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on

STATUS, IMPACTS, SOURCES AND REMEDIES OF FLOURIDE CONTAMINATION IN FRESHWATER

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CERTIFICATE

This is to certify that **Mr. VIKAS SAINI, M.Sc. (Environmental Science, 2nd Year; Registration No: - 12GNY983)** of the **Guru Nanak Khalsa College, Yamuna Nagar, Haryana,** has undergone Summer Training under my guidance and supervision from June 30 to August 30, 2016 and submitted his training report on **"STATUS, IMPACTS, SOURCES AND REMEDIES OF FLOURIDE CONTAMINATION IN FRESHWATER"**.

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Vikas Saini

(VIKAS SAINI)

CONTENTS

1. ADVERSE IMPACTS OF FLOURIDE CONTAMINATION

Fluoride is a naturally occurring element, abundant in the Earth's crust. It is not essential for growth and development of humans or other organisms. Most fluorine occurs as insoluble fluorides, but there is some ionised fluoride in soil and groundwater.

Fluorides are organic and inorganic compounds containing the fluorine element. Only inorganic fluorides are the focus of this study, particularly those which are most present in the environment and may affect living organisms.

Generally colourless, the different fluoride compounds are more or less soluble in water and can take the form of a solid, liquid, or gas. Fluorides are important industrial chemicals with a number of uses but the largest uses are for aluminium production, drinking water fluoridation, and the manufacture of fluoridated dental preparations.

There are large differences in the amount of fluoride found naturally in water supplies. Observation of large populations suggested that people drinking water high in fluoride have better dental health, and less tooth decay, than those consuming less fluoride as they drink. As a result, some countries have added fluoride to drinking water as a public health measure. This remains controversial. Some suggest that it is unnecessary, because most people receive enough fluoride from other sources. These now include fluoridated toothpastes and mouthwashes, which are widely used. In addition, there have been suggestions that adding fluoride to drinking water can produce adverse health effects, and that the environmental risks of the most common fluoridating agents have not been fully assessed.

Concentration of fluoride in groundwater in the EU is generally low, but there can be large variation in the levels in natural drinking water between and within countries. In Ireland, for example, levels vary between 0.01 parts per million (ppm), or mg/L and 5.8 ppm, in Finland between 0.1 and 3.0 mg/L and in Germany between 0.1 and 1.1 mg/L.

In Europe, Ireland and some regions in Spain and the UK currently add fluoride to drinking water, at levels ranging from 0.2 to 1.2 mg/L.

People's exposure to fluoride varies a lot, depending on levels in water, what toothpaste they use, and other factors like use of mineral water and some kinds of tea. The existing collection of risk assessments suggests that there is quite a narrow gap between the fluoride intake recommended to safeguard teeth and the maximum recommended exposure.

In Europe, exposure assessments have been made by the European Food Safety Authority (EFSA). The Authority has set upper tolerable intake levels related to levels in natural mineral waters and other common sources of fluoride. The Commission Scientific Committee on Consumer Products has also set levels for fluoride in dental products.

1.1 Health Effects

Various harmful effects were observed in a series of animal laboratory studies, such as effects on the formation and hardening of bones, and delayed fracture healing. Animal laboratory studies did not conclude that fluoride increases the frequency of any tumour. Fluoride does not cause mutations but it has been shown to cause damage to chromosomes at high doses in studies in cell cultures. This has not been shown in most studies on test animals fed with fluoride.

Drinking water containing fluoride has not affected reproduction or development of the foetus in most studies on test animals. Microscopic changes in reproductive organs have been seen at highdoses in some studies.

1.1.1 Has fluoride exposure caused cancer?

Epidemiological investigations on the effects of fluoride on human health have examined occupationally exposed workers employed primarily in the aluminium smelting industry andpopulations consuming fluoridated drinking-water. In a number of analytical epidemiological studies of workers occupationally exposed to fluoride, an increased incidence of lung and bladder cancer and increased mortality due to cancer of these and other sites have been observed. In general, however, there has been no consistent pattern; in some of these epidemiological studies, the increased morbidity or mortality due to cancer can be attributed to the workers' exposure to substances other than fluoride.

The relationship between the consumption of fluoridated drinking-water and morbidity or mortality due to cancer has been examined in a large number of epidemiological studies, performed in many countries. There is no consistent evidence of an association between the consumption of controlled fluoridated drinking-water and increased morbidity or mortality due to cancer.

1.1.2 Effects on teeth and bones

Fluoride has both beneficial and detrimental effects on tooth enamel. The prevalence of dental caries is inversely related to the concentration of fluoride in drinking-water. The prevalence of dental fluorosis is highly associated with the concentration of fluoride, with a positive dose-response relationship.

Cases of skeletal fluorosis associated with the consumption of drinking-water containing elevated levels of fluoride continue to be reported. A number of factors, such as nutritional status and diet, climate (related to fluid intake), concomitant exposure to other substances and the intake of fluoride from sources other than drinking-water, are believed to play a significant role in the development of this disease. Skeletal fluorosis may develop in workers occupationally exposed to elevated levels of airborne fluoride; however, only limited new information was identified.

Evidence from several ecological studies has suggested that there may be an association between the consumption of fluoridated water and hip fractures. Other studies, however, including analytical epidemiological investigations, have not supported this finding. In some cases, a protective effect of fluoride on fracture has been reported.

Two studies permit an evaluation of fracture risk across a range of fluoride intakes. In one study, the relative risks of all fractures and of hip fracture were elevated in groups drinking water with >1.45 mg fluoride/litre (total intake >6.5 mg/day); this difference reached statistical significance for the group drinking water containing >4.32 mg fluoride/litre (total intake 14 mg/day). In the other study, an increased incidence of fractures was observed in one age group of women exposed to fluoride in drinking-water in a non-dose-dependent manner.

1.1.3 Other health problems

Epidemiological studies show no evidence of an association between the consumption of fluoridated drinking-water by mothers and increased risk of spontaneous abortion or congenital malformation. Other epidemiological investigations of occupationally exposed workers have provided no reasonable evidence of genotoxic effects or systemic effects upon the respiratory, haematopoietic, hepatic or renal systems that may be directly attributable to fluoride exposure

2. STATUS OF FLOURIDE CONTAMINATION

Fluoride compounds are abundant in the earth's crust (0.06-0.09%) (Wedepohl,1974) and found in rocks, soils, salt, sea water and also present in rivers, lakes and almost all fresh ground water at varying concentrations. Fluoride in water exists in the dissociated form, i.e. the fluoride ion. The most common minerals are fluorite (CaF_2), Fluorapatite ($Ca_5F(PO_4)_3$) and Cryolite (Na_3AlF_6). Fluoride is an essential element, which is good for the teeth enamel and helps to prevent dental caries. In excessive doses, however, it will lead to a chronic fluoride poisoning (fluorosis). Fluoride contamination of groundwater is a growing problem in many parts of the world. High concentration of fluoride is reported both from hard rock (granites & gneisses) as well as alluvial aquifers.

In India more than 66 million people are at risk of developing fluorosis and high fluoride concentration in groundwater (greater than 1 mg/L) is widespread in the arid to semi-arid western states of Rajasthan and Gujarat and in the southern states of Andhra Pradesh, Karnataka and Tamil Nadu.

People living in such areas were drinking high fluoride water without realizing its presence, which caused various bone diseases. The cause of high fluoride in ground water is geogenic being a result of the dissolution of fluoride bearing minerals. Fluoride in ground water is mainly influenced by the local and regional geological setting and hydro geological condition. However, soil consisting of clay minerals, the influence of local lithology, aided by other factors like semi-arid climate of the region may be responsible for higher concentration of fluoride in the groundwater of the region. In sea area, fluoride containing chemical components of Ca, Mg, Na, Cl, SO4, bicarbonate, Bromide, Phosphate, Iron, Aluminium etc., Locally used agricultural pesticides and anthropogenic contamination of surface water due to many rivers carry on particulate matter on rainy seasons. Therefore it is very important to understand the mechanisms of mobilization of fluoride to be able to mitigate the problem as effectively as possible.

Tomas Blom and Elin Cederlund have been used hydro geochemistry of the groundwaters of Alappuzha and Palakkad districts with an aim to understand the mechanisms of mobilization of fluoride.

Physicochemical conditions like decomposition, dissociation, subsequent dissolution and agrochemicals might be responsible for leaching of fluoride in to the drinking water sources. In recent years, there has been an increased F-concentration in ground water causes adverse impact of human health.

Table 1: Indian states with area affected by fluoride contamination

SN	State	Area Affected (%)
1.	Assam	-
2.	Andhra Pradesh	50 - 100
3.	Bihar	30 - 50
4.	Delhi	< 30
5.	Gujarat	50 - 100
6.	Haryana	30 - 50
7.	Jammu & Kashmir	< 30
8.	Karnataka	30 - 50
9.	Kerala	< 30
10.	Maharasthra	30 - 50
11.	Madhya Pradesh	30 - 50
12.	Orissa	< 30
13.	Punjab	30 - 50
14.	Rajasthan	50 - 100
15.	Tamil Nadu	50 - 100
16.	Uttar Pradesh	50 - 100
17.	West Bengal	-

3. SOURCES OF FLOURIDE CONTAMINATION

In the environment, fluorides occur both naturally (e.g., rock weathering, volcanic emissions) and because of human activities (e.g., phosphate rock mining and use, aluminium manufacturing, drinking water fluoridation).

Fluorides can be present:

- in air, as gases or particulates;
- in water, mostly as fluoride ions or combined with aluminium;
- in soils, mainly combined with calcium or aluminium; and

Various sources of fluoride entering the body are drinking water, food, industrial exposure, drugs and cosmetics etc. However, drinking water is considered as the major contribution to fluoride entering the human body.

3.1 Drinking Water

The major source of fluoride in the groundwater is fluoride bearing rocks from which it get weathered and/or leached out and contaminates the water. Fluorides occur in three forms, namely, fluorospar or calcium fluoride (CaF_2), apatite or rock phosphate [$Ca_3F (PO_4)_3$ and cryolite (Na_3AlF_6). Concentration of fluorides is five times higher in granite than in basalt rock areas. Similarly, shale has a higher concentration than sandstone and limestone (Fig.1). Alkaline rocks contain the highest percentage of fluoride (1200 to 8500 mg/kg).

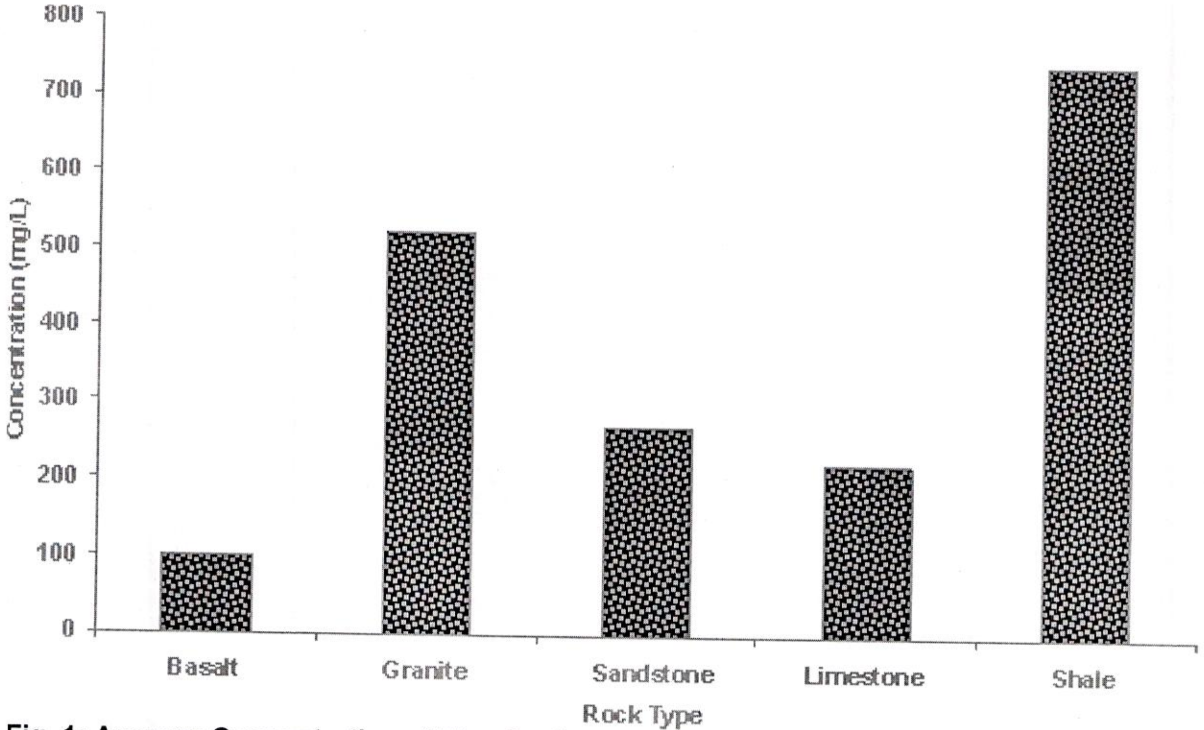

Fig. 1: Average Concentration of Fluorine in main rock types

[Source: Athavale, R.N. and Das, R.K. (1999). Down to Earth, 8(6): 24-25].

The geological survey of India has brought out considerable data which reveal that fluorite, topaz, apatite, rock phosphate, phosphatic nodules and phosphorites are widespread in India and contain high percentage of fluorides.

3.2 Food Items

Besides water, food items especially agricultural crops are heavily contaminated with fluoride as they are grown in the areas where the earth's crust is loaded with fluoride bearing rocks. The fluoride content in food material mainly depends upon:

1. fluoride level in soil
2. fluoride level in atmosphere
3. use of fertilizers and pesticides and other sources of contamination.

3.3 Industrial Exposure

Various industries involving the manufacture of phosphate fertilizers, aluminium extraction, fluorinated hydrocarbons (refrigerants, aerosol propellants etc.), fluorinated plastics (polytetrafluoroethylene etc.), petroleum refining and hydrogen fluoride manufacturing units are mainly responsible for airborne fluoride. Fluoride dust and fumes pollute the environment; inhaling dust and fumes is as dangerous as consuming fluoride containing food, water or drugs. Not only the industrial workers are affected but the people living in the vicinity of such industries may also get afflicted.

3.4 Drug and Cosmetics

The sodium fluoride containing drugs for Osteoporosis, Osteosclerosis and dental caries are in use for many years. The prolonged use of these drugs may cause fluorosis. Additionally, the toothpastes and mouth-rinses (whether labelled fluoridated or otherwise) also contain higher fluoride concentration. The fluoride content arising from raw materials used for the manufacturing of tooth-paste, namely, calcium carbonate, talc and chalk can have as high as 800-1000 mg/kg of fluoride. In the fluoridated brands of tooth-pastes, the fluoride content has been reported up to 1000-4000 mg/kg. Moreover, some of the mouth rinses are nothing but fluoridated water of a very high fluoride concentration

3.5 Human Exposure to Flourides

In drinking water, fluoride can either be naturally present due to the specific geological environment from which the water is obtained, or artificially added for the prevention of dental caries.

All foodstuffs contain at least small amounts of fluoride, but in some the concentrations can be higher. Fluoride concentration in food can be increased by the presence of fluoride in water used for its preparation.

In dental products such as toothpaste, fluoride is present in significant amounts.

The consumption of foodstuffs and drinking water is the principal route of exposure to fluoride for adults, while the ingestion of toothpaste by young children makes a significant contribution to their total intake of fluoride.

Humans retain 60 to 90% of the fluoride taken in and accumulate almost all of it in their bones and teeth.

4. ENVIRONMENTAL STANDARDS FOR FLOURIDE FOR DRINGKING WATER

Characteristic	**Requirement (Acceptable Limit)**	**Permissible Limit in the Absence of Alternate Source**	**Method of Test, Ref to**
Fluoride (as F) mg/l, *Max*	1.0	1.5	IS 3025 (Part 60)

Source: IS 10500 : 2012

5. REMEDIAL MEASURES

Nature of drinking water is a major task in advanced days because of expansion in pollution of water bodies. Fluoride is one such pollutant that undermines living life forms, specifically people. Fluoride is vital in little amount for mineralization of bone and assurance against dental caries, higher intake reasons decay of teeth enamel called fluorosis. Fluoride enters aqueous environment by weathering of fluoride rich minerals and as through anthropogenic actions, for example, industrial drains. The issue of fluoride in water bodies is serious for tropical nations, for example, such as India, Kenya, Senegal and Tanzania. The best way to bypass this issue is defluoridation. Various methods are accessible for the removal of fluoride from water, for example, precipitation-coagulation, membrane-based processes, ion-exchange and adsorption process. The precipitation-coagulation method makes vast amount of sludge and may include leaching of undesirable components; membrane procedure are lavish and fouling is an inescapable issue. Adsorption procedures have their own particular points of interest, for example, ease and minimized water disposal. In this review, a widespread list of procedures literature has been assembled. It is apparent from a literature study of around 200 latest papers that minimal effort methods have exhibited extraordinary removal capacities for fluoride.

The popular technologies for the removal of fluoride from water include: coagulation followed by precipitation, membrane processes, ion exchange and adsorption. In coagulation, trace amounts of fluoride ions tend to remain in solution due to solubility restriction. Other shortcomings include the resulting high pH of the treated water and the generation of large amount of wet bulky sludge. The Nalgonda technique, based on precipitation processes, is also a common defluoridation technique. The limitations of theprocess are: daily addition of chemicals, large amount of sludge production, and low effectiveness for water having high total dissolved solids andhardness. Further, increase in residual aluminum in the treated water has been reported. This may endanger human health as concentrations of aluminum, a neurotoxin, as low as 8.0 × 10-2 mg/l in drinking water have been associated witth Alzheimer's disease. Membrane processes, though effective in fluoride removal, demineralise water completely, besides the high initial and maintenance costs. Ion exchange methods are efficient for fluoride removal, but a tedious and difficult process of preparation of resins as well as the high cost necessitates a search for an alternative technique. Adsorption techniques have been quite popular in recent years due to their simplicity, as well as the availability of wide range of adsorbents. Research has focused on various types of inexpensive and effective adsorption media, such as different clays, solid industrial wastes like red mud, spent bleaching earths, spent catalysts and fly ash, activated alumina, carbonaceous materials, bone charcoal, natural and synthetic zeolites and other low-cost adsorbents, with various degrees of success.

Considerable work on defluoridation has been done all over the world. The most economical adsorbent for fluoride removal from drinking water is activated alumina. Literature survey on studies for fluoride removal from aqueous solutions has revealed that zeolites and cross-linked polystyrene based ion exchange resins are effective for the removal of fluoride ion from contaminated drinking water. In the last few years, layered double oxides such as Mg–Al oxides have been used. Some researchers have reported other adsorbents like fly ash, silica gel, soil, water hyacinth, bone charcoal, zeolites, bentonite, etc which controls the fluoride contamination. They also carried out pilot scale study for the treatment of fluoride using coal particles as adsorbent materials. The amount, contact time and particle size of the adsorbent influenced the treatment efficiencies of fluoride. For the removal of fluoride, Chidambaram et al used natural materials such as red soil, charcoal, brick,fly-ash and serpentine. Each material was set up in a column for a known volume and the defluoridation of these materials were studied with respect to time. According to the maximum defluoridation capacity these materials were added proportionately to the vertical column. Ten mg/l of fluoride was passed through the column and the variation of fluoride removal for a known rate of flow was studied. They found that red soil has good fluoride removal capacity followed by brick, fly-ash, serpentine and charcoal. The main factors in red oil the dominance of very fine clays, organic matter nd rich in iron aluminum oxide in composition and have good anion exchange capacity. In general, luminum compounds are found to be good fluoride removers because of the reaction between Al and F molecules. The magnesite, apophyllite, natrolite, stilbite, clinoptilolite, gibbsite, goethite, kaolinite, halloysite, bentonite, vermiculite, zeolite(s), serpentine, alkaline soil, acidic clay, kaolinitic clay, China clay, aiken soil, Fuller's earth, diatomaceous earth and Ando soil are among the numerous naturally occurring minerals which have been studied and confirmed to adsorb fluoride from water. A novel bimetallic oxide adsorbent as synthesized by the co-precipitation of Fe (II) and Ti (IV) sulphate solution using ammonia titration at room temperature for fluoride removal from water . Mg-doped nano ferrihydrite powder, Fe (III) modified montmorillonite, iron rich laterite, Awareness generation and emphasis on importance of consuming calcium, vitamin C, E and antioxidant-rich diet can be made for minimizing the adverse effects of fluoride.

To conquer the hazardous wellbeing impact of fluorosis, different approaches for defluoridations are exists like coagulation –precipitation, membrane separation processes, ion exchange, adsorption techniques and others (electro-dialysis and electrochemical). All the approaches have their advantages and limitations and worked productively under ideal condition to remove fluoride to more noteworthy range. All the above approaches are examined briefly with their advantages and limitations.

5.1 Coagulation and Precipitation Method

Lime and alum are the most usually utilized coagulants for Nalgonda technique for defluoridation of water. Expansion of lime prompts precipitation of fluoride as insoluble calcium fluoride and raises the pH value upto 11-12. As the lime leaves a leftover of 8.0 mg F/l, it is constantly connected with alum treatment to guarantee the best possible fluoride removal. As a first step, precipitation happens by lime dosing which is trailed by a second step in which alum is added to bring about coagulation. At the point when alum is added to water, basically two reactions happen. In the first reaction, alum reacts with an alkalinity's portion to deliver insoluble aluminium hydroxide [$Al(OH)_3$]. In the second reaction, alum reacts with fluoride ions in the water. Best fluoride removal is proficient at pH range of 5.5 - 7.5. Nalgonda technique created by NEERI is coagulation – precipitation method includes an expansion of aluminium salt, lime and bleaching powder took after by quick mixing, flocculation, sedimentation and filtration. Aluminum salt is utilized to remove fluoride from water. The dosage of fluoride relies on upon the concentration of fluoride proportionately. The dosage of lime is by and large 1/20th of the dose of alum. Lime serves to shape bigger and denser flocs for fast settling. Bleaching powder is included for cleansing at the rate of 3 mg/l. It is the most generally utilized defluoridation method especially at community level.

The bucket defluoridation system based Nalgonda technique has also been developed for household utilize. The process is suitable for 20 litres of water for one day utilization. The process produces water with leftover fluoride somewhere around 1 and 1.5mg/l. Fill and draw type defluoridation system based on Nalgonda technique has also been account for. Nevertheless, co-precipitation methods in view of aluminium salts have a few advantages and limitations as follows:

Advantages

- Generally utilized technique.
- Technique is more practical when contrasted with other defluoridation technique.
- Technique is easy to understand.

Limitations

- Required chemical dosages are high ($Al(OH)3$ upto 700 – 1200 mg/l).
- Sludge transfer issue.
- Cannot accomplish the passable furthest reaches of fluoride.
- Prerequisite of talented labor
- Release of aluminium in treated water which may bring about Alzheimer's syndrome.
- Final concentration of fluoride in the treated water significantly relies on upon dissolvability of precipitated fluoride, calcium and aluminium salt.
- The utilization of aluminium sulfate expands the sulfate ion concentration greatly which prompting catharatic impacts in human

Nalgonda technique, disregarding introductory Ndiaye achievement, did not take off in light of some intrinsic issues as depicted previously. A contact precipitation defluoridation technique utilizing bone char combined with sodium dihydrogen phosphate and calcium chloride has been account for.

5.2 Membrane Process

The membrane separation process is more well known from industrial viewpoints for defluoridation of groundwater wastewater treatment and sea water desalination. In a membrane separation process, particles are isolated on the premise of their molecular size and shape with the utilization of extraordinarily composed semi-permeable membrane. The semi-permeable membrane is frequently a thin, nonporous or porous polymeric film, ceramic, or metal material or even a liquid or gas. The membrane must not dissolve, disintegrate or break. The most normally utilized membrane separation processes for removal of fluoride are reverse osmosis, nano-filtration, Donnan-dialysis and electrodialysis.

5.2.1 Reverse osmosis (RO)

RO is a physical process in which the anions are removed by applying pressure on the feed water to direct it through the semi permeable membrane. RO works at higher pressure with more prominent rejection of dissolved solids. The membrane rejects the ions taking into account the size and electrical charge. RO membrane process is the reverse of natural osmosis as a consequence of applied hydraulic pressure to the high concentration side of the solution, it forces solvent filter through the membrane, against a pressure gradient into the lower-concentration solution. In RO, utilizing a mechanical pump, pressure is applied to a solution via one side of the semi-permeable membrane to overcome inalienable osmotic pressure. The process likewise removes soluble and particulate matter, incorporating salt from seawater in desalination. In the 80's, RO membrane separation technique was effectively connected for the treatment of industrial wastewater particularly for the removal and recovery of fluoride from its effluents. More than 90% of fluoride can be removed regardless of initial flucride concentration using RO membrane separation process.

Advantages

- Technique is profoundly compelling for fluoride removal.
- RO membrane was completely recovered after every arrangement of examination.
- This strategy can remove fluoride more than 90% regardless of initial concentration.
- This strategy gives the synchronous removal of other dissolved solids.
- It efforts under wide pH range.
- No obstruction by different ions
- No chemical oblige, least labor prerequisite and least operational expense.
- The process allows the treatment and purification of water in one stage.
- It guarantee steady water quality

Limitations

- Non-attainable for rural regions.
- Expensive technique.
- Remove valuable minerals which are basically required for fitting development, remineralization is required after treatment.
- Lot of water get squandered as saline solution and expendable of salt water is an issue
- The water gets to be acidic and need pH improvement.

5.2.2 Nanofiltration membrane process

Nanofiltration (NF) is the later innovation among all the membrane processes utilized for defluoridation of water. The essential contrast in the middle of NF and RO membrane separation is that NF has somewhat bigger pores than those utilized for reverse osmosis and offer less resistance to entry of both solvent and of solute. As a outcome, pressures needed are much lower, energy prerequisites are less, removal of solute is substantially less thorought, and flow are faster. Nanofiltration membrane removes essentially the larger dissolved solids when contrasted the RO making the process more prudent. Notwithstanding over, the permeability of nanofiltration membrane is higher than RO membrane, making the performance of NF in desalination better for some brackish water. In RO membrane separation 99% of salt present in water was rejected prompting the disposal of all the fluoride ions while NF membrane separation process give incomplete defluoridation of water and optimal fluoride concentration in water can be accomplished by changing the operation conditions.

Advantages

- High productivity.
- No chemicals are needed.
- It lives up to expectations under wide pH range.
- Interference because of the presence of other ion is not observed.

- This process gives an effective barrier to suspended solids, all inorganic toxin, organic micro pollutants, pesticides and microorganism.

Limitations

- Highly expensive technique when contrasted with other defluoridation techniques.
- Prone to fouling, scaling or membrane degradation.
- It removes all the ions present in water some of which are key for the ordinary development and henceforth remineralization of treated water is needed.

5.2.3 Dialysis

Dialysis separates solutes by transport of the solutes through a membrane instead of utilizing a membrane to hold the solutes while water goes through it as in reverse osmosis and nanofiltration. The membrane pores are a great deal less prohibitive than those for nanofiltration, and the solute can be driven through by either the Donnan effect or a connected electric field. Donnan dialysis is otherwise called diffusion dialysis, is similar to ion exchange membrane however unique in relation to electro- membrane process in which the driving force is not an electric current, but rather basically a distinction in chemical potential. Concentration difference is the most obvious driving force for ion transport in Donnan dialysis. A negative ion can be driven out of a feed solution through Donnan dialysis is equipped with anion exchange membrane by utilizing a second alkaline stream. The concentration difference of hydroxide ion between the two solutions compels the hydroxide ion to diffuse into feed solution. This makes an oppositely directed electrical field driving an extraction of negative ions from the feed solution.

5.2.4 Electro dialysis

Electro-dialysis is the removal of ionic components from aqueous solutions through ion exchange membranes under the driving force of an electric. Electro-dialysis is like reverse osmosis, except current, rather than pressure, to separate ionic contaminants from water. In any case, electro-dialysis is not suitable for rural because of use of electricity. Adhikary et al. have treated defluoridation of brackish water having fluoride upto 10 ppm with TDS upto 5000 ppm with an energy necessity of < 1 KWh/Kg of salt removed and brought it to reasonable firthest reaches of 600 ppm TDS and 1.5 ppm fluoride. The advantages of the electro-dialysis are given below:

- Inexpensive pre and post treatment
- Flexible (seasonal operation)
- Low chemical request
- High water recovery Restriction
- Only separation of Ionic components
- Potential formation of H2 in the electrode rinse
- Specific power consumption for Pumping
- Necessity of concentrate treatment

5.3 Ion-Exchange Process

Fluoride can be removed from water supplies with a strongly fundamental anion-exchange resin containing quaternary ammonium functional groups. The removal takes place according to the following reaction:

$$\text{Matrix-NR}_3 + Cl^- + F^- \leftrightarrow \text{Matrix-NR}_3 + F^- + Cl^-$$

The fluoride ions substitute the chloride ions of the resin. This process proceeds until every one of the sites on the resin are possessed. The resin is then backwashed with water that is supersaturated with dissolved sodium chloride salt. New chloride ions then substitute the fluoride ions promping recharge of the resin and beginning the process once more. The driving force for the substitution of chloride ions from the resin is the stronger electronegativity of the fluoride ions.

Advantages

- High productivity (90-95 % fluoride removal).
- Retains the superiority of water.

Limitations

- Technique is exceptionally costly.
- pH of treated water is low and contains high concentration of chloride.
- Interference because of the presence of other anions like sulphate, carbonate, phosphate and alkalinity.
- Regeneration of resin is an issue on the grounds that it prompts fluoride rich waste, which must dealt with before last disposal.
- It requires longer reaction period.

5.4 Electro-Coagulation (EC) Process

Electrocoagulation is a technique for applying direct current to sacrificial electrodes that are submerged in an aqueous solution. Electro-coagulation is a straightforward and efficient technique to remove the flocculating agent produced by electro-oxidation of a sacrificial anode and generally made of iron or aluminum. In this process, the treatment is performed without including any chemical coagulant or flocculants, in this way, diminishing the amount of sludge which must be disposed. Then again, electrocoagulation is in view of the in situ development of the coagulant as the sacrificial anode corrodes because of an applied current, while the concurrent advancement of hydrogen at the cathode takes into consideration contamination removal by flotation. This technique consolidates three fundamental associated processes, operating synergistically to remove pollutants: electrochemistry, coagulation and hydrodynamics. An examination of the chemical reactions happening in the electrocoagulation process demonstrates that the main reactions occurring at the electrodes (aluminum and iron electrodes) are:

$$Al \leftrightarrow Al^{3+} + 3e^-$$

$$3H_2O + 3e^- \leftrightarrow 3/2H_2 + 3OH^-$$

Moreover, Al and OH ions produced at electrode surfaces react in the bulk wastewater to form aluminum hydroxide:

$$Al^{3+} + 3OH^{-} \leftrightarrow Al(OH)$$

Also the same chemical reactions occurring in the electrocoagulation process using iron electrodes:

$$Fe(s) \leftrightarrow Fe^{3+}_{(aq)} + 3e^{-}$$
$$3H_2O + 3e^{-} \leftrightarrow 3/2\ H_{2(g)} + 3OH^{-}_{(aq)}$$
$$Fe^{3+}_{(aq)} + 3OH^{-} \leftrightarrow Fe(OH)_3$$

The aluminum and iron hydroxide flocs for the most part go about as adsorbents and/or traps for metal ions. Thusly, they would remove with them from the solution. The core purpose of this investigation was to research of the electrocoagulation process productivity for fluoride removal from aqueous environments with iron and aluminum electrodes and determination of the impacts of voltage, pH, initial concentration of fluoride and reaction time on the removal efficiency. Electrocoagulation includes electrolytic oxidation of a proper anode material. Electro-coagulation reactor is comprised of an electrolytic cell with one anode and one cathode.

Advantages

- EC obliges basic equipment, simple to handle and less support cost.
- EC treated water is consumable, colourless and odourless.
- EC produces low sludge that is promptly settable and simple to de-water since it essentially content metallic oxides or hydroxides.
- EC produces more steady and effectively separated by filtration.

Limitations

- The 'sacrificial electrodes' are dissolved into wastewater streams as an after effect of oxidation, and should be consistently supplanted.
- The utilization of electricity may be lavish in numerous spots.
- An impermeable oxide film may be framed on the cathode prompting loss of productivity of the EC unit.
- High conductivity of the wastewater suspension is needed.
- Gelatinous hydroxide may tend to solubilize now and again.

5.5 Adsorption

Adsorption is the bond of molecules species from bulk solution for a surface of of a solid by physical or chemical forces. Adsorption procedures include the water's entry through a contact bed where fluoride is removed by ion exchange or surface chemical reaction with the solid bed matrix. As contrast with different procedures of defluoridation, adsorption method is prominent because of its straightforwardness and also accessibility of extensive variety of adsorbents. Adsorption onto solid surface is straightforward, flexible and suitable procedure for treating drinking water systems, particularly for small groups. Adsorption technique is efficient and can remove ions over an extensive variety of pH to a lower leftover concentration than precipitation. A few adsorbent materials have been attempted in the past to check their possibilities and techno-economic feasibility as defluoridating specialists. Activated alumina, activated carbon, activated alumina coated silica gel, calcite, activated saw dust, activated coconut shell powder, activated fly ash, groundnut shell, coffee husk, rice husk, magnesia, serpentine, tri-calcium phosphate, bone charcoal, activated soil sorbent, defluoron-1, defluoron-2 and so on various adsorbent materials reported in literature. The most regularly utilized adsorbents are activated alumina and activated carbon. The fluoride removing efficiency of activated alumina gets influenced by hardness, pH and surface loading (the ratio of total fluoride concentration to activated alumina dosage). The adsorption procedure can remove fluoride up to 90% and the treatment is exceptionally practical. Regeneration is needed after at regular intervals of 4–5 months and viability of adsorbent for fluoride removal reduces after every regeneration cycle. Mckee and Johnston investigated the utilization of powdered activated carbon for fluoride removal and accomplished noble outcomes. The procedure is pH dependent with noble results just at pH 3.0 or less. Hence, the utilization of this material is costly because of need of pH alteration. Activated alumina method for defluoridation is being prolifereated in a few villages by the voluntary organizations funded by UNICEF or different agencies to give safe drinking water. Sarita Sansthan, Udaypur, Rajasthan is spreading the method with the viable help of UNICEF by giving a bucket (approximately 20 L capacity) fitted with a microfilter at the bottom containing 5 kg of activated alumina. The point of interest and restriction of adsorption are given below:

Advantages

- Ease of operation.
- Adsorption procedure is worthwhile
- High productivity for fluoride removal and can remove up to 90% fluoride.
- Produce high quality water.
- Regeneration is conceivable.

Limitations

- Disposal of depleted adsorbents and concentrated regenerated makes issue.
- Interference because of the vicinity of different anions may bring about competition for active sites on adsorbent.
- Drop in removal effectiveness after regeneration step.
- .Highly pH subordinate.
- High concentration of total dissolved salts (TDS) can brings about fouling of the alumina bed.

BIBLIOGRAPHY

Agrawal, V., Vaish, A. K. and Vaish, P., *Curr. Sci.*, 1997, 73, 743–746.

Alagappan Sethuraman1, Ekwal Imam, Tesfamichael, G. Yohannes, "Fluoride contamination in estuary water villages located around SIPCOT Industrial Zone, Cuddalore District, Tamil Nadu, India",J. Mater. Environ. Sci, vol 4,issue 4, pp. 520-525, 2013.

Bureau of Indian Standards, Drinking water specification (First Revision) IS 10500, 1991.

Hussain J, Hussain I, Sharma KC "Fluoride and health hazards: community perception in a fluorotic area of Central Rajasthan (India): an arid environmentEnviron Monit Assess., vol 162, pp.1-14, 2010.

Mamatha P, Rao S M"Geochemistry of fluoride rich groundwater in Kolar and Tumkur districts of Karnataka"Environ Earth Sci., vol 61,pp.131–142, 2010.

Mukherjee, S., Pal, O. P. and Pandey, A. K., *Bhu–Jal News*, 1995, 10, 1–6.

Srikanth, R., Khanam, A. and Rao, A. M. M., *Fluoride*, 1994, 27, 93–96.