



A Review on Study of fluoride content in groundwater of Warora region and fluoride removal by adsorption techniques

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ABSTRACT

Fluoride is a persistent and non-biodegradable pollutant that accumulates in soil, plants, wildlife and humans. Therefore, the removal of fluoride with the best technology and optimum efficiency is required. This study highlights the efficiency of various materials for the removal of fluoride from water. The study evaluates the suitability of low-cost sheet adsorbents, moringa seeds and potter's clay for effective remediation of fluoride-contaminated water. In the present study, various low cost adsorbents are used for the removal of fluoride from water. Fluoride is an essential element for dental health and bone growth, while excess fluoride is a problem for human health. Various methods and techniques have been used by researchers over the decades to control fluoride ions. The study indicates that removal of fluoride from aqueous solution depends on pH, contact time, particle size and dose of adsorbent. Fluoride is an ion of the chemical element fluorine which belongs to the halogen group. Fluoride has a significant mitigating effect against dental caries if the concentration is approximately 1 mg/l. However, continuing consumption of higher concentrations can cause dental fluorosis and in extreme cases even skeletal fluorosis. The WHO guideline value for fluoride in drinking water is 1.5 mg/l (WMO, 2004). High fluoride concentrations are especially critical in developing countries, largely because of lack of suitable infrastructure for treatment.

Keywords- Fluoride, Adsorption, Freshwater, Groundwater, UNICEF, Warora Region

1. INTRODUCTION

Groundwater is the most important source of water to meet the requirement of consumption for drinking water, irrigation. India is the largest user of groundwater in the world. It uses an estimated 230 cubic kilometres of groundwater per year - over a quarter of the global total. More than 60% of irrigated agriculture and 85% of

drinking water supplies are dependent on groundwater. Fluorine is widely dispersed in nature. It is about 0.06 to 0.09 % of component on Earth's crust and is estimated to be the 13th most abundant element on our planet.

In Chandrapur district of eastern Maharashtra State, Central India fluoride contamination occurs mainly in Warora, Korpana and Rajura areas. In Warora area large

number of cases of dental fluorosis and skeletal fluorosis are reported. Mottled teeth, stiff joints and muscular pains are also commonly reported in the villages. Geologically the area is underlain by mixed rock types ranging in age from Archean to Cretaceous. The main rock types are Archean granitic-gneisses; Vindhyan meta-sedimentaries represented by limestones, shales and cherts; Lower Gondwana sandstones and shales; as also limestone, sandstone and shales belonging to Lameta Beds. The youngest lithounits occur in the northern part of the study area belonging to the Deccan Trap lava flows. Detailed groundwater quality studies of the Warora area carried out during and post-monsoon seasons (2012) with special emphasis on fluoride contamination are reported here to know the latter's source, intensity and extent. A total of 57 bore well and dug well samples were collected from 32 villages. 88% of the samples show fluoride concentration more than the maximum permissible limit (i.e. more than 1.5 mg/l), out of which 52% of the samples show concentrations higher than 2.0 mg/l. Fluoride concentrations of more than the permissible limit were recorded in 30 villages, whereas the highest was observed in the village Yeoti (5.3 mg/l). Groundwater samples from shales and limestones of Lameta Formation and from basaltic lava flows show the highest concentrations of fluoride. Further, presence of high concentrations of fluoride in the above mentioned shallow aquifers in the area rules out the possibility of deeper gneissic aquifers as potential source of fluoride. Physico-chemical conditions along with leaching of fluoride bearing minerals from shallower lithostratigraphic horizons like those of Lameta Beds are likely to be responsible for higher concentration of F-into the groundwater of Warora area.

Fluoride is an essential constituent for both humans and animals depending on the total amount ingested or its concentration in drinking water. The presence of fluorine in drinking water, within permissible limits of 1.0 to 1.5 mg/l, is beneficial for the production and maintenance of healthy bones and teeth, while excessive intake of fluoride causes dental or skeletal fluorosis which is a chronic disease manifested by mottling of teeth in mild cases, softening of bones and neurological damage in severe cases. Warora being the polluted city in India (Indian Express, dated:- November 2016) hence all the ecological parameter should be checked. Warora city

have a large number of coal mines, open cast mines, ferro alloy plants, thermal power station. All these leads to a lot of mining work going on. Hence it is inferred that there must be groundwater contamination. Groundwater contamination could be due seepage of various metals, ions. Fluorspar is metallic mineral found in various places in Warora which is the major source of fluoride seepage in ground water. Hence fluoride content analysis for Warora region is required to be done.

Fluoride contamination in groundwater has been recognized as one of the serious problems worldwide. Fluoride is classified as one of the contaminants of water for human consumption by the World Health Organization (WHO), in addition to arsenic and nitrate, which cause large-scale health problems. Various minerals, e.g., fluorite, biotites, topaz, and their corresponding host rocks such as granite, basalt, syenite, and shale, contain fluoride that can be released into the groundwater. Thus, groundwater is a major source of human intake of fluoride. Besides the natural geological sources for fluoride enrichment in groundwater, various industries are also contributing to fluoride pollution to a great extent. The industries which discharge wastewater containing high fluoride concentrations include glass and ceramic production, semiconductor manufacturing, electroplating, coal fired power stations, beryllium extraction plants, brick and iron works, and aluminum smelters. The effluents of these industries have higher fluoride concentrations than natural waters, ranging from ten to thousands of mg/L. The fluoride content in ground water tends to increase due to heavy withdrawal of water for agriculture purpose, poor recharging, low rainfalls and pollution from industrial effluents. India has declared fluorosis as an epidemic and has banned the use of water for drinking and cooking if the fluoride content is more than 1.5 mg/L. In this project work, we are trying to understand the techniques of removing fluoride using various adsorbent.

Scarcity of pure water is well known. The water may be polluted by natural sources or by industrial effluents. We can say healthy environment is the cost of healthy life. If the quality is sufficiently degraded, it becomes unusable and the effect is the same as a quantitative loss. The control of water quality has become overriding

consideration in providing adequate water supplies for continuous use. The World Health Organization (1996) has set a guideline value of 1.5 mg/l as the maximum permissible level of fluoride in drinking waters. However, it is important to consider climatic conditions, volume of water intake, diet and other factors in setting national standards for fluoride. As the fluoride intake determines health effects, standards are bound to be different for countries with temperate climates and for tropical countries, where significantly more water is consumed, continued global growth, health and welfare.

Rajiv Gandhi National Drinking Water Mission solves the problem of fluoride in rural areas, with great support from external agencies, particularly UNICEF. However, even with the great interest in fluoride in India, it is not easy to arrive at an accurate or reliable estimate of the number of people at risk. This is because of the difficulty of sampling groundwater from India's many millions of hand pumps. Existing sampling are selective but unstructured, taking some villages from districts and some of the many pumps in each village (UNICEF, 1999).

Adsorption and ion-exchange:

Adsorption processes involve the passage of water through a contact bed where fluoride is removed by ion exchange or surface chemical reaction with the solid bed matrix. After a period of operation, a saturated column must be refilled or regenerated. The different adsorbents used for fluoride removal include activated alumina, carbon, bone charcoal and synthetic ion exchange resins.

Objectives Of The Study:

1. Survey of groundwater samples and collection.
2. Characterization of groundwater on the basis of fluoride content.
3. Detection of fluoride and to remove excess of fluoride ion (F-) from groundwater.
4. To adopt adsorption technique for removal of fluoride from water.
5. To select proper adsorbent material.
6. To prepare adsorbent and to characterize the adsorbent by using modern techniques.
7. To study optimum dose for removal of fluoride content from water.

2. LITERATURE REVIEW

[1] Fan et al. (2003) studied fluoride adsorption on to a number of minerals such as fluorite, calcite, quartz, iron activated quartz and compared their fluoride uptake capacities. Fan et al. (2007) took advantage of the extremely sensitive analysis available for the radioisotope ^{18}F (10-13 mg) to look closely at the deposition of fluoride on calcite, hydroxyapatite and fluorite along with quartz and iron (III)- activated quartz from very dilute solution (0.025–6.34 ppb). Their experimental data suggested that among the selected materials, calcite is a surface fluoride adsorbent within that low fluoride concentration range and less effective than all the other solids except untreated quartz. The fluoride did not appear to exchange with carbonate beyond an initial surface reaction.

[2] Das et al., (2005) worked on activated titanium rich bauxite for defluoridation of water. Titanium bauxite was activated and with different dose of adsorbent it was used for defluoridation. Different parameters were tested in batch experiment.

[3] H.S.Parmar et al.,(2006) investigated adsorption of fluoride on untreated and aluminium chloride/calcium chloride treated corn cobs powder. Untreated powdered corn cobs did not show remarkable adsorption but aluminium treated corn cobs (Al- ccp) had good adsorption capacity. Effective pH range for the fluoride adsorption was found to be 5.0–6.5 and all the experiments were carried out at pH ca. 6.5. The breakthrough fluoride capacity was found to be 18.9 mg/g and 15.12 mg/g for Ca-ccp with Al-ccp, respectively, at initial fluoride concentration of 12.60 mg/L. The fluoride was found to leach out up to 25% using 0.1 M NaOH. The experimental results revealed that leaching of Ca^{2+} and Al^{3+} was negligible.

[4] Mohan et al., (2007) Non-viable algal Spirogyra IO1 was also studied for its fluoride sorption potential. The Langmuir maximum sorption capacity of fluoride was 1.272 mg/g. Fluoride sorption was dependent on the aqueous phase pH and higher fluoride uptake was exhibited at lower pH and such behavior was attributed to positively charged surface of adsorbent at lower pH which facilitated fluoride sorption, probably by the anionic exchange process.

[5] **S.V. Ramanaiah et al., (2007)** worked on biomass of *Anabaena fertilissima* and *Chlorococcum humicola*. They found maximum biosorption of Ca^{2+} at 50 mg Ca^{2+}/L with both *Anabaena fertilissima* (2.8 mg Ca^{2+}/g dry wt.) and *Chlorococcum humicola* (4.4 mg/g). Adsorptive studies were also carried out using waste fungal biomass (*Pleurotus ostreatus* 1804) derived from laccase fermentation process for defluoridation from aqueous solution.

[6] **Sathish et al., (2007)** impregnated zirconium on coconut shell carbon (ZICSC) and used for fluoride removal from water by. The fluoride adsorption by ZICSC was above 90% for the entire pH range of 2–9. The Langmuir maximum capacity of ZICSC for fluoride was 7.51 mg/g at pH 6.0.

[7] **Pandey et al., (2012)** studied the biomass of the natural plant *Tinospora cordifolia* which showed good capacity of fluoride biosorption, highlighting its potential for the drinking water treatment process. pH had a strong effect on biosorption capacity and the optimum pH was found to be 7. The biosorption was rapid and equilibrium was achieved within 120 min. The uptake capacity of fluoride was found to be 25 mg/g. The results indicate that Langmuir and Freundlich sorption models were good agreement with the experimental results. This biosorptive material is very useful to reduce fluoride within standard WHO permissible limit (1.5 mg/L) at neutral pH. [20]

[8] **Davila-Rodriguez et al., (2012)** reported a detailed fluoride adsorption study in packed columns with chitin and chitin-based biocomposite. An empty bed contact time (EBCT) of 20 min was determined as adequate. The initial fluoride concentration of the artificially prepared influent was 5.1 mg/L. About 200 and 300 bed volumes of contaminated water were treated before saturation of packed columns with biocomposite or chitin, respectively. Fluoride was desorbed from the fluoride exhausted chitin and biocomposite by using a NaOH solution as eluent: the regeneration efficiencies were 85% and 84% for chitin and biocomposite, respectively.

[9] **Regassa et al. (2016)** carried out batch mode study for fluoride removal from ground water and aqueous solution samples by natural coal. pH is 2 for optimal removal efficiency of fluoride when coal is physically and chemically activated and pH is 4 for natural coal. Maximum adsorption capacity of fluoride is 5.9, 8.36 and 11.35 mg/g for natural, physical and chemical activated

coal in their order written from Langmuir model. The adsorbents from fluoride contaminated groundwater indicated that natural coal (NC), physically activated coal (PAC) and chemically activated coal (CAC) can be utilized as a powerful, ease adsorbent to removal of fluoride from groundwater.

[10] **Ayoob et al. (2016)** used Nalgonda technique for defluoridation. The dose of lime taken was 1/20th part of filter alum. 3mg/l bleaching powder was added to the raw water to ensure disinfection. It is a “fill and draw type” defluoridation technique is designed for community application, in India, 20-40 million gallon have been used for fluoride endemic areas.

3. PROPOSED METHODOLOGY

(1) Collection and Preparation of Adsorbents:

Tulsi leaves

Tulsi leaves will be plucked from the plant. Washed with the tap water and dried at room temperature without exposure to sun. Grinded in the mixer and sieved from a 600 micron stainless steel sieve.

Moringa Seeds

Moringa oleifera (Drumsticks) will be washed with tap water, peeled off to take out the seeds. The seeds dried at room temperature without exposure to sun. Grinded in the mixer and sieved from a 600 micron stainless steel sieve.

Tea Leaves

Used tea leave will be collected. Dried at room temperature without exposure to sun. Grinded in the mixer and sieved from a 600 micron stainless steel sieve.

Pottery Clay

Pottery clay will be collected from a local pottery maker. All the lumps removed from the sample and manually tamped for uniformity of clay. Dried in the sunlight.

Instruments To Be Use In Testing:

Fluoride Testing Kit

FluoridetestingKitbyRakiroBiotechSysPvt.Ltd.Having anaccuracyofupto0.1mg/litwill use in theproject.

Direction for using the test kit is given on the kit itself.

The direction given on the test kit will be as follows.

- Take 10 ml of filtered water sample in the test jar, provided.
- Add 1 drops of FD1. Mix well. If a yellow colour does not appear, then add FD2a drop wise till you get yellow

colour.

- Now add FD2b till the solution become colourless.

Add 5 drops more of FD2b.

- Add 1 spoonful of FD3, mix well to dissolve.
- Now drop wise add FD4L, counting the number of drops while mixing until the colour changes from yellow to the distinct pink colour.
- Observe this colour change against a white background held below the test jar.
- If the expected fluoride of the test sample is more than 2 ppm, then use FD6 instead of FD4L.

Calculations:

$$\text{Fluoride as ppm} = 0.1 * (\text{No. of drops of FD4L}) \\ = 1.0 * (\text{No. of drops of FD 6})$$

For these experiments 100 ml of a solution containing Cu(II), Zn(II), and Pb(II) at 1ppm to 20ppm concentrations will be added with the adsorbent and stirred continuously at 250 rpm speed in a electromagnetic stirrer. for 24 hours at 40 degree constant temperature. Then the sample is allowed for settlement till clear water is seen on the surface, the sample will filtered and final concentration of metals will be measure from the analysis using a Perkin-Elmer Model Analyst 200 atomic adsorption spectrometer. The experimental parameters affecting the bioaccumulation of Cu (II), Zn and Pb (II) species will examined. The effect of pH on the ability of rice husks to adsorb metal ions will be investigated. For this purpose, the pH values of the Cu (II), Zn and Pb (II) solution are varied from 2 to 6. In order to evaluate the treatment efficiency for other metals, after establishing the optimal conditions for Cu, Zn and Pb(II) laboratory effluent treatment. Thus, the initial and final concentrations of these metals will be determined, and the results shall be recorded.

4. CONCLUSION

- To provide a adsorbent which locally available as well as cheap in nature. Hence various adsorbents will be tested to get best results.
- Verify that low cost bio-adsorbents can be effectively used for removal of fluoride from water.
- To study Moringa Seeds (drum sticks), Tulsi, Tea leaves, Pottery have good fluoride removal capabilities and discuss the comparative results .

- Will get data on various adsorbents that will be tested, and verify whether adsorbents effectiveness depends on surface area or not.
- Will get the optimum dose for various adsorbent for best results of fluoride removal.

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Conflict of interest statement

Authors declare that they do not have any conflict of interest.

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