

# REMOVAL OF FLUORIDE FROM GROUNDWATER USING LOW COST NATURAL ADSORBENTS: A REVIEW

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**Abstract-**Weathering of rocks, wastes from industrial establishments and geochemical responses the fluoride relates with the ground water. Many techniques such as precipitation, adsorption, ion-exchange, membrane process help in defluoridation of water. Among all of above fluoride removal strategies, adsorption technique is most appropriate for drinking water treatment. Some adsorbents such as activated carbon and alumina, agricultural and industrial wastes etc. have been used to maintain permissible range of fluoride in water by adsorption method. Use of plant related materials and agricultural wastes as adsorbents are commonly involved in adsorption technique since these materials are easily available with biodegradable nature and also they are inexpensive materials. The main idea behind this review paper is to give new views regarding the defluoridation in aqueous solutions by adsorption method using natural adsorbents which was analyzed by several researchers. In this review paper, the efficiency of different natural adsorbents has been reviewed and their effect of pH, initial fluoride concentration, temperature, contact time has been studied on fluoride sorption. It is obvious from the review that the various adsorbents have confirmed excellent ability of defluoridation. Treatment technology which have been used are solely based upon the social, economic and financial aspects of the procedure.

**Key words:** Defluoridation, adsorption, adsorbent, Langmuir, Freundlich, Isotherms

## 1. INTRODUCTION

Water is very important and important requirement in day to day life. In many portions of the world, fluoride contaminated drinking water is supposed as an important public health subject. Presence of fluoride in groundwater is very harmful which indicates a probable hazard to human health. Dependent on the measure of fluoride consumed or its presence in drinking water, it is considered as an important constituent for both humans and animals. According to World Health Organization (WHO) and IS: 10500, the safe and permissible limit of fluoride in drinking water should be between 1.0 to 1.5 ppm. Fluoride has double effect, both good and bad. Fluoride concentration between of 0.5-1.0 mg/l, is helpful for the creation and upkeep of teeth and healthy bones, but the fluoride content greater than 1.5 ppm causes dental and skeletal fluorosis. Fluoride in abundance causes comfort problems to the regular habitat. Thus awareness on fluoride removal, using finest possible technique with maximum efficiency is required to be studied. Among different systems practiced in water defluoridation, adsorption strategy possesses a noticeable commercial in fluoride removal, as this technique simple and adoptable locally. Use of plant originated materials and agricultural waste products as adsorbents are highly embraced that those materials are accessible in abundance, ease materials, biodegradable and regular in presence. As cost is important consideration, investigators explored the likelihood of using unlike inexpensive adsorbents that are abundant, promptly available and are found from waste constituents. This review paper summarizes that different adsorbents and their adsorption limits which have large capability for the fluoride removal from natural groundwater conditions and furthermore assesses the rationality of low cost natural adsorbents to effectively remove fluoride from drinking water. The potential for removal of fluoride from water using natural adsorbents is very vast and is reviewed in the present paper.

## 2. DEFLUORIDATION METHODS

Many orthodox defluoridation techniques have been designed in the past to remove fluoride from the groundwater. The major techniques which have been commonly used are Adsorption, Precipitation/Coagulation, Ion exchange and membrane process. Adsorption technique includes sorption of fluoride ions on the surface of any active adsorption materials. The fluoride ions are retained on the material surface through physical, chemical or ion exchange mechanism. Some commonly used adsorbents which have been widely used are the following Activated Alumina, Bone char, Calcined clay and natural adsorbents like tamarind seeds, tulsi leaves, coconut shell etc. Ion exchange method includes exchange of fluoride ions with other non-harmful

ions by use of ion exchangers. In the precipitation (coagulation) technique some materials like aluminium salts are used to precipitate fluoride ions from the water. In the membrane process, the water is passed through a semi permeable membrane to remove fluoride ions. A semi permeable membrane is used to remove fluoride ions from the water. Osmotic pressure is applied for the effective removal. In India especially rural areas, Nalgonda technique is used to defluoridate the water. In this technique, Aluminium salt, lime and bleaching powder is added to the water followed by the rapid mixing, flocculation, sedimentation, filtration and disinfection. Aluminium salts is used in the form of aluminium sulphate (alum) or aluminium chloride.

### 3. DEFLUORIDATION USING INEXPENSIVE NATURAL ADSORBENTS: REVIEW

**Jain et al. (2013)** studied the defluoridation of water utilizing bio adsorbents. The author investigated the effectiveness of several treated natural adsorbents, for example, Neem leaf powder (NL), guava leaf powder (GL), black berry seed powder (BB), Neem bark powder (NB), rice husk (RH). The analysis has followed batch process adsorption mechanism. The adsorption kinetics followed the first order rate system for RH, GL and NB however BB and NL followed second order rate mechanism. All adsorbents followed Freundlich and Langmuir models isotherms. The adsorbents used were effective, inexpensive for removing fluoride from water and removal high fluoride limit. These alternative adsorbents were found to offer good and useful media for efficient fluoride removal from water and also mixed adsorbents gave good outcomes when compared to single adsorbents when used. [1]

**Sharad Sharma et al. (2014)** also measured the defluoridation from water utilizing bio adsorbents. The author stated that the finely crushed dry neem leaves, crushed pimple leaves, dry ground-nutshells in powdered form, rice husk and wheat husk as adsorbent for fluoride removal [2]

**Ravi Kumar et al. (2014)** studied the fluoride removal in aqueous system utilizing moringa olifera seeds. Coagulation with aqueous distillate of moringa olifera seed cake powder reduced the fluoride concentration of fluoride in water below 1mg/l but the turbidity after the reaction became quite high which was removed to permissible limit using the double filtration technique.. When the compound coagulants prepared by including alum and starch with moringa olifera used for coagulation of fluoridated water, the fluoride content reduced below 1mg/l and the turbidity was also below the acceptable limit. So it was found that compound adsorbents removed fluoride without increasing the turbidity. [3]

**Sudhanshu Kannaujia et al. (2015)** measured the defluoridation in groundwater through carbonized punica granatum carbon CPGC. The author supposed that CPGC has good properties for the adsorption of fluoride ions from aqueous solutions. The contact time for fluoride removal was found to be 75 min. The particle size was a main constraint which affected the sorption for fluoride on CPGC as the adsorption of fluoride particles increases as the particle size decreases. The author stated that CPGC can be used as an adsorbent for removal from groundwater where fluoride related issues exist [4]

**Mekala suneetha et al. (2015)** inspected the removal of fluoride from polluted water using active carbon got from barks of vitex negundo plant. Nitric acid activated carbon acquired from the vitex negundo plant barks was perceived as an effective adsorbent. The adsorption procedure is totally fitted in Langmuir adsorption isotherm with great correlation coefficient value and furthermore shows monolayer adsorption. The adsorption kinetics followed pseudo-second- order kinetics equation. The methodology was greatly successful in the defluoridation technique. [5]

**Gandhi et al. (2012)** researched the fluoride removal using chalk powder, ragi seed powder, horse gram seed powder, pine apple peel powder, orange peel powder, red soil, multhani matti. The adsorption limit is more at lower concentrations as compared to higher concentration. Decreasing order of fluoride removal is chalk powder, pine apple strip powder, orange strip powder, horse gram seed powder, red soil, ragi seed powder and multhani matti. [6]

**P.S. Harikumar et al. (2012)** studied the potential of vetiver root for defluoridation in the activated form. The experimental data obtained from the vetiver root was very rightly fitted into the Freundlich and Langmuir isotherms. The activated vetiver root is easily available and is found in the Kerala district of India which is rich in the biodiversity. Effect of important controlling factors was studied on the fluoride sorption [7]

**S.Chidambaram et al. (2013)** studied the fluoride removal using natural soil. The red soil was placed as column and water was passed from the above and the sand was also added to improve the porosity of the red soil. The effect of controlling

factors was studied and graphs were plotted between different parameters and the fluoride removal efficiency. It was found that natural soil was effective in the removal of fluoride from the groundwater to a large extent. [8]

**Fufa et al. (2013)** investigated the defluoridation of groundwater using termite mound containing aluminium, iron, silicon and titanium oxides. The adsorption followed the pseudo second order equation. The studies also showed that fluoride loaded termite mound can be regenerated without significant loss of metals. Termite mound was also easily available and cheap which offered significant cost related advantages. [9]

**Aash Mohammad et al. (2014)** investigated defluoridation of synthetic water by using banana peel, groundnut shell and lemon peel. The sweet lemon peel, banana peel and groundnut shell nullified 94.34 % of the fluoride from the synthetic water. [10]

**Bhaumik et al. (2012)** inspected the eggshell powder for the fluoride removal from the groundwater. The highest adsorption occurred between pH 2.0 to 6.0. The data best fitted in the Langmuir isotherm model, displaying monolayer sorption on the homogenous surface. The Thermodynamic data also showed that the process of the sorption was exothermic with the release of the heat energy [11]

**Gourouza et al. (2014)** investigated the defluoridation of the water using charred beef shoulder blade bones. The conclusion of adsorption shows that the beef calcined bone is a precursor material, suitable for the defluoridation of aqueous solutions. It was revealed that the mass of fluoride adsorbed on the adsorbent depends on the adsorbent dose, the initial fluoride concentration and the contact time. [12]

**Chakrabarty et al. (2012)** inspected defluoridation of contaminated drinking water utilizing neem charcoal adsorbent. This adsorbent is known as an effective adsorbent for the defluoridation of groundwater sources. The biosorbent was effective in the fluoride removal of 10mg/l fluoride initial concentration from aqueous solution with efficiency of 94%. The equilibrium was achieved in 180 minutes. The author perceived that the adsorption efficiency depends on pH with maximum adsorption achieved at pH of 5.0. [13]

**Kumari et al. (2015)** examined defluoridation using shorea robusta. Sal leaf powder demonstrated to be a very effective adsorbent for defluoridation at optimal pH of 7.5. The fluoride particles have a tendency to adsorb on the surface of sal leaf powder. The conclusion recommends that the pore diffusion is to be considered as important factor in the study. The uptake of leaf powder adsorbent of 0.3mm and 1mm increased from 0.0192 mg/g to 0.154mg/g and 0.0134mg/g to 0.124mg/g independently with the increase in original concentration of 1.8 mg/l to 5mg/l. SEM combined with EDX characterizations of biosorbents displays the sign for internal circle messes and gives a clear picture of progress in morphology when fluoride treatment that confirms adsorption of fluoride on the sal leaf powder [14]

**Mamilwar et al. (2012)** inspected the removal of fluoride from groundwater using babool bark. Inspection on the effects of different parameters such as dose, contact time, pH, temperature etc. was done. The result showed that the babool bark powder in concentration of 5g/l removed 77.04 % of fluoride from 5 mg/l of concentration at pH of 8.0 and contact time of 8 hours. The pseudo-second-order and pseudo first order model fitted well with the experimental data. [15]

**Renu singh et al. (2008)** examined the fluoride removal in drinkable water using brick powder as an adsorbent. The effect of adsorbent dosage on fluoride sorption was observed at pH of 8 for 60 min. The fluoride removal was found to accelerate from 43.1% to 56.7 % for 0.21 to 2.01g/100 ml dosage [16]

**Ranjeeta Soni et al. (2013)** observed the removal of fluoride water using red mud. According to the result, the author came to the conclusion that the red mud can remove about 1.15 mg/l of fluoride from the water. The water quality is also not affected as it is a natural adsorbent. The taste and quality of the treated water always remained same. [17]

**Sivasankar et al. (2010)** discovered fluoride removal using enacted and MnO<sub>2</sub>-shielded tamarind shell. In the batch method, the elements of fluoride sorption, as for pH, [F]<sub>0</sub> and sorbent portion was contemplated. The suitability of pseudo-first order for ATFS and Ritchie-second order for MTFS was acknowledged. The kinetics data fitted well with Temkin isotherm for ATFS and Langmuir isotherm for MTFS. The collaboration of co-particles in the defluoridation limit of the adsorbent was studied. Column experiments were finished at a constant fluoride concentration of 2 mg/flow rate at other depths of the bed. [18]

**Bina Rani et al. (2012)** examined the defluoridation of water utilizing brick powder as an adsorbent. Adsorbent efficiency of brick powder was observed for the fluoride removal from potable water samples of different concentrations. The author inferred that the adsorption of fluoride on brick powder adsorbent from aqueous solution was considered as first order reaction and the mechanism of the removal of fluoride on adsorbent was found to be complex. Presence of other ions in groundwater didn't influence the defluoridation procedure, in this way, showing that the brick powder is an appropriate and economical adsorbent for fluoride. [19]

**Telkapalliwar et al. (2016)** envisioned the fluoride removal from aqueous solution by utilizing inexpensive bark and wood based bio-adsorbents. The fluoride removal has been comprehensively separated into two segments managing the removal of fluoride by bark based and wood based bio adsorbents. The most significant after effects of broad examinations on different factors, for example, pH, contact time, temperature and initial fluoride concentration changes the fluoride removal effectiveness of adsorbents alongside the different isotherm models and kinetic models likewise reviewed. [20]

**Bhagawati et al. (2012)** examined the fluoride removal utilizing the activated carbon prepared from almond shell. Defluoridation utilizing activated carbon preparation from almond shell with KOH activation in packed bed down flow column was investigated. The impact of different operating parameters, for example, bed height, pH, flow rate, temperature and adsorption limit were investigated. The author focused on chemical characteristics of almond shell, SEM images, and surface area analysis. The fluoride removal from synthetic sample was 63% and 68% respectively for CGAC and AGAC for initial fluoride ion concentration of 2mg/l. The adsorption equilibrium was very much related by BET isotherm model. [21]

#### 4. PROPOSED RESEARCH AREA

The use of bagasse powder obtained from the sugarcane can be effectively used for the defluoridation of groundwater. Bagasse is used as an adsorbent which adsorbs fluoride ions from the water. Bagasse powder is added to the water for suitable contact time and fluoride concentration is determined finally and reduction of fluoride concentration in the water is determined. In addition, the effect of different parameters such as adsorbent dose, temperature, contact time and pH on the fluoride removal efficiency is determined. The optimum conditions of fluoride removal is calculated. The mechanism of fluoride removal is studied and the adsorption data is fitted into Langmuir and Freundlich isotherms and the coefficient of correlation is found out. Kinetics of the mechanism is observed and studied thoroughly.

The advantage of bagasse for the removal of fluoride includes its easy availability and cheap availability. Bagasse can be easily obtained from the sugar mill in the form of powder directly or it can be obtained from juice shops locally and crushed into the powder form. The bagasse powder after that is treated with 0.1N HCL and 0.1N NaOH to impart neutral nature to the powder. Also powder is kept in desiccator to remove the moisture prior to its use as adsorbent. The study aims to find the suitability and feasibility of bagasse powder as defluoridating agent to be used at local or wide level.

#### 5. CONCLUSIONS

Based on the past studies of the fluoride removal using natural and inexpensive adsorbents, it can be inferred that the orthodox procedures of fluoride removal from the water can be replaced with the natural and inexpensive adsorbents which are easily available. The old techniques used for fluoride removal such as Nalgonda technique, Activated Alumina etc. had certain disadvantages such as requirement of salts and reagents for the defluoridation process. Hence adsorbents prepared from naturally available materials and wastes can be utilized for defluoridation. Some commonly used adsorbents which have been utilized are Rice husk powder, Neem powder, Tulsi powder, Eggshell powder, Activated carbon etc. The studies suggested that these adsorbents are no less effective in defluoridation technique as compared to old orthodox processes.

The future perspectives include research about other natural adsorbents which can remove fluoride from water. Some adsorbents which can be investigated include Bagasse powder obtained from sugarcane husk, Pineapple peel powder, Wheat husk powder, Sand etc. Before reaching to any conclusion, the effect of pH, contact time, Adsorbent dosage, Temperature, Initial fluoride concentration etc. on the fluoride sorption needs to be studied very thoroughly. Sometimes it has been also found from the past studies that mixture of different adsorbents has improved the removal efficiency as compared to removal efficiency when adsorbents was used singly.

So, it can be concluded that further study needs to be evaluated in identifying the different adsorbents which can remove fluoride from the groundwater and also their suitability in the rural areas and cost effective measures to remove extra expenses which have been commonly encountered in defluoridation technique. Many adsorbents and waste products still are in dark, which need to be discovered in the defluoridation strategy.

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