fluoride removal under different operating conditions such as pH, contact time, initial fluoride concentration, temperature, surface charge, etc. were discussed. Considerable amount of this paper discusses about various natural and low cost adsorbents available in nature, their possible potential in removing the fluoride and their adsorption mechanisms for fluoride removal.

***Key words* - Fluoride contamination, Defluoridation, Natural Adsorbents, Adsorption.**

I. INTRODUCTION

Fluoride ion contamination in groundwater has been identified as one of the most serious problems globally [1]. Fluoride is a halogen group of mineral and is natural constituent of the environment. Fluoride is the most electro negative elements and is never present in the elemental form. In the order of frequency of occurrence of the elements it is in seventeenth place and presents in 0.06% to 0.09% of the earth's crust [2].

Fluorides exist as a number of minerals, such as fluorspar, cryolite, fluorapatite and their corresponding host rocks such as granite, syenite, basalt and shale by which they can be released into the groundwater. Fluoride concentration can be present in many waters but higher concentrations mostly present in ground waters. Some areas contain fluoride rich minerals where ground water fluoride concentration is up to about 10 ppm, in some cases much higher fluoride can also be found. Many countries of the world can be found with high fluoride concentrations especially in regions of India, South America, China and Central Africa, but high concentrations can be occurred locally in many parts of the world. Most of the food materials contain some fluoride in minute concentrations. All types vegetation contains some fluoride that got absorbed from soil and water. Tea contains higher fluoride concentration which is on average 100 mg/kg. [3]

Wastewater with high fluoride concentrations is generated from ceramic and glass production, electroplating, coal fired power stations, brick and iron works, beryllium extraction plants, semiconductor manufacturing and aluminium smelters. The concentration of fluoride in natural waters is ten to thousand times lower than the industrial waste effluents [4].

Table 1. Drinking Water Standard for Fluoride by Different Authorities. [5]

S. No.	Authority	Permissible Limit (mg/l)
1	WHO (international standard)	0.50 – 1.5
2	Bureau of Indian Standards (IS-10500)	1.0-1.5
3	Indian Council of Medical Research (ICMR)	1.0-2.0
4	Central Public Health and Environmental Engineering Organisation (CPHEEO)	1.0-1.5
5	US Public Health	0.7-1.2

1.1 Fluoride in Indian Scenario

India is one of the 23 countries in the world, where health problems are caused due to fluoride contaminated groundwater. A report of UNICEF recognizes the fluoride problem in 177 districts present in 20 States of India. Andhra Pradesh is one of the State in which fluorosis is endemic. Total population of India would be more than 1330 million in 2020 with an expectedincrease the world's water resource. The surface water resource in India is scarce till the groundwater is deep in some places which is difficult to obtain. Almost 90% of drinking water demands are fulfilled from groundwater only. The most seriously affected areas are Andhra Pradesh, Punjab, Haryana, Tamil Nadu, Rajasthan, Gujarat and Uttar Pradesh. The highest fluoride concentration in India observed is 48 mg/L in Rewari District of Haryana [6].

Rivers flowing through half of the country of India are reported to contain fluoride contentration varying from 0.1 to 12.00 ppm [7]. People belonged to several districts of Rajasthan and Assam is forced to use water with fluoride concentration up to 44 ppm and 23 ppm for drinking and other purposes [8]. In Andhra Pradesh, districts of Anantapur, Srikakulam, Kurnool and some parts of the Kadapa district are affected places by fluorosis. Some parts Anantapur suffers with considerable cases of fluorosis. The socially and economically backward rural population in Anantapur district has been extremely vulnerable to fluorosis due to presence fluoride in ground water sources beyond limits. [9]

India is intensely suffering from fluoride problem. So defluoridation of drinking water supplies is essential. Several methods or technologies available for the defluoridation of drinking water supplies such as coagulation-precipitation, ion exchange, membrane technology (reverse osmosis, nano-filtration), adsorption etc. Most of these methods creates high operational and maintenance costs, secondary pollution (such as generation of toxic sludge) and complicated treatment procedure [10].

In India most of the rural people are below poverty line who can't afford the expensive technologies. Nalgonda technique based on coagulation and precipitation is one of the popular and inexpensive techniques widely used for removing fluoride from water in India. In this process the addition of prescribed quantities of alum, lime, and bleaching powder to raw water, followed by rapid mixing, flocculation, sedimentation, filtration, and disinfection. After adding alum and lime to the raw water forms an insoluble aluminium hydroxide floc and get sediment. The limitation of this technique is high residual aluminium concentration up to 2–7 mg/Lin the treated water which is much more than the WHO standard 0.2 mg/L [11]

On comparison adsorption is the better process available. But still the adsorbents available in market such as activated carbon, activated alumina, silica etc. is expensive. So there is a need to identify the suitable low cost adsorbents such as fly ash, brick powder, clay minerals etc. so that it would be economical, simple in design and operation and feasible for the community water supply.

II. EFFECT OF FLUORIDE CONTAMINATION

2.1 Effect of Fluoride Contamination on Human Health
2.1.1 Dental and skeletal fluorosis

Fluoride ion is the strongest electronegative element, which is attracted to positively charged calcium in teeth and bones. Major health issues caused by fluoride are dental fluorosis, teeth mottling, skeletal fluorosis and deformation of bones in children and adults [12]. The fluoride concentration in drinking water limited to 1 ppm and 1.5 ppm. Too lower concentrations below 0.5 ppm causes dental caries, both in children and in adults. The higher concentration beyond 1.5 ppm creates more serious effects on skeletal tissues by decreasing the bone density. Skeletal fluorosis (bone structure changes adversely) may be observed when drinking water contains 3–6 ppm, particularly with high water consumption. Crippling skeletal fluorosis usually develops when drinking-water contains concentration greater than 10 ppm. It is estimated that about 200 million people worldwide depend on drinking water with fluoride concentrations that exceed the WHO guideline of 1.5 ppm [3]. The high fluoride concentration manifests as an increase in bone density leading to calcification of ligaments and thickness of long bones. The symptoms include mild rheumatic/arthritic pain in the muscles and joints to severe pain in the cervical spine region along with rigidity and stiffness of the joints. The disease may be manifested in an individual at subclinical, chronic or acute levels. The severity of fluorosis depends on the concentration of fluoride in the drinking water, daily intake, climatic conditions and continuity and duration of exposure [13].

2.1.2 Other ill-effects on human health

Excess intake of fluoride causes various diseases such as arthritis, osteoporosis, brittle bones, infertility, cancer, brain damage, Alzheimer syndrome, and thyroid disorder [14]. Fluorosis is a common symptom of high fluoride accumulation can be manifested by mottling of teeth in mild cases and embrittlement of bones and neurological damage in severe cases. There are some reports indicates the interference of fluoride with DNA synthesis. The higher concentrations of fluoride can also interfere with carbohydrates, proteins, lipids, vitamins and mineral metabolism. Fluoride toxicity may occur by several ways. During digestion, fluoride initially acts on the intestinal mucosa and form hydrofluoric acid in the stomach causig gastro-intestinal irritation and erodes mucous layer. The gastro-intestinal tract is the earliest and most commonly affected organ system. Fluoride can also interfere with different enzymes disrupting oxidative phosphorylation, coagulation, glycolysis and neurotransmission. It is found that individuals with kidney disease have a higher susceptibility to the long term toxic effects of fluoride. In addition, fluoride acts as poison to kidney function when present at high doses over short-term exposures in both animals and humans. It has also been concluded by several research groups that fluoride has the ability to interfere with the function of the brain and pineal gland. Major site of fluoride accumulation in the body is Pineal gland, with higher concentrations of fluoride than that of teeth or bone. Fluoride exposure causes bladder cancer among workers exposed to excess fluoride at the workplace. Thyroid activity, effects on reproduction and birth defects also knownto be influenced by fluoride [15]. Fluoride is more toxic than lead. Even in small concentrations it accumulates to cause damage the brain and development of children. Also produces abnormal behaviour in human beings and reduces human IQ [16].Keeping the view of toxic effects of fluoride on human health, there is an urgent need to find out an effective and clean technology for the removal of excess fluoride from drinking water.

2.2 Effect of Fluoride Contamination in Animals

Animal studies on mice and rodents shows that the application of fluoride increases the risk of getting cancer. Particular attention has been given to bone cancer, especially osteosarcoma, because of concentration of ingested fluoride in the bones. Some attention has also been given to cancers of the kidney, stomach and thyroid, because fluoride is usually absorbed in the stomach and can be concentrated in the kidneys and thyroid. It also has effect on reproduction and birth defects in animals [14] [15]. It causes abnormal behaviour in animals [16].

Aquatic animals such as fish and invertebrates consume fluoride directly from the water and lesser mounts through food [17]. Fluoride toxicity in fishes depends on the increasing fluoride concentration in the aquatic medium, exposure time and water temperature. Fluoride toxicity decreases with increasing intra specific fish size and water content of calcium and chloride [18]. Although it may be removed through excretory

systems, it tends to be accumulated in the exoskeleton for invertebrates and in the bone tissue for fishes [29]. Lethal concentrations of fluoride cause acute intoxication in fish and bring symptoms of fluorosis before death [20].

Domestic animals like dairy cows also exhibited the symptoms of dental fluorosis and skeletal fluorosis. In these animals, colic, excessive urination, inutermittent diarrhoea, repeated abortions, irregular reproductive cycles, and stillbirths were also found as signs of nonskeletal fluorosis [21]. Toxic effects of fluoride in cattle (Bostaurus), buffaloes (Bubalus bubalis), sheep (Ovisaries), goats (Capra hircus), horses (Equusca ballus), camels (Camelus dromedaries) and donkeys (Equusa sinus) was observed. The prevalence and severity of fluorotoxicosis in both man and animals varies greatly from place to place and region to region, even in areas with similar concentrations of F in the drinking water. Numerous determinants appear to be responsible for variations in Fluoride toxicity [22].

2.3 Effect of Fluoride Contamination in Plants
Fluoride contamination in plants takes place by supplying the fluoride contaminated water. This fluoride has many effects on the plants differs from one species to another. It decreases the yield of the crop. It also reduces the quality of the crop. It reduces the weight of grain, fruit, produce, or quantity of sugar, acid, starch, fats, or protein per unit mass. There by the quality of the produce also affected. The contaminated produce is capable of biomagnifying at one or another level in the food chain and finally reaches to human beings [23].

Fluoride increases or decreases the growth of algae, depending upon the concentration, exposure time and nature of algal species. Some algae tolerate high fluoride concentration levels up to 200 mg/l. The toxic action of fluoride on algal growth is that its ions can affect nucleotide and nucleic acid metabolism governing processes of algal cell division [24].

Fluoride ions levels vary widely even between samples of the same kind of food. Some foodstuffs such as vegetables and fruits normally contain fluoride though at low concentration (0.1 mg/kg -0.4 mg/kg) and thus contribute to fluoride intake by man. Higher levels (up to 2 mg/Kg of fluoride) have been found in barley and rice [25]. Leafy vegetables are particularly susceptible to air borne fluoride ion and this accounts for wide variations in the contents of vegetables grown in different areas. Cereals usually contain less than 1ppm fluoride, where fluoride tends to accumulate in the outer layer of the grain and in the embryo [26].
The fluoride contents of both leaf and root vegetables do not differ appreciably from those of cereals with the exception of spinach which is unusually enriched in fluoride. Potato peelings can contain as much as 75% of the total fluoride in the whole tuber. Tea is one of the most fluoride enriched drinks with about two thirds of the fluoride in leaves being soluble in the beverage [27]. Phosphate fertilizers especially the super phosphates are most important source of fluoride in agricultural lands [28]. Fluoride ion intake into roots largely depends on the concentration of fluoride ion in the soil and on the type of soil. In spraying experiments leaves contain more fluoride concentration than stems and stems more than fruits [29].

Absorbed fluoride can be transferred from roots to aerial parts, where it can cause physiological, biochemical, and structural damages. The cell collapse resulting from fluoride accumulation depends not only on the plant species, but also on fluoride content in plant organs. Some plant species such as Gladiolus (Gladiolus grandiflorus) and Freesia (Freesia sp.) developed toxicity symptoms at F concentrations less than 20 µg F/g. dry weight. However other plants such as Elderberry (Sambucus nigra) and Camellia (Camellia japonica) did not show any toxicity symptoms at up to 3600 µg F/g dry weight. Fluoride toxicity symptoms such as leaf necrosis, leaf drop, tip burning, reduction in chlorophyll production and finally death of plants at lethal dosage of fluoride [30] [31].

III. METHODS FOR DEFLUORODATION OF WATER
To reduce the impact of fluoride contamination, different methods for defluoridation exists like coagulation and precipitation, ion exchange, membrane separation and adsorption technique. Each approach has their own advantages and limitations and worked productively under ideal condition to remove fluoride.

3.1. Coagulation and Precipitation

Lime and alum were the mostly utilized coagulants in Nalgonda technique of defluoridation of water. Expansion of lime enhances the precipitation of fluoride as insoluble calcium fluoride and raises the pH up to 11 – 12.

$$Ca(OH)_2 + 2F^- \rightarrow CaF_2 + 2OH^- \qquad (3.1)$$
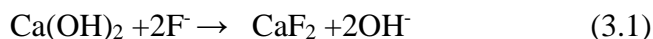
As the lime leaves a leftover fluoride, it was continuously connected with alum treatment to give the best possible fluoride removal. In first step, precipitation happens and lime dosing was utilized. In second step alum was added to bring coagulation. Up on the addition of alum, two reactions have been happened. In the first reaction, alum reacts with an alkalinity's portion to give insoluble aluminium hydroxide [$Al(OH)_3$]. In the second reaction, alum reacts with fluoride ions present in the water. Best fluoride removal is proficient at pH range of 5.5 – 7.5 [32][33].

Nalgonda technique was created by National Environmental Engineering Research Institute (NEERI) is coagulation – precipitation method that includes the expansion of salt of aluminium, lime and bleaching powder took after quick mixing, followed by flocculation, sedimentation and filtration. Aluminium salt was used to remove fluoride from water. The dosage of fluoride depends on upon the concentration of fluoride. The dosage of lime is up to 1/20th of the dose of alum. Lime gives bigger sized and denser floc for rapid settling. Bleaching powder is included for cleansing at the rate of 3ppm. It is the mostly utilized defluoridation method at community level [34].The residual aluminum in waters ranges from 2.01 to 6.86 mg/L under different operating conditions. Any amount over 0.2 mg/L of aluminum in drinking water can cause serious health problems, including dementia [35]

3.2 Ion Exchange

Ion exchange technique involves the removal F by adsorption along with exchanging ions. The basic reason is the fluoride concentration is lower than other ions present in water. Cation exchange resins are more selective in nature for F removal than anion exchange resins [36]. The type of resin decides the defluoridation capacity and selectivity for F removal. The fluoride removal is influenced by the loading of metal ions depending on the variations in their properties [37]. Thus, it is difficult to increase the defluoridation capacity of ion exchange resins and enhancing the F selectivity simultaneously. Ion exchanger Indion FR 10 has considerable F removal capabilities. It was chemically modified with Ce^{3+}, Fe^{3+}, La^{3+}, and Zr^{4+} species to study their feasibility for defluoridation. The maximum fluoride removal capacity of all the modified resins was around 0.5 mg/g. The modified Indion FR 10 with Na^+ and Al^{3+} by loading the metal ions with H^+ type of resin [38] [39]. The order of exchange capacity for the strongest base resins as $HCrO_4^-$ (maximum)> CrO_4^{2-} > ClO_4 > SeO_4^{2-} > SO_4^{2-} > NO_3^- > Br^- > (HPO_4^{2-}, $HAsO_4^{2-}$, SeO_3^{2-}, CO_3^{2-}) > CN > NO > Cl^- > PO_4^{2-} > HCO_3^- > OH^- > CH_3COO^- > F^- [40]. Ion exchanger obtained from double hydrous oxide ($Fe_2O_3.$ $Al_2O_3.xH_2O$) by the sol-gel method from raw materials that are easily available, which was used for adsorption of F, Cl , Br, and BrO_3 simultaneously. It was found that the pH effect of Fand Br depends on ion speciation. Sorption all these anions were effective in the pH range of 3-10. The F^- adsorption of 88 mg/g was the highest among all species [41].

3.3 Membrane Separation (Reverse Osmosis and Nano Filtration)

In membrane process the water containing high fluoride or pollutant concentration is passed through a semi-permeable membrane. The membrane removes pollutant molecules or ions on the criteria of size and electric charge. The pollutants that are removed from the water are collected as retentate and clean water is recovered as permeate. Semi permeable membrane separates pure solvent from solution. The solvent would start flowing from the solution towards the pure solvent when the pressure applied on the solution is more than the osmotic pressure. This phenomenon is called reverse osmosis.

Nano-filtration is a new process in contrast to reverse osmosis, ultrafiltration and microfiltration, and it is much suitable in treating industrial wastewaters. The operation is similar with reverse osmosis, but nano-filteration is operated at lower pressures yielding more flux compared to reverse osmosis. Nano-filtration removes monovalent ions upto 60% where as reverse osmosis membrane remove up to 90%. Reverse

osmosis process can completely demineralize water with very low monovalent ions but its limitations are high operating pressure, high energy equirements and low permeate flux [42].

The performance of a low energy reverse osmotic membrane with a nano-filtration membrane is evaluated. A membrane filtration plant of16 to 25 m3/hr capacity in Finland is constructed to control F and Al concentration in portable water. The comparative removal was upto 95 and 76% for F and Al. Reverse osmosis requires excess feed pressure of 16 bar than thenano-filtration [43].
Study of a large scale RO plant for three years in southern Finland where the system was operation pressure of 6 -11 atm and temperature range of 5-11 ^{0}C, which was possible with nano-filtration membrane. This resulted in lower power consumption and without using a scaling inhibitor the plant was operated at the recovery of 80% [44].

Nano filtration membranes like NF90 and NF400 were used to remove F from ground water. The water quality achieved by the NF400 membrane was found with lower F content. For higher F content removal, a double layer was used to reduce it to an required level. The recovery rate corresponding to 100 m^3/h is 84%, F removal of 97.8% at the pressure of 10 bar [45].

3.4 Adsorption
The process of accumulation of one molecular species on the surface of the other solid materials in the bulk solution called adsorption. Adsorption technique has been quite popular due to its simplicity and availability of wide range of adsorbents. Adsorption on the solid surface is a simple, versatile, and appropriate process for treating drinking water systems, especially for small communities. Adsorption technique is considered as economical and can remove ions over a wide range of pH to a lower residual concentration compared to precipitation [46][47]. The following are the three essential steps of adsorption:

(i) Diffusion or transport of fluoride ions to the outer surface ofthe adsorbent from bulk solution across the boundary layer surrounded by the adsorbent particle, called external mass transfer;

(ii) Adsorption of fluoride ions on the particle surfaces;

(iii) The adsorbed fluoride ions exchange with the structural elements present inside adsorbent particles depending upon the chemistry of solids, or the adsorbed fluoride ions are transferred to the internal surfaces for porous materials (intra particle diffusion) [48].

Adsorption process is effective, efficient, economical regenerative and no sludge generation when compared with the other methods available [49]. Many low cost adsorbents have also been employed for fluoride removal like alumina, red mud, clays, soils, activated carbon, calcite, brick powder, activated coconut-shell, activated kaolinites, oxides ores, modified chitosan, bone char, and some other low cost materials [50]. These low cost adsorbents are classified into natural geological minerals, industrial wastes, construction materials and plant bio materials. These are discussed in detail in below section.

IV. LOW COST ADSORPTION MATERIALS

4.1. Adsorption by Natural Geological Minerals
Coal: Various abundantly available inexpensive natural materials have been explored as adsorbents for defluoridation. The adsorption efficiency of 3 different coal based sorbents fine coke (FC), bituminous coal (BC) and lignite (LN) was evaluated for fluoride removal in water. BC and FC showed higher efficiency of fluoride removal at acidic pH. LN is effective at pH range 6–12. At a fluoride concentration of 90 mg/dm3, the fluoride removal efficiencies of the 3 adsorbents ranged between 77.0% and 85.0% [51] .The adsorption capacity of coal based adsorbents was between 6.9 and 7.44 mg/g. when low grade Assam coal was used for fluoride removal, the optimum dose of adsorbent was 1.25 g/100mL with 85% fluoride removal [52].

Bauxite: Bauxite was used for defluoridation at the optimum adsorbent dose of 1.8 g/50ml and equilibrium was reached in 90 min with the optimum pH of 6. At optimum conditions the fluoride removal efficiency was 94% and the experimental data fitted well with Langmuir isotherm model. High alumina (81.5%) content in bauxite has been responsible for the removal of fluoride [53]. The adsorption of fluoride on

thermally activated titanium-rich bauxite (TRB) at temperatures 300 ^{0}C - 450 ^{0}C the adsorption capacity of TRB is increased. Adsorption was fast and maximum level was reached 90 min. The uptake of fluoride increased with increasing pH up to 5.5–6.5 and decreased thereafter. The presence of other ions in drinking water does not affect the fluoride uptake from aqueous solution [54].

Clay minerals: Fluoride can be removed effectively by montmorillonite clay. Other clay minerals such as laterite, kaolinite and bentonite can also be effectively used for the fluoride removal. In montmorillonite clay the fluoride uptake was found maximum at pH 2, and it decreased with increase in pH. Fluoride adsorption is maximum when the particle size of 75 microns. The Langmuir maximum adsorption capacity at different temperature for fluoride was 1.485–1.910 mg/g [55].

Zeolites: They have also been used for the fluoride removal from drinking water. Zeolite containing surface-active sites created by exchanging Na^+ bound zeolite with La^{3+} orAl^{3+} as they show good affinity for fluoride. The removal of fluoride by Al^{3+} exchanged zeolite took place byan ion-exchange mechanism; while fluoride removal in La^{3+} exchanged zeolitehappened by physical adsorptionwhich are assessed bythe Dubinin-Radushkevitch (D-R) isotherm parameters. Fluorideremoval from water was enhanced by the solution bicarbonate content and pH. In bicarbonate buffered the system the pH increasehas been reduce the affinity of the active sites for fluoride adsorption.The efficiency of adsorbents was reduced in natural groundwater samples comparedwith the stock solution. Al^{3+}exchanged zeolite was superior compared to La^{3+}exchanged zeolite in fluoride removal within the tested concentration range [56].

Dolomite: The calcinations temperature influence the surface chemical composition of dolomite as it has considerable effect on the resulting sorption density of fluoride. At higher concentrations of fluoride, precipitation controles the adsorption process, and thus adsorption of fluoride for the sample calcined at 1173 K was higher and for lower concentrations of fluoride, the adsorption process is not influenced by precipitation, and the maximum adsorption was observed for the sample calcined at 973 K [57].

4.2 Adsorption by Industrial Wastes

Red mud: Red mud, an industrial waste gives maximum fluoride adsorption at pH 5.5 and equilibrium reached in 2 hrs. The fluoride removal depended on chemical nature and interaction of fluoride with metal oxide surfaces [58]. The defluoridation by using red mud and acid treated red mud with 5.5 M HCl for drinking have been used. At pH 5.5 the fluoride removal is maximum and the equilibrium obtained within 2hrs. The lower and higher fluoride adsorption limits were 3.12 and 6.29 mg/g [59]. Modified red mud with $AlCl_3$ (MRMA) was modified by heat activated red mud (MRMAH).The adsorption capacities of MRMA and MRMAH were 68.07 and 91.28 mg/g, which were much higher as compared to red mud (13.46 mg/g). At the pH 7-8 the fluoride adsorption is higher. The adsorption process was best fitted to Langmuir isotherm. The fluoride adsorption of granular red mud in both batch and column studies was done [60]. The highest fluoride adsorption in batch study was 0.644 mg/g for the initial fluoride concentration was 5 mg/L, at pH 4.7 and equilibrium was obtained within 6hrs, while the column study shows the efficiency of adsorption was more and it was 2.05 mg F$^-$/L for a flow rate of 2 mL/min. The recovery of column adsorbent has been made by pumping 0.2M of NaOH solution through the adsorbent media [61]. With zirconium hydroxide modified red mud porous material (RMPM) maximum adsorption was achieved at pH 3 and the equilibrium was achieved within 1hr. The adsorption capacity was 0.6 mg/g. The fluoride adsorption procedure was all around fitted with pore diffusion models and pseudo-second-order rate kinetics. The regeneration of adsorbent was done by using NaOH solution at pH 12 and the recovery ratio was 90%. [62]

Fly ash: The calcium hydroxide treated fly ash (CFA) for fluoride removal in batch study removes more than 80% fluoride. Fluoride concentration is decreased from 10 mg/L to 3 g/L in contact time of 120 min. At pH 7 fluoride removal was higher. The Langmuir adsorption capacity was 10.86 mg/g and the chemisorption process followed by pseudo second ordered kinetic. This process was endothermic and increase of temperature increases the removal efficiency [63]. The study of the batch adsorption capacity of was observed that between pH 2 to 12 fluoride adsorption decreases continuously. The pH influence on

fluoride removal in both studies was different due to the variations in fly ash compositions and experimental conditions [64].

Bottom ash: The adsorption capacity of bottom ash for fluoride removal is investigated with batch and column studies. The maximum efficiency of 73.5 % was achieved at 70mg/100ml bottom ash dosage where the optimum contact time was 105min. The pH was 6 with the maximum efficiency of 83.2 %. During the column studies the increase in fluoride ion uptake is observed with an increase in the bed height as contact time increases. The linearity of the BDST plot assures the applicability of the BDST Model to continuous column studies [65].

Waste carbon slurry (a fertilizer industry waste): The fluoride removal capacity of waste carbon slurry, a waste from fertilizer industry was investigated. The adsorption capacity of fluoride was initially increased up to pH of 7.58 and then decreased to pH of 9.68 and drastic decrease observed when the pH is increased to 11.6. Maximum fluoride adsorption capacity on carbon slurry was observed when the initial fluoride dosage is 15 mg/l and adsorbent dose of 1 g/l is 4.861 mg/g. Langmuir maximum sorption capacity was obtained as 4.3–5.5 mg/g at various temperatures. The breakthrough capacity of column was to be 4.155 mg/g obtained at a flow rate of 1.5 mL/min. Under alkaline conditions at pH of 11.6 desorption was achieved from exhausted carbon slurry [66].

Coal mining wastes: The fluoride removal capability of coal mining wastes was investigated. The Langmuir maximum adsorption capacity of this adsorbent was reported to be 15.67 mg/g. The removal of fluoride was favourable at low pH and the optimum pH for adsorption was found to be 3.5 [67].

Spent bleaching earth: It is a solid waste generated from the edible oil processing industry. It was treated with acid and can be used as an adsorbent for fluoride removal. The Langmuir maximum adsorption capacity of treated spent bleaching earth was obtained to be 7.752 mg/g. With the increasing pH Fluoride removal got decreased and maximum fluoride removal was obtained at pH of 3.5. Ions like PO_4^{3-}, SO_4^{2-} and NO_3^- influenced the fluoride adsorption capacity of acid treated SBE adversely [68].

4.3 Adsorption by Construction Material:

Brick powder: Brick powder (BP) was tested for fluoride removal and compared that with the commercially available activated charcoal (CAC). The adsorption of fluoride by brick powder (BP) was found to be in range of 51.0–56.8% within pH range 6 to 8. In case of commercially available activated charcoal, increase in pH decreased the adsorption capacity. Fluoride removal capacity of brick powder was due to the chemical interaction of the metal oxides with fluoride under suitable pH conditions. The percentage of fluoride removal from synthetic sample got increased from 29.8 to 54.4% for brick powder and increased from 47.6 to 80.4% for commercially available activated charcoal when the contact time got increased from 15min to 120 min [69].

Hyderated cement (ordinary portland cement): The fluoride removal capacity of cement hydrated at different time intervals from aqueous solution is investigated with the help of batch adsorption studies. Hydrated cement shows significant fluoride removal over a wide range of pH values from 3 to 10. The maximum fluoride removal was 92.37% with 10gm/l dosage of hydrated cement by maintaining contact time 24 hours and initial fluoride concentration as 5.9 ppm. The experimental data obtained from batch adsorption experiments was best fitted with the linearly transformed Freundlich and Langmuir isotherms [70]. The fluoride removal capacity of Portland cement was investigated by casting cubes and cured them for 28 days. After that they were grounded into powder and batch and column studies were performed.28 day old cement cube powder removed fluoride much faster and better than raw cement. About 92.6% of fluoride in 100 ppm wastewater was removed by 1% dose of the cement powder at pH 12. The removal efficiencies of raw cement and lime were 47.3 and 96.4%. In column experiments the column was filled with 1–2 mm cement powder and hydrofluoric acid wastewater of pH 3.3 was passed through it and initial fluoride concentration maintained at 1150 ppm got reduced to 15 ppm [71].

Gas concrete: The fluoride removal by adsorption on the gas concrete took place at pH 6.9. Less adsorption occurred in acidic medium due to the formation of weakly ionised hydrofluoricacid. The fluoride removal by gas concrete took place due to adsorption and precipitation byAl^{3+} and Ca^{2+} ions. By using gas concrete96% fluoride removal was achieved. The X-ray spectroscopy revealed that the attraction between fluoride and gas concrete particles electrostatic (columbic) in nature. The pH was increased from 6.9 to 8.9, and thereby an increase in fluoride adsorption was observed. [72].

Broken concrete cubes: The fluoride removal from groundwater using broken concrete cubes as an adsorbent material was investigated by performing batch studies. In batch adsorption study broken cube was found to remove 80% fluoride with contact time of 120 minutes. The adsorbent dose of 6mg/100ml was made and pH is maintained at 7. In column experiment the influent fluoride concentration of 8mg/l at pH of 7 is made. The effluent fluoride concentration was reached up to 1.5mg/l at volume of 26 litres [73].

Lightweight concrete: The fluoride removal capacity of light weight concrete is investigated where the specific sorption of fluoride on concrete was explained with the help of ligand exchange reaction. Fluoride sorption was high at pH 6.9 and the Langmuir maximum sorption capacity for fluoride was 5.15 mg/g. The presence of high percentages of silica and aluminium made the light weight concrete an effective adsorbent for fluoride removal [74].

4.4 Adsorption by Biomass
4.4.1 Adsorption by agriculture wastes
Rice husk ash: The fluoride removal capacity of activated rice husk ash (ARHA) was investigated. Rice husk ash was prepared by cleaning and drying rice husk ash collected from the rice mill at 100°C for 8 hrs using an electric oven. After that it was crushed to obtain 250μm size for the fluoride removal using batch technique. The Langmuir adsorption capacity was to be 0.402mg/g and it follows pseudo second order kinetics. The equilibrium was obtained within 100 minutes with the fluoride removal of 88.30% [75]. The fluoride removal using rice husk ash coated with aluminium hydroxide was also investigated. Here the initial fluoride concentration was 10–60 mg/L and adsorbent concentration is 0.1g.while pH was maintained at 7. Experiments were conducted at the temperature of 27°C for contact time of 1hr. The adsorption study infers the adsorption capacities of modified rice husk ash and column study were found to be 15.08 and 9.5 mg/g. The results indicate that pH is maintained at 5for maximum fluoride removal [76].

Maize ash: Maize husk ash can be utilized as an adsorbent for removing fluoride from raw water in batch studies. The fluoride adsorption is found to be 86% at an agitation rate of 250 RPM while maintaining pH 2. The dosage of adsorbent was 2.0 g/50 ml at equilibrium time of 120mins. While studying the adsorption, Redlich- Peterson isotherm model (R>0.981) was best applied compared to Langmuir, Freundlich and Temkin model [77].

Activated bagasse carbon, saw dust, wheat straw: The applicability of activated bagasse carbon (ABC), sawdust raw (SDR) and wheat straw raw (WSR) has been investigated for fluoride removal and comparison was made with commercial activated carbon (CAC). The uptake of fluoride by CAC, ABC, SDR and WSR were 57.6, 56.4, 49.8 and 40.2%. Initial fluoride concentration of aqueous solution of 5 mg/L and pH is 6. Contact period considered was 60 minutes and adsorbent dosage was 4 g/L. Freundlich isotherm was best fitted with the experimental data. The pseudo-second-order reaction was suitable for kinetic study [78]. The capability of bagasse, modified bagasse using 1 M of $NaHCO_3$ and chitosan has been investigated for fluoride removal from water. The modified bagasse removes more than 90% of fluoride at optimum condition when pH is maintained at 7, adsorbent dosage of 2 g/L, contact time of 60 minutes and initial fluoride concentration of 5 mg/L. The Langmuir adsorption capacity of modified bagasse, bagasse and chitosan were 9.033, 2.034 and 1.463 mg/g, respectively [79].

Zirconium impregnated groundnut shell, coconut shell coconut fibre and activated charcoal: The fluoride removal capacity of zirconium impregnated groundnut shell, coconut shell coconut fibre and activated charcoal was investigated in a continuous down flow column at the constant flow rate of 0.6-0.7 l/hr. The

zirconium ion impregnated coconut fibre showed maximum fluoride adsorption and groundnut shell and coconut shell carbon has decreasing order of fluoride adsorption. Initial fluoride concentration of 8 mg/l of volume 21 litre test solution and another solution of concentration 2.47 mg/l of volume 6 lit treated with zirconium impregnated groundnut shell brought down the fluoride concentration less than 1.5 mg/l. For zirconium ion impregnated coconut fibre the optimum condition for the batch study of was achieved by maintaining the pH of 4 and stirred continuously for 6 hours and adsorbent dosage is 20 g/l. zirconium impregnated groundnut shell was regenerated by treating with 0.02 M of NaOH solution [80].

Cashewnut sheath: The removal of fluoride from water by activated carbon derived from cashewnut sheath (CSC) and commercial activated carbon (CAC) which was treated with 2% of aluminium sulphate solution in batch and column studies was considered. The maximum fluoride removal percentage of CSC was 87.6% for an adsorbent dosage of 8 g/L at an optimum pH of 6.9 with a contact time of 16 hr. CAC could remove 56% of fluoride with adsorbent dosage of 14g/L at pH 6.9 and contact time of 6h. The Freundlich adsorption equation was best fitted for CSC and CAC [81].

4.4.2 Adsorption by Plant Biomass

Tamarind (Tamarindus indica): *Tamarindusindica* fruit shells (hard pod shells) were activated by ammonium carbonate and then carbonized. This material is used for fluoride removal when the BET surface area of 473 m2/g. The experiments revealed that for pH values between 3 and 7, the fluoride uptake capacity of ammonium carbonate activated fruit shells in stirring experiments was increased from 1.84 mg/g to 16.0 mg/g. Fluoride uptake capacity reduces below 7 pH and above 12 pH with 3.12 mg/g and 5.14 mg/g for shaking and stirring dynamic studies..The defluoridation capacities of activated and MnO_2coated tamarind fruit shell with the help of batch and column sorption techniques investigated. At an optimum pH value 6.5, the fluoride removal capacity of the sorbents was 1990 mg/kg when the contact time is 30 min, [82] [83].

Vetiver (Chrysopogon zizanioides): The fluoride removal capacity of the powder of the vetiver root was investigated as an adsorbent. In the fluoride stock solution of 2 mg/Lat pH range of 6.0 to 7.0, Vetiver had removed 80 to 90% of fluoride from water. Langmuir and Freundlich isotherms are well fitted with the equilibrium data obtained [84].

Durva grass (Cynodon dactylon): The fluoride removal capacity of Durva grass (*Cynodondactylon)* as adsorbent is investigated by performing batch studies at the constant temperature of 25-32°C.The fluoride concentration of 3.0 mg/L, dosage of adsorbent was 1.5g, pH is maintained neutral andontact time 105 minutes. The maximum removal of fluoride was 83.77 %. Various adsorption isotherm models were applied to investigate the adsorption data. The adsorption process followed Redlich-Peterson isotherm and Langmuir isotherms. This material has superior adsorptive capacity and effective when compared with the other natural adsorbents [85].

Indian Gooseberry (*Phyllanthusemblica):* The fluoride removal from aqueous solution is investigated using Indian Gooseberry (*Phyllanthusemblica)*as adsorbent. At neutral pH with adsorbent dose 0.75g and initial fluoride ions concentration of 3 ppmthe highest adsorption capacity was obtained. The removal of fluoride was observed to be 82.1%. The adsorption of fluoride was heterogeneous in nature [86].

Guava (Psidium guajava): The fluoride removal capacity of Guava Seeds (PsidiumGuajava) from Aqueous Solutions is investigated. Maximum adsorption occurred at pH5.0 to 8.0.The adsorption process was found to be endothermic in nature.Adsorption process is followed by Langmuir and Freundlich adsorption isotherm models. The fluoride sorption kinetics using guava seed at different temperature is described by pseudo-second order model. The Langmuir model was much suitable to the isotherm's experimental data which indicates it as chemical adsorption [87].

Drumstick (Moringaoleifera): The fluoride removal efficiency of alkali and acid treated drumstick (*Moringaoleifera*) seed powder from aqueous solution has been investigated. The fluoride removal capacity of alkali treated adsorbent was better than acid treated adsorbent. At the initial concentration of 10 mg/L,the

optimum dose of 400mg/L alkali treated adsorbents removed 76 and 68%. The particle size adsorbents were 212 and 600 μm at pH of 8 and contact time of 2 and 2.5 hrs [88].

V. CONCLUSIONS

The effect of fluoride contamination on human, animals and plants are studied in the literature. For the biological metabolism some amount of fluoride is required for the living organisms. Every organism has some amount of fluoride in its body. Plants get fluoride through the soil and water, human and animals get fluoride through plant or animal based food and water. Its concentration beyond the required concentration leads to fluoride contamination and it affects the human and animal health and also growth in plants. Fluoride ion from plants can be biomagnified to animals and finally reach human through the food chain. So the defluoridation for drinking water supplies is essential along with irrigation and livestock water to prevent biomagnification of fluoride.

Removal of fluoride even for drinking water itself is a costly process. So for the regulation of fluoride in livestock or irrigation water require much cheaper and effective technology. Adsorption process is one of such technology which makes use of cheaper natural adsorbents for fluoride removal. This adsorption process is also simple and can be easily adopted by an individual or communities at large scale. Other processes such as reverse osmosis, membrane technologies maybe effective but they are costlier compared to adsorption. In coagulation and precipitation process some unwanted harmful ions are produced. This may give some negative results regarding health.

Adsorbents are derived from natural geological minerals, industrial wastes, construction materials or wastes and plant bio materials. Geological minerals such as clay, dolomite or serpentine have removal efficiency up to 70 percent when used without pre-treatment. The fluoride removal efficiency is increased by pre-treatment of geological adsorbents. Some adsorbents are generated from industrial waste materials such as fly ash is better removal of fluoride in water. This percentage removal of fluoride up to 85 % but some industrial wastes contains traces of heavy metals from different industries which has other adverse effect. Biomass adsorbents after pre-treatment like pyrolysis have high fluoride removal capacity compare to other adsorbents. It was easy to acquire in large quantities of bio mass but difficult to pre-treat them. Most of the adsorbents performed better when suitable thermal or chemical pre-treatment in fly ash, red mud, bleaching earth, sugarcane baggase and in some plant based bio adsorbents.

The operating parameters like pH, contact time, particle size of adsorbents, and dosage of adsorbents are effecting the percentage removal of fluoride. In most of the cases operating parameters in range of pH range of 6 to 8, contact time of 15 to 120 min, 3 to 8 % (w/v) percent dosage of adsorbent to achieve high fluoride removal. There is much scope for research in this area to explore of different materials as adsorbents and to find methodology to increase activity of adsorbents to remove the fluoride ions.

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