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A REVIEW ON SOURCES, OCCURRENCE, HEALTH EFFECTS AND TREATMENT METHODS OF FLUORIDE CONTAMINATED WATER

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Abstract- High intake of fluoride above the permissible limit of 1.5 mg/L through drinking water is responsible for skeletal, dental fluorosis and some other health effects in humans. If the intake is below 1 mg/L, it causes dental carries in the teeth. In this paper various natural and anthropogenic sources of fluoride are discussed in short. Worldwide occurrence of fluoride contaminated water is also discussed. Health effects like effects on bone, reproductive effects, dental effects, neurological effects, renal effects, gastrointestinal effects are discussed in brief. Techniques which are being used nowadays for the removal of fluoride from the contaminated water are discussed with their advantages and disadvantages. These techniques are divided into four categories i.e. Adsorption, Precipitation, Membrane-based and Ion Exchange. Various materials which have been used by different researchers are reviewed and tabulated along with their efficiencies or capacities in removing fluoride.
KeyWords: Fluoride; Sources; Occurrence; Health Effects; Treatment Methods

1. INTRODUCTION

In the periodic table of elements, fluorine is the lightest, most electronegative element and it is also most reactive due to its electronegative nature. Due to oxidizing nature and more tendency to acquire a negative charge, it is not found in nature in its elemental state[1]. It is generally found in the form of fluorides and it forms fluoride ion in the solution. It forms mineral complexes with cations. Fluoride ions have the same size and radius as hydroxide ions [1]. As hydroxyl group is most common as a subunit in all mineral structures of living creatures, it can replace fluoride ion by its hydroxide ion in teeth and all bone structures[2]. Due to this fluoride gets accumulated very easily in the body which causes fluorosis. Since fluoride has high reactivity it found in nature in many mineral complexes like fluorspar (Fluorite or Calcium Fluoride CaF_2), cryolite (Sodium Aluminum Fluoride Na_3AlF_6) rock phosphate (salts rich with PO_4), apatite, mica, hornblende, and others. Fluorite is the most common mineral form of fluoride found in igneous and sedimentary rocks. It is recognized as a thirteenth most common element in the earth crust. Its concentration in seawater is around 1.2-1.4 mg/L, in ground waters its concentration is up to 67 mg/L and in surface waters, it is less than 0.1 mg/L. It is also found in foods especially fishes and tea[3].In groundwater, high and low concentrations occur depending upon the nature of rocks and occurrence of fluoride-bearing minerals. High fluoride concentrations are expected to occur in ground waters from calcium poor aquifer and in areas where fluoride-bearing minerals are common [4]. This paper aims at reviewing the recent research work which is going on the fluoride and sharing the sources, occurrence and health effects on human due to high fluoride intake, with the global scientific community, to bring down the importance of drinking water having fluoride within the acceptable limit, into focus.

2. OCCURRENCE

Waters with high fluoride concentrations occur in large and extensive geographical belts associated with a) sediments of marine origin in mountainous areas, b) volcanic rocks and c) granitic and gneissic rocks [1]. The most well-known and documented area associated with volcanic activity follows the East African Rift system from the Jordan valley down through Sudan, Ethiopia, Uganda, Kenya and the United Republic of Tanzania. In rift valley system most of the lakes like soda lakes have high fluoride concentration from 1600 mg/L to 2800 mg/L in Kenya lake elmentaita and Nakuru respectively and up to 690 mg/L in Tanzanian Momella soda lakes [5].In Sri Lanka concentrations up to 10 mg/L in Dry Zone, associated with dental and skeletal fluorosis have been reported. In the Wet Zone, the intensive rainfall and long-term leaching of fluoride and other minerals from the crystalline bedrock are probably responsible for much lower concentration [1]. The volcanic areas of Nairobi, rift valley, and central provinces have maximum groundwater fluoride concentration up to 30 to 50 mg/liter. Most of the sampled well and boreholes were providing drinking water and the prevalence of dental fluorosis in the most affected areas was observed to be very high [6]. Groundwater having high fluoride concentration associated with metamorphic and igneous rocks such as granite and gneisses have been reported in India, Pakistan, West Africa, Thailand, China, Sri Lanka, and Southern Africa. InChina endemic fluorosis has been reported in all 28 provinces, autonomous regions, and municipalities except Shanghai. List of countries having skeletal and dental fluorosis problem due to exposure to fluoride

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through drinking-water is given in table 1. Groundwater in India has fluoride concentration more than the permissible limit 1.5 mg/L is a very big health problem. List of districts in India having excess fluoride in the groundwater is given in table 2. Around 90 % rural population of India is using this water for drinking and domestic purposes due to which very large population of India is facing health problems like dental and skeletal fluorosis caused by high concentration of fluoride [7].

Argentina	Eritrea	Indonesia	Mexico	Pakistan	Spain	Turkey
Brazil	Ethiopia	Israel	Niger	Saudi Arabia	Sri Lanka	Uganda
Canada	Germany	Japan	Nigeria	Senegal	Sudan	Tanzania
China	India	Kenya	Norway	South Africa	Thailand	USA

Table 1: List of countries having skeletal and dental fluorosis problem due to fluoride intake through drinking-water [1].

Serial Number	State Name	Total Affected Districts	Names of Affected Districts
1.	Andhra Pradesh	16	All districts except Adilabad, Nizamabad, Srikakulam, West Godavari, East Godavari,Vishakhapatnam, Vizianagaram
2.	Assam	2	KarbiAnglong, Nagaon
3.	Bihar	5	Daltonganj, Gaya, Rohtas, Gopalganj, PaschimChamparan
4.	Chhattisgarh	2	Durg, Dantewara
5.	Delhi	7	Central, South, West, East, South-west, North West, North East zones.
6.	Gujarat	18	All districts except Dang.
7.	Haryana	11	Rewari, Faridabad, Karnal, Sonipat, Jind, Gurgaon, Mahendragarh, Rohtak, Kurukshetra, Kaithal, Bhiwani.
8.	Jammu& Kashmir	1	Doda.
9.	Jharkhand	4	Giridih, Palamau, Pakur, Sahabganj.
10.	Karnataka	14	Dharwad, Gadag, Bellary, Belgaum, Raichur Bijapur, Gulbarga, Chikmaglur, Mandya, Bangalore (rural), Mysore, Manglore, Kolar, Shimoga.
11.	Kerala	2	Palghat, Allepy
12.	Maharashtra	8	Chandrapur, Bhandara, Nagpur, Jalgaon, Buldhana, Amravati, Akola, Yavatmal
13.	Madhya Pradesh	13	Shivpuri, Jhabua, Mandla, Dindori, Chhindwara, Dhar, Vidisha, Sehore, Raisen, Mandsour, Neemuch, Ujjain, Seoni
14.	Orissa	18	Phulbani, Koraput, Dhenkenal, Angur, Boudh, Nayagarh, Puri, Balasore, Bhadrak, Bolangir, Ganjam, Jagatpur, Jajpur, Kalahandi, Keonjhar, Kurda, Mayurbhanj, Rayagada
15.	Punjab	9	Mansa, Faridkot, Bhatinda, Muktsar, Moga, Sangrur, Ferozpur, Ludhiana, Amritsar
16.	Rajasthan	32	All districts
17.	Tamil Nadu	8	Salem,Erode,Dharmapuri, Coimbatore,Tiruchirapalli, Vellore, Madurai, Virudunagar
18.	Uttar Pradesh	7	Unnao, Agra, Meerut, Mathura, Aligarh, Raibareli , Sonbhadra
19.	West Bengal	7	Birbhum, Bardhman, Bankura, Purulia, Malda, U.Dinajpur & D.Dinajpur

Table 2: States in India along with their districts having excess fluoride in groundwater[7].

3. SOURCES OF FLUORIDE

Sources of fluoride are of two types anthropogenic as well as natural. Both types of sources are discussed below in detail.

3.1 Natural Sources

Fluoride in the environment is found in many mineral complexes form due to the high reactivity of fluorine. Weathering of minerals, marine aerosols, and emissions from volcanoes are the main natural sources of fluoride in the environment [8, 9]. An estimated annual release from volcanoes through passive degassing and eruptions ranges from 60 to 6000 kilotons, approximately 10 percent of this total annual release goes directly into the stratosphere. Annually an approximate amount of 20 kilotons of fluoride may be found in marine aerosols [8]. Inorganic fluoride is generally found in parent rocks[10].In acidic conditions, some of the fluoride minerals are broken down generally, due to weathering [11]. Calcium fluoride & fluorapatite ($Ca_5(PO_4)_3F$) dissolve very slowly [12].In calcareous & alkaline soils mineral fluorophlogopite (mica; $KMg_3(AlSi_3O_{10})F_2$) is stable [13].

3.2 Anthropogenic Sources

Hydrogen fluoride, Calcium fluoride, Phosphate fertilizers, Sodium Hexafluorosilicate, and Sulfur hexafluoride the anthropogenic sources of fluoride. Each of them is discussed below in brief.

3.2.1 Hydrogen Fluoride

Annual estimated world consumption of hydrogen fluoride is more than one million tonnes [14]. It is manufactured from calcium fluoride. Synthetic cryolite, chlorofluorocarbons, motor gasoline alkylates, aluminum fluoride (AlF_3) all uses hydrogen fluoride for their production. Nuclear industry uses uranium hexafluoride (UF_6), uranium tetrafluoride (UF_4) which are synthesized using hydrogen fluoride [15]. Hydrogen fluoride is also used in petrochemical manufacturing processes, etching, and cleaning glass, etching semiconductor devices, cleaning brick and aluminum and tanning leather [16].

3.2.2 Calcium Fluoride

Calcium fluoride is the principal fluoride-containing mineral used in industries [10]. During 1972-1978 estimated average annual production of calcium fluoride range from 118000 to 225000 tonnes was identified from production data confined to the USA [9].In 1989 an estimated consumption of calcium fluoride as fluorspar in Canada was 180000 tonnes. In the USA the estimated consumption of CaF_2 was 1063000 tonnes in 1977 [9]. CaF2 is used as a raw material for the production of hydrofluoric acid. It is used in glass, steel, and enamel production industries as flux [15].

3.2.3 Phosphate Fertilizers

A major source of fluoride contamination of the agricultural soils is phosphate fertilizer. Rock phosphates contain 3.5 percent fluorine and are used for manufacturing of the phosphate fertilizers [17]. Some of the fluorides are lost into the atmosphere during the manufacture of phosphate fertilizers due to acidulation process. In final fertilizer, fluoride content is reduced by diluting it with ammonium ion (ammoniated phosphates) and sulfur (superphosphates). Between 1.3 to 3.0 % fluorine is found in the final product [18].

3.2.4 Sodium Hexafluorosilicate

For fluoridation of the drinking water, sodium hexafluorosilicate is used. It gives fluoride ions by getting hydrolyzed when it is dissolved in the water. It should meet standards of purity for drinking water chemicals while used for fluoridation of the drinking water [3].

3.2.5 Sulfur Hexafluoride

In Canada annually, more than 110 tonnes of sulfur hexafluoride is imported [19]. Sulfur hexafluoride is used as a current interrupting and an insulating medium in electrical switchgear such as power circuit breakers, in various components in electrical substations [19]. More than 90% of the total imported amount of sulfur hexafluoride into Canada is used for the production of magnesium and the remaining amount is used in the manufacturing of electrical switchgear [19].

4. HEALTH EFFECTS OF EXCESS FLUORIDE

Excess fluoride intake has many health effects: All these effects are discussed below in short.

4.1 Effects on Bone

Most pertinent outcomes of the adverse effects of the long-term exposure of humans to excess fluoride are effects on bone (skeletal fluorosis and fracture) [3]. Ingested fluoride influences the physical structure & chemical composition of bone [20].Skeletal accumulation of fluoride due to long-term exposure and its effects on non-neoplastic bone disease, especially bone fractures and skeletal fluorosis is the most serious effects in human [21].

4.1.1 Skeletal Fluorosis

Long-term exposure to the increased level of fluoride concentration by inhalation and ingestion both causes skeletal fluorosis. In preclinical phase slight increase in bone mass occurs, in first and second phase osteosclerosis of cancellous bone, chronic joint pain, the stiffness of joints, sporadic pain and calcification of ligaments occurs. The third phase is crippling fluorosis in which limited movement of joints, skeletal deformities, neurological deficits, muscle wasting, intense calcification of ligaments occurs [22, 23]. The occurrence of endemic skeletal fluorosis in northern, eastern, central, and southern Africa China, India, has been reported which is mainly due to following reasons:

- Consumption of foodstuff which is naturally rich with high fluoride content
- Eating of foodstuffs which are prepared by water containing increased fluoride level
- Drinking water which is having a significant amount of fluoride

- Indoor burning of the coal which is rich with fluoride [22-24].

4.1.2 Skeletal Fracture

When a person is under continuous exposure to fluoride then the cumulative accumulation of fluoride occurs in the bones and bones become heavier and brittle [25]. Denser bone is not a better bone [26] because it is brittle or fragile than normal bone. This increase in brittleness and density of bones causes an increase in the risk of skeletal and hip fracture.

4.2 Reproductive Effects

Many studies have been done to know the relationship between ingested fluoride and birth rates. But very few of them conclude that ingested fluoride has some effect on birth rates so further study is required. Study of a database of 30 regions which were from nine states of United States where fluoride in drinking water was more than 30 mg/L concluded that there is a decrease in birth rates with an increase in fluoride ingestion [27].

4.3 Dental Effects

It is well known that fluoride has both types of effects on dental health beneficial as well as harmful. For the formation of dental caries fluoride has an inverse relation with fluoride intake and for the prevalence of dental fluorosis, it has a positive relationship with the intake of fluoride [28].

4.3.1 Dental Caries

People using fluoridated water are affected very less by dental carries but those who don't use fluoridated water used to be affected more. The difference in caries prevalence for both fluoridated water users and non-fluoridated water users has become very narrow. Fluoride prevents dental caries formation by becoming incorporated into the crystal lattice of enamel, improving the stability of the lattice and by furnishing the enamel so that it becomes less soluble to acid demineralization. If saliva and dental plaque contain fluoride then it hampers the demineralization and supports the remineralization which takes place at the tooth surface[3].

4.3.2 Dental Fluorosis

Intake of the increased level of fluoride leads to dental fluorosis which occurs during tooth development age normally up to the age of 6 to 8 years. This condition is called as hypoplasia of dental enamel which results from the amalgamation of excessive fluoride into the dental enamel. The extremity of dental fluorosis is usually ranged from mild to severe depending upon the level of fluoride exposure. Small white areas appear in the tooth enamel in the case of mild dental fluorosis. Pitting and staining of teeth appears in the case of severe dental fluorosis. Amalgamation of excess fluoride into enamel alters the rheological structure and affects cellular metabolic processes associated with normal enamel development which ultimately affects normal maturation of the enamel [29, 30].

4.4 Neurological Effects

Intake of excess fluoride affects the intelligence quotient of children's as mentioned in the studies conducted in China [31-34]. Children who consumed a high level of fluoride (2 mg/L) scored less in comparison of those who consumed a low level of fluoride (1 mg/L) in the tests related to the intelligence. In India, an inverse relationship was found between intelligence quotient of school children's and concentration of fluoride in their urine [35].

4.5 Renal Effects

Renal system excretes most of the excess body fluoride and it is exposed more to higher fluoride concentrations than other body organs [36]. So this can be affected more by fluoride toxicity than other organs. 18700 People living in a region of India, where fluoride concentration in drinking water ranged from 3.5 to 4.9 mg/L, were examined and it was found that patients with clear signs of skeletal fluorosis were 4.6 times more likely to develop kidney stones [37].

4.6 Gastrointestinal Effects

Nausea, vomiting, diarrhea, and abdominal pain have been reported as gastrointestinal effects due to acute fluoride toxicity [38, 39].

5. METHODS OF FLUORIDE TREATMENT

There are mainly four methods of treatment of fluoride and these are ion exchange, membrane-based processes, precipitation, and adsorption. All these methods are discussed below in detail.

5.1 Ion Exchange

Both cation and anion exchange resins have been used for the removal of fluoride. Resin has chloride ion which is replaced with fluoride ion in the water. This removal takes place according to the following reaction:

$$Matrix - NR_3^+Cl^- + F^- \rightarrow Matrix - NR_3^+F^- + Cl^-$$

This reaction continues until all the sites get filled by fluoride ion. Once the resin gets saturated with fluoride ions then it can be recharged using water having dissolved NaCl salt. Fluoride ions get replaced with chloride ions and come out of the resin this is due to high electronegativity of the fluoride than chloride. This recharged resin can be used again for the removal of fluoride [40]. Ion exchange resins which have been used for the removal of fluoride from water are given in table 3.Where, q_{max} is the maximum fluoride adsorption capacity of the resin. Chelating resin, namely Indion FR 10 (IND) was found to be an effective sorbent for fluoride removal than an anion exchange resin Ceralite IRA 400 (CER) because of its specificity towards fluoride when both were compared in effectiveness[41].

Advantages of Ion Exchange Technique

- Removes fluoride up to 90–95%.
- Retains the taste and color of water intact.

Limitations of Ion Exchange Technique

- Efficiency is reduced in presence of other ions like sulfate, carbonate, phosphate, and alkalinity due to an increase in the ionic competition.
- Regeneration of resin is a problem because it leads to fluoride-rich waste, which has to be treated separately before final disposal.
- The technique is expensive because of the cost of resin, pretreatment required to maintain the pH, regeneration and waste disposal.
- Treated water has a very low pH and high levels of chloride.

Ion exchange resin	Initial F^- (mg/L)	q_{max}(mg/g)	References
Indion FR 10	4	1.35	[41]
Ceralite IRA 400	4	1.64	[41]
Polyanion (NCL)	8.1	1. 04	[42]
Amberlite IR-120	50	4.63	[43]
Amberlite XAD-4TM	5	95.74	[44]

Table 3: Ion exchange resins which have been used for the removal of fluoride from water

5.2 Membrane-Based Processes

A membrane-based process like Reverse Osmosis is one of the most widely used processes for the removal of fluoride from the water. It is being used in both communities as well as household level. Reverse Osmosis is a physical process in which pressure is applied to the feed water to pass it through the semipermeable membrane for getting water with less fluoride concentration. The process is the reverse of natural osmosis as a result of the applied pressure to the concentrated side of the membrane, which overcomes the natural osmotic pressure. RO rejects ions based on charge and size. RO membrane subjects to fouling and can act as media for microbial growth and produces concentrated brine discharge that should be disposed of safely. Nanofiltration is a relatively low-pressure process that removes larger dissolved solids as compared to reverse osmosis. Conversely, RO operates at high pressure with the greater rejection of all dissolved solids [40]. For Nanofiltration, the membranes have slightly larger pores than those used for reverse osmosis and offer less resistance to passage both of solvent and of solutes. As a consequence, pressures required are much lower, energy requirements are less, removal of solutes is much less exhaustive, and flows are faster [45]. Both RO and NF were found effective for fluoride removal from soft, high fluoride groundwater[46]. Electrodialysis (ED) is a membrane process similar to RO, except that ED uses an applied dc (direct current) potential electric current instead of pressure, to separate ionic contaminants from water[47]. List of membrane-based processes which are being used in removing fluoride from water is given in table 4.

Advantages of Membrane-Based Processes

- There is not any interference by other ions.
- The membrane can work in a wide range of pH.
- No chemicals are required and very little maintenance is required.
- This process provides treatment and disinfection both in one step.
- Membrane process is highly effective in fluoride removal and provides an effective barrier to suspended solids, inorganic pollutants, pesticides, and microorganisms etc.
- The process is simple, operated automatically and minimum manpower is required.

Disadvantages of Membrane-Based Processes

- It removes all ions from water but some minerals are necessary for proper growth, remineralization is required after treatment.
- This process is expensive than other treatment methods.

- A lot of water is wasted as brine.
- Disposal of brine is a very big problem.
- Water becomes acidic and needs pH correction.

Membrane process	Initial F^- (mg/L)	Removal (%)	References
	3	63	[48]
Electrodialysis	20.6	96	[49]
	7.72	99	[50]
Reverse Osmosis	4	95	[46]
Nano Filtration	4	76	[46]
Reverse Osmosis	460	98	[51]

Table 4: List of membrane-based processes and their efficiencies in removing fluoride.

5.3 Precipitation

Precipitation process involves the addition of chemicals and formation of fluoride precipitates. Aluminum salts (e.g. Alum), lime, Poly Aluminium Chloride, Poly AluminiumHydroxysulfate are some of the frequently used materials in defluoridation by precipitation technique. Nalgonda technique is the best example of defluoridation by precipitation method. This method was developed by the National Environmental Engineering Research Institute (NEERI), Nagpur India. This method is being used widely in India at community and domestic level both. Nalgonda Technique involves the addition of Aluminium salts, lime, and bleaching powder followed by rapid mixing, flocculation, sedimentation, filtration, and disinfection[42]. Addition of lime leads to precipitation of fluoride as insoluble calcium fluoride and raises the pH value of water up to 11–12 [40].

$$Ca(OH)_2 + 2F^- \rightarrow CaF_2 + 2OH^-$$

In the first step, precipitation occurs by lime dosing which is followed by a second step in which alum is added to cause coagulation. When alum is added to water, essentially two reactions occur. In the first reaction, alum reacts with some of the alkalinity to produce insoluble aluminium hydroxide [$Al(OH)_3$]. In the second reaction, alum reacts with fluoride ions present in the water. The best fluoride removal is accomplished at a pH range of 5.5–7.5[52].

Advantages of Precipitation Technique [53]

- Regeneration of media is not required.
- Chemicals used are easily available.
- Can be used for treating water at community and domestic level both.
- This process is economical also.
- Applicable in batch as well as in continuous operation.
- Local semi-skilled workers can be readily employed.
- Highly efficient in removing fluoride from a high level to a desirable level.
- Simultaneous removal of color, odor, turbidity, bacteria and organic contaminants occurs.
- The simplicity of design, construction, operation, and maintenance.
- Little wastage of water and least disposal problems.
- Needs a minimum of mechanical and electrical equipment.

Disadvantages of Precipitation Technique

- Desalination is required when raw water has total dissolved solids more than 1500 mg/L.
- Raw water hardness should be less than 600 mg/L otherwise desalination is required.
- A large amount of alum is needed to remove fluoride.
- A large amount of sludge is produced as compared to electrochemical defluoridation[42].
- Daily addition of chemicals is required.
- Treated water had residual aluminum ranging from 2.01 to 6.86 mg /L in Nalgonda technique [54].
- It converts a large portion of ionic fluoride (67–87%) into the soluble aluminum complex and practically, removes only a small portion of fluoride in the form of precipitates (18–33%). These soluble aluminum fluoride complexes are toxic in nature[55].
- Due to organoleptic reasons, users do not like the taste of treated water[40].

5.4 Adsorption

Adsorption is the process by which ions or molecules present in one phase get accumulated on the surface of another phase. The material being concentrated is called adsorbate and the adsorbing solid is called adsorbent. There are two general types of adsorption:

5.4.1 Physical Adsorption
This is due to weak forces of attraction or van der walls forces between molecules. The adsorbed molecule is not affixed to a particular site on the solid surface but it is free to move from one surface site to another and can form several layers on the surface of the adsorbent. It is reversible in nature i.e., desorption can occur.

5.4.2 Chemical Adsorption
This is due to result of much stronger forces comparable with those leading to the formation of chemical compounds. Molecules are not free to move from one site to another and can form an only monomolecular layer. This type of adsorption is seldom reversible.

Adsorbent	Dose (gm/L)	Initial F^- (mg/L)	Efficiency/q_{max}	References
Hydrated cement	10	5.9	2.6 mg/g	[56]
Broken concrete cubes	60	8	80 %	[57]
Cement paste	1	100	92.6 %	[58]
Brick Powder	6	3.1	48.7 %	[59]
Alum impregnated activated alumina	8	20	40.3 mg/g	[60]
Alum impregnated brick powder	20	10	1.84 mg/g	[61]
Alum sludge	8	25	5.3 mg/g	[62]
Mixed rare earth oxides	4	50	12.5 mg/g	[63]
Red mud	2	21.28	82 %	[64]
Titanium rich bauxite	1	10	3.8 mg/g	[65]
Activated alumina	4	13.8	1.45 mg/g	[66]

Table 5: Adsorbents and their efficiencies in removing fluoride from water.

5.5Adsorption Isotherms
Adsorption isotherms are used for understanding the mechanism and quantifying the distribution of the adsorbate between the liquid phase and solid adsorbent phase at equilibrium during the adsorption process. The Langmuir, Freundlich both isotherms are most commonly used in adsorption studies. Langmuir isotherm equation is expressed as:

$$q_e = \frac{q_{\max}}{1+bC_0} C_e$$

Where, q_e is the amount of adsorbate adsorbed at equilibrium per unit weight of adsorbent (mg/g). Ceis the equilibrium solute concentration mg/L; q_{max} and b are Langmuir constants which are related to saturated monolayer adsorption mg/g and binding energy or affinity parameter of the sorption system respectively. The corresponding linear form of the equation is:

$$\frac{1}{q_e} = \frac{1}{bq_{\max}C_e} + \frac{1}{q_{\max}}$$

This empirical model assumes uniform surface having equivalent adsorption sites with no lateral interactions between the adsorbed species. Thus, Langmuir isotherm refers to homogeneous sorption, where each molecule has equal sorption activation energy. In order to evaluate the feasibility of the process, the Langmuir isotherm can be described in terms of the dimensionless constant; separation factor or equilibrium parameter

$$R_L = \frac{1}{1+bC_0}$$

Where, C_0 is initial concentration (mg/l).There are four probabilities for the R_L value: (i) for favorable adsorption $0 < R_L < 1$, (ii) for unfavorable adsorption $R_L>1$, (iii) for linear adsorption $R_L = 1$ and (iv) for irreversible adsorption $R_L = 0$. Freundlich model is extremely used for experimentally determining the adsorption capacity (K_f) and considers multilayer sorption on heterogeneous surfaces. The Freundlich isotherm is formulated as:

$$q_e = K_f C_e^{\frac{1}{n}}$$

Where q_e is the adsorption capacity (Milli gram of adsorbate per gram of adsorbent), C_e is the concentration of adsorbate in solution (mg/L), K_f is the measure of adsorption capacity and 1/n adsorption intensity. Slope and intercept give the values of 1/n and K_f, which are the empirical constants dependent on several environmental factors. This equation is conveniently used in the linear form by taking the logarithmic of both sides as given in the following equation:

$$\ln(q_e) = \frac{1}{n}\ln(C_e) + \ln(K_f)$$

A plot of $\ln(q_e)$ against $\ln(C_e)$ yielding a straight line indicates the confirmation of Freundlich isotherm for adsorption. The constants can be determined from the slope and the intercept. Many adsorbents have been used by researchers for removing fluoride from water and brief detail of some of them is given in table 5. Researchers are trying locally available materials for fluoride treatment; still, researches are going on to find a locally available, cheaper, abundant and efficient adsorbent media.

Advantages of Adsorption Process

- Treatment using the adsorption process is cost-effective.
- Locally available materials can also be used as an adsorbent material.
- This process has high efficiency.

6. CONCLUSION

- Fluoride removal technologies have been reviewed in brief.
- Drinking fluoride-safe water is necessary for ensuring good health. De-fluoridation of the fluoride contaminated water should be done for ensuring the good health.
- Methods of removal of fluoride have been divided into four categories i.e. Adsorption, Precipitation, Membrane-based and Ion Exchange.
- Community-based de-fluoridation should be encouraged so that community can get the same quality water with better quality control. Places where community defluoridation is not feasible, residence should be motivated and educated to adopt the most suitable domestic defluoridation technique.
- Nalgonda technique should be used in the all rural areas of India where the alternate source of safe drinking water is not available. Community-based de-fluoridation plants should be established by the Indian government.
- Technique for community de-fluoridation should be adoptable, acceptable & economic to the community.
- Electrodialysis, nanofiltration, reverse osmosis has been discussed as membrane-based techniques with their fluoride removal efficiencies.
- Adsorption is also a very suitable method for de-fluoridation because it is cost-effective, eco-friendly, simple and a locally available material can also be an adsorbent.
- More research work should be done to find locally available, cheaper, abundant and efficient adsorbent media.
- Adsorbents such as hydrated cement, Aluminium impregnated carbon, mixed rare earth oxides, Activated alumina, Cement paste, Titanium rich bauxite, Alum sludge, Brick Powder & Broken concrete cubes with their fluoride removal efficiency have been reviewed.
- More focus should be given to the use of waste materials as adsorbents such as Alum sludge and red mud so that they can be used as a low-cost adsorbent.
- All the above techniques remove fluoride under specific conditions. Removal efficiency can vary depending upon the geographical, chemical and economic conditions.
- Every technique should be tested with the water to be treated before applying it in the field because one technique which is fit for the one place may not be fit for the other place.

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