

# A Review on Defluoridation of Water through Natural Adsorbents

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**Abstract:** Fluoride is often described as a 'double-edged sword' as an adequate ingestion is associated with dental caries, where an excessive intake leads to dental, skeletal and soft tissue fluorosis. Defluoridation of water done by natural adsorbents such as Drumstick seeds (*Moringa Oleifera*), Roots of vetiver grass, Tamarind seeds, coconut shell carbon, rice husk carbon and algae like *Ulva fasciata* species. Algae traditionally used as food supplement and are generally safe. Tamarind seed is a household material and is left as waste after removing tamarind pulp, this material is familiar with all kinds of people. It is a simple viable defluoridation adsorbent that could be adopted easily by villagers. Tamarind seed sample in the free and fluoride loaded conditions were characterized by SEM (Scanning Electron Microscope) and FTIR (Fourier-Transform Infrared spectroscopy). Roots of Vetiver grass are another product have traditionally used for water purification. The roots were effective and could remove as much as 70% of fluoride from a sample. Drumstick seeds (*Moringa Oleifera*) act as a coagulant. They have been traditionally used for purification of turbid water. They have remarkable defluoridation efficiency, which was higher than that of activated Alumina. Natural adsorbents are easily available and are economic, which makes defluoridation process affordable, thus people can attain a good oral hygiene at affordable cost.

**Keywords:** Adsorbents, Affordable, Defluoridation, Tamarind seed

## 1. Introduction

Fluoride is a highly volatile element which is found in earth crust in different forms of compounds. Fluoride is acquired by humans worldwide mainly through two sources one is ground water and other through dietary sources. It has been reported that in India, China, Sri Lanka, Holland, Italy, Mexico, West Indies, Spain, North and South America there is a high level of fluoride in ground water. Ground water is the prime source and meets the needs of 60% of Indian households. So the quality of ground water can be potentially affected over 100 million households, rich and poor, urban dwellers and villagers alike. (susheela 1999)<sup>1</sup>

According to World Health Organisation (WHO) maximum acceptable fluoride concentration in drinking water is 1.5 mg/L. However according to Indian standard 1996, drinking water is considered to be safe for human consumption, if the concentration does not exceed 1.0mg/L.<sup>2</sup> Excessive fluoride consumption causes many health hazards. For example dental fluorosis at initial stage (WHO 1970, 1974).<sup>3,4</sup> Chronic intake of excessive fluoride ion causes severe damage. Bone stiffness, rheumatism and stimulating permanent crippling known as skeletal fluorosis (Waldcott 1973) and kidney damage (Odnal 1973).<sup>5,6</sup> Considering the fact that fluorosis is an irreversible disease which has no cure. The generation can only be protected from the disease through prevention.

Prevention can be achieved by following methods<sup>7</sup>

- Removal of fluoride from water (defluoridation) by using suitable techniques.
- Locating alternative sources of safe water.
- Bringing in water from distant, safe sources.
- Prevention of industrial fluorosis done by rigorous enforcement of procedures to minimize industrial fluoride pollution.

For water treatment, coagulants are used which may be chemical or naturally occurring, some studies on natural coagulants have been carried out and various natural coagulants were produced or extracted from animals, plants and microorganisms. Biosorbents are alternative biomasses that can be effectively utilized. As they offer low operating cost and minimization of the volume of chemical and/or biological sludge to be disposed<sup>8</sup>. Alternatives of chemical coagulants are Tamarind seed, *Moringa Oleifera*, *Tinospora Cordifolia*, coconut shell charcoal, Rice Husk Charcoal, *Ulva Fasciata* and others.

## 2. Biosorbents used in Defluoridation of Water

**Tamarind Seed:** Tamarind fruit tree is usually found in all regions of India and used as a household product. To produce the adsorbent powder, Tamarind seed soaked in water for one hour to remove the adhering pulp, then washed with tap water and then with distilled water, dried in an air oven at 110°C for an hour, micronized in a flour mill and sieved to get particle size 75, 150 & 300 meshes ASTM (American Standard Test Sieve Series). The adsorbent was now used for defluoridation of standard fluoride solution sample. Defluoridation of water is done by using an ordinary two-tier water tank with a clay filter for water purification. The tamarind seed powder is encapsulated between the clay filter, the water in the upper tank passes through the sand filter slowly at its own rate and collected in the bottom tank. The previous studies found that the adsorption capacity of tamarind seed is 18mg/g/L which means that for treating one liter of water of fluoride concentration 1mg/L, 0.055g of Tamarind seed is required. The binding of fluoride to Tamarind Seed may be due to electrostatic attraction and hydrogen bonding.<sup>9</sup>

**Effect of pH** - There is greater possibility of coulombic interaction between fluoride ion and Tamarind seed surface at pH 7.0 as the surface is positively charged. It was found

that the sorption process attain equilibrium in less than 60 minutes. It is seen that sorption of fluoride is most appreciable in the pH range of 6.0 – 8.0 with the peak value at pH 7.0.<sup>9</sup>

**Effect Of Temperature** - When there is increase in temperature there is decrease in the percentage sorption. This may be due to weakening of adsorptive forces between tamarind seed and fluoride ion. Previous study shows that temperature is an unfavourable factor for fluoride sorption on Tamarind seed.<sup>10</sup>

**Effect of particle size & adsorbent Dose** - If there is increase in the particle size, there is decrease in the sorption level. The large size particles tend to open tiny cracks and channels on the particle surface of the sorbent and provide more sorption sites and surface area leading to greater sorption.<sup>9</sup> Amount of adsorbent significantly influences the extent of fluoride adsorption. This increase in loading capacity is due to the availability of higher number of fluoride ions per unit mass of adsorbent.<sup>11</sup>

**Moringa Oleifera**<sup>12</sup>:- It is commonly known as drumstick which was grown in all parts of India so it was easily available for peoples. Several studies have been conducted to show that *Moringa Oleifera* was used as natural adsorbent material in Defluoridation of water. *Moringa Oleifera* adsorbent powder is prepared by grinding the seed of drumstick and then further treated by adding *Moringa Oleifera* seed powder to 1N HNO<sub>3</sub> for acid treatment and 0.5N NaOH for Alkali treatment. The mixture was boiled for about 20 minutes. Washing of the powder sample was carried out by using distilled water until maximum color was removed and clear water is obtained and finally powder sample was dried again in an oven at 50°C for 6 hours

In case of acid washed adsorbents maximum removal efficiency was 39% at pH 1 whereas in case of alkali washed adsorbents maximum removal of fluoride was 51% at pH 10. Therefore at pH 8, the percentage removal of fluoride was 13% and 49.5% for acid washed and alkali washed adsorbents respectively. The contact time was varied from 0.5 to 2.5 hours for alkali treated *Moringa Oleifera* seed powder of 600 $\mu$  and 212 $\mu$  respectively. It is seen that the contact time using adsorbents with different particle size. Results show that for 212 $\mu$  alkali treated *Moringa Oleifera* biosorbent, the maximum removal efficiency of fluoride was 76% at 400mg/lit whereas maximum removal efficiency of fluoride was 40% at 50 mg/lit. Similarly for alkali treated *Moringa Oleifera* adsorbent, the maximum removal efficiency of fluoride was found to be 68% at 400 mg/lit.

**Tinospora Cordifolia**<sup>13</sup>:- The plant is locally available in rural as well as urban areas. *Tinospora Cordifolia* was collected and washed with deionized water to remove dirt and other particulate matter then cut into small pieces, sundried for 7 days then kept in a hot air oven at 60°C till dryness. It was then powdered and sieved through 1.18  $\mu$ m sieve for getting uniform size biosorbent.<sup>13</sup> Biomass dose is an important parameter owing to its effect on efficiency and amount of fluoride removed per unit weight of adsorbent. The fluoride adsorption increased with the

increase in amount of the adsorbent as higher doses of the adsorbent provided more active sites. Optimum fluoride removal efficiency was found to be 7 g/50ml of adsorbent dose. Further increase in doses does not result in the considerable increase in de-fluoridation. The pH of the aqueous solution was found an important controlling parameter in the adsorption process. This was adjusted by adding 0.5N HCL or 0.1M NaOH. The effect of pH (3-8) on the removal of fluoride for a constant biosorbent dosage of 7g/50ml and fluoride ion concentration of 5 mg/L. The percentage adsorption of fluoride ion was found to maximum at pH 7 and then it decreased with a further increase of pH. This adsorbent material is very useful to reduce fluoride within standard permissible limit of 1.5 mg/L (WHO) at neutral pH. The variation in percentage removal of fluoride with time was studied using the solution of fluoride with initial concentration of 5 mg/L, adsorbent dosage 7 g at pH 7. On increasing the contact time with adsorbent, the percentage removal of fluoride was found to increase till 120 min. Further increase in time will decrease the capacity of fluoride removal.

**Ulva Fasciata**<sup>14</sup>:- Algae are traditionally a food supplement and are generally safe. The algal *Ulva Fasciata* sp. used as biosorbent in the experiments is generally grown profusely on rocks of tidal zone of coastal belts and its availability is easy without any practical investment. *Ulva Fasciata* sp. as adsorbent is environmentally safe and practically economical. The algae collected were washed with deionized water several times to remove impurities. Then washed algae were completely dried in sunlight for 10 days. The resulting product was directly used as adsorbent. The dried algae were then cut into small pieces and were powdered using domestic mixture. The powdered materials in the range from 75- 212  $\mu$ m particle size were then directly used as adsorbent without any pretreatment. The rate of fluoride adsorption by the nonliving cells was very rapid reaching almost 90% of the maximum absorption capacity within 45 minutes of contact time. Fluoride uptake increases by increasing adsorbent dose. The increase in adsorbent dose from 0.1 to 0.5 g resulted in an increase in absorption of fluoride. This is because of fluoride due to the availability of more binding site for complexation of fluoride ion. The adsorption of fluoride on *Ulva Fasciata* sp. decrease from with the increased particle size from 200 to 72  $\mu$ m at an initial concentration of 5 mg/L.

**Rice husk charcoal**:- Rice husk is an organic waste and a major by-product of the rice milling and agro-based biomass industry. Rice husk is a cellulose-based fiber and contains approximately 20% silica in amorphous form. The ash of rice husk contains silica, which is a highly porous structure and is lightweight, with high specific surface area. According to study done by C.M. V Vardhan et al shows that as contact time increases, percent removal also increase initially and reduce gradually with time and attains almost equilibrium condition in nearly 180 minutes and remains more or less constant thereafter. A maximum of 83% removal could be accomplished by rice husk.<sup>16</sup> Under the treatment of low concentration of potassium hydroxide, both the adsorbents gave better result than high concentration of potassium hydroxide. Under the treatment of high concentration of potassium hydroxide, the adsorbents have less tendency to

adsorb the fluoride but the pH values of the resultant solution gets increased. The investigation revealed the fact that among these two adsorbents paddy husk charcoal showed the better results than coconut shell charcoal.<sup>15</sup>

**Coconut Shell Charcoal:-** Coconut plant are grown in coastal regions of Indian subcontinent and being used in different forms. The coconut shell was a huge waste product produced in coconut oil industries so it being converted to charcoal for different uses like domestic fuel, industrial fuel and also used in laundries. Some of the studies in recent years shows that coconut shell charcoal is being used for Defluoridation of water. As coconut shell in rural India from the agricultural sector, there is nil explanation in procurement of this raw material and hence we have a low cost charcoal proportion procedure. About 100g of crushed coconut shell was taken and kept for about 3hr in a muffle furnace at 300 – 400°C at which all of the material was completely carbonized. The carbonized material was cooled, powdered and kept in a beaker of 2L capacity, 200 ml of concentrated sulphuric acid was gradually added to it. The activated charcoal left overnight and washed free of acid and dried at 110 °C for 2hr then sieved as to pass through 40 mesh and retain on an 100 mesh. Stock solution of fluoride was prepared by dissolving 2.21g of sodium fluoride in 1000 ml of double glass distilled water. Then stock solution was then appropriately diluted to get the test solution of desired fluoride concentration. Sodium fluoride solution equivalent to 6.5 mg/l (4L) was percolated through carbon bed at the rate of 4L/hr by outflow control. One liter lots of the effluent were collected successively and fluoride was estimated in each of these lots by ion selective electrode method. The activated charcoal when impregnated with ZrOCl<sub>2</sub> results to be an effective defluoridating agent for treating effluents of lower fluoride concentration from 10 – 2 mg/L.<sup>17</sup>

### 3. Conclusion

According to the previous results and discussion above, the selection of a suitable adsorbent for defluoridation unit can be made at a domestic level. The experimental investigations clearly suggested that abundantly available and low cost materials like Tamarind Seed, seed extract of Moringa Oleifera, rice husk, coconut shell *Tinospora Cordifolia* and *Ulva Fasciata* are having effective defluoridating property. It was found that the adsorption capacity of tamarind seed is 18mg/g/L which means that for treating one liter of water of fluoride concentration 1mg/L, 0.055g of Tamarind seed is required. Results show that for 212µ alkali treated Moringa Oleifera biosorbent, the maximum removal efficiency of fluoride was 76% at 400mg/lit whereas maximum removal efficiency of fluoride was 40% at 50 mg/lit. Similarly for alkali treated Moringa Oleifera Biosorbent, the maximum removal efficiency of fluoride was 68% at 400 mg/lit. So it was concluded that Tamarind seed was easily available and highly effective in Defluoridation of water at domestic level.

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