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Effective Low Cost Adsorbents for Removal of Fluoride from Water: A Review

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Abstract: ***Drinking water contamination by fluoride is recognized as a major public health problem in many parts of the world. In fact, although fluoride is an essential trace element for animals and humans, excessive fluoride intake may cause adverse health effects. The present survey highlights on efficiency of different materials for the removal of fluoride from water. The most important results of extensive studies on various key factors (pH, agitation time, initial fluoride concentration, temperature, particle size, surface area, presence and nature of counter ions and solvent dose) fluctuate fluoride removal capacity of materials are reviewed. This paper investigates the potential health risks involved with both lower and higher concentrations of fluoride in drinking water, as well as posing possible measures of mitigation to eliminate such harmful threats. Also, this paper describes brief discussions on various low cost adsorbents used for the effective removal of fluoride from water.***

Keywords: Fluoride, Adsorption, Low cost Adsorbents, Contact time, Environmental Impact, pH**.**

1. Introduction

Pure water is scarce and is not easily available to all. The water may be contaminated by natural sources or by industrial effluents. One such a contaminant is fluoride. Geological formation is the main source of fluoride in the groundwater. Fluoride is a naturally occurring compound derived from fluorine, the 13th most abundant element on Earth. It is found in rocks, soil, and fresh and ocean water. Fluoride occurs naturally in public water systems as a result of runoff from weathering of fluoride-containing rocks and soils and leaching from soil into groundwater. Atmospheric deposition of fluoride-containing emissions from coal-fired power plants and other industrial sources also contributes to amounts found in water, either by direct deposition or by deposition to soil and subsequent runoff into water.

The major sources of fluoride in ground water are fluoride bearing rocks such as fluorspar, cryolite, fluorapatite and hydroxylapatite. The fluoride content in the ground water is a function of many factors such as availability and solubility of fluoride minerals, velocity of flowing water, pH, temperature, and concentration of calcium and bicarbonate ions in water [1]. The other sources of fluoride occurrence in water are industrial discharge from aluminum industries, phosphate industries, coal plants as well as due to water, food, air, medicament and cosmetics. The total inorganic fluoride emissions from various industries are given in Table 1.

Removal of fluoride from water is important because of the ill effects it causes. Exposure to fluoride in drinking water has a number of adverse effects on human health including crippling skeletal fluorosis that is a significant cause of morbidity in a number of regions of the world. Fluoride is more toxic than lead, and just like lead, even in minute doses, accumulates in and is damaging to brain/mind development of children, i.e. produces abnormal behavior in animals and reduces IQ in humans [2].

Fluoride if taken in small amount is usually beneficial, but the beneficial fluoride concentration range for human health is very small. Depending on the concentrations and the duration of fluoride intake, it could have positive effect on dental caries [3]. On the contrary, long term consumption of water containing excessive amounts of fluoride can lead to fluorosis of the teeth and bones.

Table 1: Estimated Total Inorganic Fluoride Emissions from Major Industries

Sources	*Emissions Tons/year*
Steel	40100
Ceramics	21200
Phosphate fertilizer and processing	18700
Aluminium Industries	16000
Combustion of coal	16000
Non Ferrous metal foundries	4000

The excessive intake of fluoride may cause dental [4] and skeletal disorders [5]. Fluoride ion is attracted by positively charged calcium ion in teeth and bones due to its strong electro negativity which results in dental, skeletal and no skeletal forms of fluorosis i.e. high fluoride ingestion, in children as well as adults. Fluorosis in mild version can be evidenced by mottling of teeth and in high version by embrittlement of bones and neurological damage [6], in some of the cases it may even interfere with carbohydrates, proteins, vitamins and mineral metabolism and to DNA creation as well if intake excessively [7]. Studies have shown that major of the Kidney diseases have a great inclination of toxicity of fluoride. On high doses and short term exposure fluoride can exterminate the kidney function. Several research groups have also shows that fluoride can interfere with the function of pineal gland as well as of brain. Pineal gland is one of the major fluoride accrued site in body with concentration more than that of teeth and bones. Workers exposed to high fluoride concentration areas are diagnosed with bladder cancer [8]. Various diseases such as osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, Alzheimer syndrome, and thyroid disorder can attack human body on excessive intake of fluoride. Fluoride contamination in ground water is a world-wide issue . The information regarding occurrence of fluoride in ground water in India is given in Table 2.

Table 2: Summarized Information on the Occurrence of Excessive Fluoride in Ground Water in India

State	*No. of Habitation with excess fluoride*	*State*	*No. of Habitation with excess fluoride*
Andhra Pradesh	7548	Madhya	201
Gujarat	2378	Orissa	1138
Karnataka	860	Punjab	700
Kerala	287	Rajasthan	16560
Meghalaya	33	Tamilnadu	527
Haryana	334	Uttar	1072
Himachal Pradesh	488	West Bengal	21

Excessive presence of fluoride in potable water continues to be a serious public health concern in many parts of the world, including India. Adsorption has shown considerable potential in defluoridation of wastewater. The viability of such technique is greatly dependent on the development of suitable adsorptive materials. Within last few years, the plant based bioremediation approach to improve the quality of water has become an area of intense study. Bioremediation is recognized as a cost-effective and environmental friendly option for cleanup of contaminated water [9].

According to current knowledge, a fluoride concentration of about 0.5 mg/L is beneficial in preventing dental caries during tooth development, while levels higher than 1.5 mg/L may result in fluorosis or other health problems [10]. A maximum fluoride concentration of about 4 mg/L is considered adequate for the prevention of skeletal fluorosis. A secondary maximum contaminant level of 2 mg/L is recommended to minimize the "cosmetic" risk of dental fluorosis, which can occur when fluoride is incorporated into enamel. The World Health Organization (WHO) guidelines suggest optimum levels of fluoride concentration at 1 and 1.5 mg/L for warmer and cooler climates, respectively (WHO).

Nowadays, biosorption method is very effect/attractive technique for removal of fluoride from water. This technique involves the low cost adsorbents (also called biosorbents) such as rice husk, saw dust, moringa olifera extract, red mud and goose berry etc.

2. Conventional methods for fluoride removal

Treatment of water and wastewater containing fluoride ions requires a suitable and effective method. Membrane filtration**,** precipitation, nanofiltration, ion-exchange, electro coagulation, flotation, reverse osmosis and adsorption have been used for fluoride removal. Most of these methods have high operational and maintenance cost, low fluoride removal capacities, lack of selectivity for fluoride, undesirable effects on water quality, generation of large volumes of sludge and complicated procedures involved in the treatment. Among these methods, adsorption is the most effective and widely used method because it is universal, has a low maintenance cost, and is applicable for the removal of fluoride even at low concentrations. In recent years, considerable attention has been focused on the study of fluoride removal using natural, synthetic and biomass materials such as activated alumina, fly ash, alum sludge, chitosan beads, red mud, zeolite, calcite, hydrated cement, attapulgite, and acid-treated spent bleaching earth.

Reverse osmosis is an excellent choice for the reduction of fluoride. Using a cellulose acetate/cellulose triacetate (CA/CTA) membrane, rejection rates of 80-90 percent are achievable when the pH is in the 4-8.5 range. Thin Film Composite membranes (TFC) will yield a higher rejection rate (up to 95 percent) in the 3-11 pH range. Both the CA/CTA and TFC membranes should be operated at a minimum membrane pressure differential of at least 30 psi.

Defluoridation methods can be broadly divided into three categories according to the main removal mechanism:

- Chemical additive methods
- Contact precipitation
- Adsorption/ion exchange methods

2.1 Chemical additive methods

These methods involve the addition of soluble chemicals to the water. Fluoride is removed either by precipitation, co-precipitation, or adsorption onto the formed precipitate. Chemicals include lime used alone or with magnesium or aluminum salts along with coagulant aids. Treatment with lime and magnesium makes the water unsuitable for drinking because of the high pH after treatment. The use of alum and a small amount of lime has been extensively studied for defluoridation of drinking water [11]. The most popular method for removal of fluoride from water is the Nalgonda technique [12], involves adding lime (5% of alum), bleaching powder (optional) and alum ($Al_2(SO_4)_3.18H_2O$) in sequence to the water, followed by coagulation, sedimentation and filtration. A much larger dose of alum is required for fluoride removal (150 mg/mg F-), compared with the doses used in routine water treatment.

Nalgonda technique is carried out with easily available chemicals and the method is economically attractive. The limitations of the method are varying alum doses depending on fluoride levels in water, daily addition of chemicals and stirring for 10-15 min, which many users may find difficult.

2.2 Contact Precipitation

Contact precipitation is a recently reported technique in which fluoride is removed from water through the addition of calcium and phosphate compounds. The presence of a saturated bone charcoal medium acts as a catalyst for the precipitation of fluoride either as CaF_2, and/or fluorapatite. It gives high efficiency.

2.3 Adsorption/ion-exchange method

In the adsorption method, raw water is passed through a bed containing defluoridating material. The material retains fluoride either by physical, chemical or ion exchange mechanisms. The adsorbent gets saturated after a period of operation and requires regeneration.

A wide range of materials has been carried out for fluoride uptake such as Bauxite, magnetite, kaolinite, serpentine, various types of clays and red mud are some of the naturally occurring materials were studied. The general mechanism of fluoride uptake by these materials is the exchange of metal lattice hydroxyl or other anionic groups with fluoride. Fluoride uptake capacity can be increased by certain pre-treatments like acid washing, calcinations, etc. The merits and demerits of some of the defluoridation methods are summarized in Table 3.

3. Selection of adsorbent

To select a suitable defluoridation method following criteria need to be considered:

- Fluoride removal capacity
- Simple design
- Easy availability of required materials and chemicals
- Acceptability of the method by users with respect to taste and cost

4. Low cost adsorbents

Different low cost adsorbent materials are available for effective removal of fluoride from water. The naturally available adsorbents are horse gram powder, ragi powder, multhani matti, red mud, calcined clay, concrete, pine apple peel powder, chalk powder, orange peel powder, rice husk, redmud, Moringa oleifera extract, goose berry, activated alumina coated silica gel, activated saw dust, activated coconut shell carbon, coffee husk, bone charcoal, activated soil sorbent, etc. are some of the different materials investigated for adsorptive removal of fluoride from water.

Freshly fired brick pieces are used for the removal of fluoride in domestic defluoridation units. The brick bed in the unit is layered on the top with charred coconut shells and pebbles. Water is passed through the unit in an up flow mode. It is reported that efficiency depends on the quality of the freshly burnt bricks [13]. The unit could be used for 25-40 days, when withdrawal of defluoridated water per day was around 8 liters and raw water fluoride concentration was 5 mg/l.

Activated carbon prepared from various raw materials (rice husk, wheat husk) exhibits good fluoride uptake capacity [14]. But the adsorption process is highly pH dependent and is effective at pH less than 3.0 and there is little removal at neutral pH of 7.0. A maximum of 83 percent removal could be accomplished by rice husk and attains almost an equilibrium condition in nearly 180 minutes (3 hours).

Table 3: Merits and Demerits of some Defluoridation methods

Method	*Merits*	*Demerits*	*Estimated relative cost*
Nalgonda	Low technology, adaptable at point of use & point of source level	• Large quantity of sludge • High chemical dose • Dose depend on F- level • Daily addition of chemicals and stirring in point of source units	Low – media
Bone Char	Local available media	• May impart taste and odour and result in organic leaching if not prepared properly • Requires regeneration periodically • Effected by high alkalinity • May not be acceptable in some countries	Low – media
Activated Alumina	Effective, much experience	• Periodic regeneration • Skilled personnel for plant operation • Properly trained staff for regeneration of point of use units • Suitable grades may not be indigenously available in less developed countries	Medium – High
Contact precipitation	Not much experience	• Algal growth can occur in phosphate solution • Bone char used as a catalyst may not be acceptable in many countries	High – Very high
Brick	Low cost technology	• May not be universally applicable	High – Very high
Reverse osmosis	Can remove other ions	• Skilled operation • Interference by turbidity • High cost	Very High

Marginal variation in fluoride removal by rice husk over pH range of 2 to 10. Removal of fluoride by rice husk decreased continuously as pH was increased from 2.0 to 12.0 as depicted decrease in removal of fluoride in pH range of 2.0 to 10.0 was low i.e., 12.8% whereas removal of fluoride deceased significantly from pH 10.0 to 12.0. The amount of Fluoride adsorbed increased with increase in dose and maximum 84% removal was accomplished at a dosage of 6g/L.

The use of bone charcoal or bone char (carbonized animal bone) is reported to be an effective means for the reduction of fluoride. Bone charcoal contains a carbon structure while supporting a porous hydroxyapatite matrix (a calcium phosphate hydroxide in crystalline form which is rich in surface ions which can be readily replaced by fluoride ion). Regeneration of this material can be accomplished by a two percent sodium hydroxide rinse and a backwashing cycle. Reduction of fluoride using bone charcoal is somewhat pH dependent; the challenge water should be below 6.5 pH to suppress any ion competition.

Fluoride removal was 100% in initial 4 hrs in case of the two flow rates 10ml/min and 5ml/min. Effluent Fluoride concentration dose to 1mg/l in 8.3 hours in case of the flow rate which was maintained at 10ml/min, whereas for the effluent Fluoride concentration to reach 1mg/l it took 15 hours at a flow rate of 5ml/min. Further to reach 100% exhaustion, it took 13 hours and 40 hours respectively for flow rates of 10ml/min and 5ml/min [15].

Fluoride removal by coagulation is of chemical nature due to formation of chemical complexes, between the fluoride ions and the long chained polymers present in Moringa oleifera. Removal of fluoride by MOE increased from 75% to 89% as pH was increased from 3 to 6. From pH 6 to 12 the Fluoride removal decreased from 89% to 77%. It may be observed that percentage removal of Fluoride is optimum at pH of 6.0.

A batch and column studies will be carried out for the removal of fluoride from aqueous solution using bottom ash as adsorbent [16]. The bottom ash is a waste material obtained by thermal power generation plants after combusting solid fuels. It is an undesired collected material, which is transported and dumped near the surrounding land. The equilibrium time decreases with the temperature without much increase in fluoride ion uptake. The time to reach equilibrium was slightly affected by the temperature of fluoride solution. Maximum adsorption by the bottom ash was observed at pH 6.0.

Multhani mitti is known as montmorillonite and it contains grains of fine sand particle. They contain complex multi centre crystalline structures of oxides and hydroxide of magnesium, aluminum, zinc and silicon and it is known as Fullerene mud and rich in lime.

Horse gram seed consists of higher trypsin inhibitor and heamagglutinin activities and polyphenols. These components are responsible for adsorption it is an effective adsorbent for removal of fluoride.

Red soil has a high porosity and iron oxides, and chemical reactants of fluoride which may form other useful products. The maximum adsorption of fluoride occurred over the pH range 5.0-7.0. This spread is more suitable for practical application when compared with the specific pH value of 4.7 for red mud [17]. The fluoride adsorption process took place in two stages. The first rapid stage in which 70-80% adsorption was achieved in 20 min, and a slower second stage, with equilibrium attained in 2 h. The first stage was due to the initial accumulation of fluoride at the mud surface, as the relatively large surface area was utilized. With the increasing occupation of surface binding sites, the adsorption process slowed. The second stage was due to the penetration of fluoride ions to the inner active sites of the adsorbent.

Orange peel chemical composition as well as some trace elements, ascorbic acid, carotenoids dietary fiber, total polyphenols and their antiradical efficiency, using the 2,2-diphenyl-1-picrylhidracyl (DPPH) were assessed in the dried peels of orange (Citrus sinensis), due to certain porosity of orange peel powder adsorbs fluoride from aqueous solution.

Ragi seeds are the low cost material act as a bioadsorbent and it consist of proteins, fat, and fiber. These components are responsible for fluoride adsorption from aqueous solution.

Chalk is the form of Calcium carbonate with minor amount of silt and clay As Calcium carbonate decomposes only at 900^{o}C, the adsorption taking place Chalk powder due to certain porosity adsorbs fluoride from aqueous solution. The percentage removal of fluoride using various low cost adsorbents is shown in Table 4 [18].

Table 4: Percentage Removal of fluoride with Different Adsorbents

S. No.	*Adsorbents*	*Initial Concentration of fluoride in mg/L*	*Final Concentration of fluoride in mg/L*	*% Removal*
1	Red mud	12	3.4	71
2	Pine Apple peel powder	12	1.6	86
3	Orange peel powder	12	2.5	79
4	Horse gram powder	12	3	75
5	Chalk powder	12	1.6	86
6	Ragi seed powder	12	4.2	65
7	Multhani mitti	12	5.2	56
8	Concrete	12	5.6	53

The Phyllanthus emblica sample (powdered seed), common name, Indian gooseberry material was dried at 378-383K for 24 hours. It was washed with doubly distilled water to remove the free acid and dried at the same temperature for 3 hours. Later the dried adsorbent was thermally activated in Muffle furnace at 1073K (here we avoid acid treatment for charring). The resulting product was cooled to room temperature and sieved to the desired particle sizes. Finally, the product was stored in vacuum desiccators until required. The adsorption of fluoride increases with time and gradually attains equilibrium after 75 minutes. At neutral pH, the success rate of defluoridation was observed as 82.1 percent for the 3 ppm initial fluoride concentration at the optimal adsorbent value. Also the presence of bicarbonate ions interfere the defluoridating property of this adsorbent but this interference is insignificant for other co-anions [19].

5. Conclusions

This paper provides an overview of various low cost adsorbents used for the effective removal of fluoride from water. Most of the adsorbents performance is depend on the pH and temperature. The removal capacity increases by increasing dose of the adsorbent and decreasing size of the adsorbent. The new treated adsorbents are also available and hope that it will encourage even more rapid and extensive developments for the treatment of fluoride.

References

[1] D. K. Malay and A. J. Salim, "Comparative Study of Batch Adsorption of Fluoride Using Commercial and Natural Adsorbent", Research Journal of Chemical Sciences,Vol. 1, pp. 68-75, 2011.

[2] A.S. Parlikar, S.S. Mokashi, "Defluoridation Of Water by Moringa Oleifera- A Natural Adsorbent", International Journal of Engineering Science and Innovative Technology (IJESIT) Vol. 2, pp. 245-252, 2013.
[3] Mahramanlioglu M, Kizilcikli I, Bicer IO "Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth", J Fluorine Chem, Vol. 115, pp. 41–47, 2002.
[4] Gonzales C, Hotokezaka H, Karadeniz EI, Miyazaki T, Kobayashi E, Darendeliler MA, Yoshida N "Effects of fluoride intake on orthodontic tooth movement and orthodontically induced root respiration" Am. J Ortho Dentofacial Orthop, Vol. 139, pp. 196–205, 2004.
[5] Solangi IB, Memon S, Bhanger MI "Removal of fluoride from aqueous environment by modified amberlite resin". J Hazard Mater, Vol. 171,pp. 815–819, 2009.
[6] Fan X, Parker DJ, Smith MD "Adsorption kinetics of fluoride on low cost materials", Water Res, Vol. 37, pp. 4929–4937, 2003.
[7] Zhou Y, Yu C, Shan Y "Adsorption of fluoride from aqueous solution on La^{3+} impregnated crosslinked gelatin", Sep Purif Technol, Vol. 36, pp. 89–94, 2004.
[8] Islam M, Patel RK "Thermal activation of basic oxygen furnace slag and evaluation of its fluoride removal efficiency", Chem Eng J, Vol. 169, pp. 68–77, 2011.
[9] Vaishali T and Dinesh K, "A critical study on efficiency of different materials for fluoride removal from aqueous media", Chemistry Central Journal, Vol. 7, pp. 51-65, 2013.
[10] Dean H.T., "Endemic fluorosis and its relation to dental caries", Public Health Rep., Vol. 121, pp. 213–219, 2006.
[11] Jamodei AV, Sapkal VS, Jamode VS "Defluoridation of water using inexpensive adsorbents" J Ind Inst Sci, Vol. 84, pp. 163–171, 2004.
[12] W.G. Nawlakhe, R. Paramasivam, "Defluoridation of potable water by Nalgonda technique", Current Science, Vol. 65, pp.743-748, 1993.
[13] R Singh, S P Raghuvanshi, C.P. Kaushik, "Defluoridation of Drinking Water using Brick Powder as an Adsorbent", Asian Journal of Chemistry Vol. 20, pp. 5818-5826, 2008.
[14] McKee, R.H. and Jhonston, W.S., "Removal of fluorides from drinking water", Industrial engineering Chemistry, Vol. 26, No.8, pp.849-850.
[15] C.M.Vivek Vardhan, J.Karthikeyan, "Removal of Fluoride From Water Using Low-Cost Materials", Fifteenth International Water Technology Conference, IWTC-15, pp. 1-14, 2011.
[16] S. T. Ramesh, R. Gandhimathi, P. V. Nidheesh and M. Taywade, "Batch and Column Operations for the Removal of Fluoride from Aqueous Solution Using Bottom Ash", Environmental Research, Engineering and Management, Vol. 2, PP. 12-20, 2012.
[17] R. Soni, Dr. Shikha M., "Removal Of Fluoride From Drinking Water Using Red Mud", International Journal of Scientific & Technology Research Vol. 2, PP. 120-122, 2013.
[18] N. Gandhi, D. Sirisha, K.B.C. Shekar Smita A., "Removal of Fluoride From Water and Waste Water By Using Low Cost Adsorbents", International Journal of Chem.Tech. Research, Vol.4, pp. 1646-1653, 2012.
[19] Veeraputhiran V. and Alagumuthu G., "Treatment of High Fluoride Drinking Water Using Bioadsorbent", Research Journal of Chemical Sciences, Vol. 1, PP. 49-54, 2011.

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