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Studies on the Defluoridization Competency of a Mixture of Raw Vermiculite and *Strychnos potatorum linn.* Seeds

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ABSTRACT

The incidence of dental and skeletal fluorosis due to excessive ingestion of fluoride through drinking water is increasing alarmingly in various parts of the world. Though several defluoridization techniques having different principles of actions such as reverse osmosis, ion exchange and chemical treatments are available, none is found to be ideal due to cost effective, sludge transfer, maintenance of pH and demineralization after treatment and non-attainable for rural regions. Hence, the search for new methods to selectively remove fluoride from the drinking water sources still continues. Earlier, we have reported that treatment with raw vermiculite, a type of mica, at a mesh size of 80 significantly adsorbed the fluoride present in the water samples. Strychnos potatorum Linn., commonly known as Nirmali, is a medium-sized, glabrous tree well known for its seeds which are 10-13 mm. in diameter and approximately weigh about 1-1.5 g. In the traditional system of medicine, the nirmali seeds are used to clear the muddy water through its coagulant action. This property was attributed to the presence of anionic polyelectrolytes having -COOH and free -OH surface groups that are present in the seed protein. In order to circumvent the disadvantages such as odour and mild turbidity associated with vermiculite, in the present study we have prepared a new adsorbent mixture comprising of the raw vermiculite and S. potatorum seeds in the ratio of 70: 30 (w/w) and found that the mixture possess significant defluoridization capacity than the raw vermiculite. *The treatment with mixture significantly improves the taste, odour and turbidity.*

Keywords: Fluorosis, Defluoridization, Raw vermiculite, *Strychnos potatorum*.

INTRODUCTION

Water is an essential requirement for all the living creatures and it occupies a major part of the earth. The maintenance of good health of human being mainly depends on the quality of drinking water [1]. It has been estimated that only 0.6% of the globally available water is existing as fresh water sustainable for human consumption [2]. Unfortunately, this fresh water is increasingly contaminated by both lithogenic and anthropogenic pollutants. Among the various pollutants, the presence of fluoride in the drinking water in excess than the permissible limit is termed as fluorosis and is becoming a major contributory factor from the health point of view [3]. The incidence of fluorosis has been reported in many parts of the world especially India, China and Pakistan. Fluoride enters the aqueous environment mainly by weathering of fluoride-rich minerals and through anthropogenic activities [4]. Though the fluoride ingestion at low levels helps to reduce the solubility of apatite crystals in the bone and makes the structural system strong, excessive fluoride consumption is a detriment to bones and causes skeletal fluorosis which elicits severe pain and stiffness in joints [5]. Likewise, excessive chronic intake of fluoride, especially during tooth development, causes mild to severe dental fluorosis [6].

Fluoride exerts its toxicological effects even at the molecular level which ultimately results in increased apoptosis, impairment of glucose and protein metabolism and chronic oxidative stress [7]. Consumption of drinking water with permissible fluoride content (WHO 1.5 mg/l; BIS 1 mg/l) is the only option to prevent fluorosis and there is no established treatment for dental and skeletal fluorosis [8]. To overcome the hazardous wellbeing effects of fluorosis, several approaches for defluoridization have been proposed and their advantages and limitations were reported in detail. It is perceptible from a literature survey of more than 200 recent research articles that minimal efforts methods have exhibited extraordinary removal capacities for fluoride [9]. However, the major restrictions of the available defluoridization methods mainly include upkeep costs, the prerequisite of talented labor, issues related to sludge transfer, maintenance of pH and demineralization after treatment and non-attainable for rural regions.

The traditional system of removing fluoride from drinking water is liming and the attending precipitation of fluoride. Coagulation and precipitation method (Nalgonda technique) of defluoridization using lime and alum is suitable for 20 l of water for one-day utilization [10,11]. The membrane process involves reverse osmosis (RO), Nano-filtration (NF), Donnan- dialysis and electrodialysis is best suited for industrial waste water treatment particularly for the removal and recovery of fluoride from its effluents [12-14]. Reverse osmosis (RO) using the semi permeable membrane is capable of removing more than 90% of fluoride regardless of initial fluoride concentration [15]. Nano filtration (NF) is the later innovation of RO which essentially removes the larger dissolved solids at a relatively less pressure applied [16,17]. However, RO and NF techniques are highly expensive methods. Dialysis and electro dialysis is based on the removal of ionic components from aqueous solutions through ion-exchange membranes under the influence of an electric field [18-20]. Fluoride can be selectively eliminated from the water with the aid of costly anion exchange resins such as amberlite IRA-400, Indion FR10, Ceralite IRA-400, titanium oxohydroxide and aluminium loaded duolite C-467 [21-24].

Among the various defluoridization techniques, adsorption method is considered as more prominent because of the availability, accessibility and affordability of a variety of natural adsorbents. A few adsorbents which have been studied in the past include, activated alumina, activated charcoal, activated alumina coated with silica gel, activated saw dust, activated coconut shell powder, groundnut shell, bone charcoal and activated soil sorbent [25-28]. Earlier, we have extensively studied the defluoridization efficacy of vermiculite, a type of mica comprised of aluminium /iron/ magnesium/ silicate mixture. It is unearthed as a material composed of thin layers. We have reported that the raw vermiculite at a particle size of 80 mesh shows the maximum defluoridizing effect at acidic pH [29]. Several reports are available in the literature regarding the use of vermiculite, acidic and basic fly ashes, bauxite and xeolite for their defluoridizing efficacy [30-33].

In the recent past, several researchers have used plant materials as adsorbents for the removal of fluoride ions [34]. *Strychnos potatorum Linn*., commonly known as Nirmali, is a medium-sized, glabrous tree known for its seeds. The seeds are sub-spherical in shape and 10-13 mm. in diameter and approximately weigh about 1-1.5 g. The horizontally split seed shows that the endosperm is translucent white and has the same shape as the seed. Sanskrit writings mentioned in Sushruta Samhita from India reported that the seeds of *S. potatorum* were used to clarify turbid surface water over 4000 years ago [35,36]. In the traditional system of medicine, the nirmali seeds are used to clear the muddy water due to their coagulant action. This property was attributed to the presence of anionic polyelectrolytes having -COOH and free -OH surface groups that are present in the seed protein. On average, the seed binds 0.5 mg of the respective metals per 1.0 g of the seed [37]. A major polysaccharide consisting of a 1: 7 mixture of galactomannan and galactan was found to be responsible for its water purifying properties [38,39]. Further, the seed extract is non-toxic and widely used for the treatment of various ailments like jaundice, bronchitis, diabetes, conjunctivitis, chronic diarrhoea, dysentery etc. which in turn due to the presence of biologically active phytochemicals present in them.

In view of the potential credentials bestowed with vermiculite as well as the seeds of *Strychnos potatorum*, in the present study, an attempt has been made to combine these two natural adsorbents in the ratio of 70: 30 w/w and evaluate the defluoridizing capacity of the vermiculite and *S. potatorum* mixture.

MATERIALS AND METHODS

Collection and preparation of adsorbent materials

Raw vermiculite samples with different particle sizes were obtained from Tamil Nadu Minerals Limited, Ambattur, Chennai and used for the present study (Figure 1). Based on our earlier studies with respect to particle size and the defluoridization capacity, the raw vermiculite was powdered to obtain the particle size of 80 mesh using agate motor [29]. *S. potatorum* seeds were collected from an organic shop in Mylapore, Chennai and authenticated by Prof. J. Muthumary, a taxonomist in Centre for Advanced Studies in Botany, University of Madras, Guindy Campus, Chennai (Figure 2). The seeds were dried in a hot air oven for 24 h at 50ºC. The seed coat was selectively removed and powdered to obtain a 100 mesh size [40]. After standardization by using different proportions, the raw vermiculite and *S. potatorum* seeds were mixed in the ratio of 70: 30 w/w using mortar and pestle and used as the adsorbing material for defluoridization studies.

Figure 1: Raw vermiculite

Figure 2: *Strychnos potatorum linn.* seeds

Column adsorption study

A column size of about 80 cm in height and 3 cm in diameter capable of accommodating 30 ml of water with an outlet fitted with a stopper at the bottom was selected to perform column adsorption study and the column was fixed to a stand [29]. A plug of cotton is placed to the bottom of the column and slurry of silica was prepared and poured into the column carefully so that silica will not pass through the column [41]. The columns were carefully packed with 15 g of either the raw vermiculite or the adsorbent mixture containing raw vermiculite and powdered *S. potatorum* seeds in the ratio of 70: 30 w/w. The water samples were allowed to stand in the column for 30 min.

Fluoride assay

A stock solution (100 mg/l) was prepared by dissolving 221 mg NaF (analytical grade) in 1 l of distilled water [42]. From the stock solution, three different concentrations of fluoride solutions namely 3 ppm, 4 ppm and 5 ppm were prepared for defluoridizing analysis. The flow rate was adjusted to 2 ml/min. The effluent fluoride solutions were collected and analyzed for fluoride content [43]. All the experiments were carried out in triplicate and the solutions for defluoridization as well as fluoride analysis were prepared by an appropriate dilution from the stock solution [44]. Fluoride content in the water samples before and after defluoridization was carried out with an Orion ion analyzer (Orion modal 720- pH-fluroimeter, USA) equipped with a fluorine selective electrode.

All reagents were of analytical-reagent grade and distilled. De-ionized water was used throughout the studies. Sodium fluoride (AR, BDH) was used as the source of fluoride. A stock solution of fluoride was prepared by dissolving 2.21 g of sodium fluoride and the solution was made up to 1 l in a standard flask [45]. By constructing the cell using the fluoride ion-selective electrode and the calomel reference electrode in a solution of fluoride at pH 5.35, adjusted with total ionic strength adjusting buffer (TISAB), the cell potential can be determined.

For the preparation of Total Ionic Strength Adjustment Buffer (TISAB), approximately 500 ml of water was added to 57 ml of analytical reagent grade Glacial acetic acid, 58 g of analytical reagent grade NaCl and 0.03 g of sodium citrate. The solution was titrated to pH 5.0-5.5 using analytical reagent grade 5 M sodium hydroxide and finally made up to 1 l. The TISAB buffer was transferred to a plastic container and stored in a refrigerator [46]**.** The fluoride standards were prepared by dilution from Orion Research 0.1 M Fluoride Activity Standard. Ten milliliters of a standard 1.0 ppm fluoride solution was pipette into a beaker and 10.0 ml of TISAB was added. The solution was stirred and the electrode potential determined after three minutes. The same 1: 1 mixing procedure was used with other standards and with unknowns [47]**.**

RESULTS AND DISCUSSION

Access to clean drinking water at an affordable price is a great concern in many developing countries. In India, fluoride is a major inorganic pollutant of natural origin found in groundwater [48]. Endemic fluorosis has been reported from 20 states spreading over 65% of the total Indian rural habitations. About 120 million people in India are affected and more than 200 million are exposed to the risk of developing endemic fluorosis. In Tamil Nadu state, several districts are reported to have high fluoride contamination and the prevalence of dental and skeletal fluorosis is endemic [49]. Defluoridization is the process which selectively removes excess fluoride from the water. Most of the defluoridization methods proposed and adopted worldwide are based upon the principles of precipitation, adsorption and ion exchange. However, the defluoridization methods developed so far lack viability at the end-user level due to one or more reasons such as high cost technology, limited efficiency, unnoticeable breakthrough, deteriorated water quality and taboo limitations [50]. Additionally, the shortcomings of most of these methods are high operational and maintenance costs, low fluoride removal capacity, lack of selectivity for fluoride, undesirable effects on water quality, generation of large amounts of sludge and complicated procedure involved in the treatment [51].

The most commonly adopted method in India, the Nalgonda technique of community defluoridization, is based on the precipitation process and is very efficient and cost effective. However, the major disadvantages of Nalgonda technique are daily addition of chemicals, a large amount of sludge production, least effective with water having high total dissolved solids (TDS) and high hardness [52]. Besides, it converts a large portion of ionic fluoride (67-87%) into soluble aluminium complex and practically, removes only a small portion of fluoride in the form of precipitate (18-33%). Therefore this technique is erroneous. Residual aluminium ranging from 2.01 to 6.86 mg/ l was also reported in Nalgonda technique, which is a major disadvantage to human health as aluminium is a potent neurotoxin capable of causing Alzheimer's disease and has strong carcinogenic properties. Hence, the search for a new defluoridization method continues [53].

Earlier, we have studied the defluoridization capacity of raw and exfoliated vermiculite having different particle sizes and found that treatment with raw vermiculite at a mesh size of 80 significantly adsorbed the fluoride present in the water samples. In order to circumvent the disadvantages such as odour and mild turbidity associated with the defluoridization using raw vermiculite, in the present study, we have prepared a new adsorbent mixture comprising of the raw vermiculite (80 mesh size) and powdered *S. potatorum* seeds, a traditionally used water purifier, in ratio of 70: 30 (w/w) and assessed its suitability to selectively remediate fluoride contaminated groundwater. Vermiculite is a micaceous mineral, comprised of an aluminium/iron/magnesium/silicate mixture. It is excavated as a material composed of thin layers. The chemical formula of vermiculite is $(Mg,Ca)_{0.7}(Mg,Fe^{3+},Al)_{6.0}[(Al, Si)_8O_{20}](OH)_4.8H_2O$. Structurally, vermiculite contains a central octahedral coordinated layer of magnesium and iron ions which lies between two inward pointing sheeting of linked SiO_4 terahydrate [54]. It is characterized by a high water-holding capacity as a result of its large surface area: volume ratio, a low bulk density, nearly neutral pH and a high cation exchange capacity attributed to its platy structure [55]. Vermiculite shows very weak bonding due to various cations between the sheets, therefore they show a great expansion, especially in wet condition [56]. Factors such as adsorbed water, exchangeable cations as well as anions and the sheet structure composed of layers made favorable for employing vermiculite as a successful defluoridating agent.

S. potatorum seed powder can effectively remove turbidity of muddy water, remediate fluoride [57] chromium (IV) [58] lead [59] and cadmium [60]. The unique fluoride adsorption property of *S. potatorum* seeds is attributed to the presence of polyelectrolytes, proteins, lipids, carbohydrates and especially the alkaloids containing –COOH and free -OH surface groups [61,62]. The removal of fluoride from aqueous solution by using *S. potatorum* seeds has been reported in batch technique. The influence of pH, adsorbent dose, contact time, co ions, speed and initial concentration on the adsorption has also been reported [58].

The removal of fluoride was expressed with Langmuir and Freundlich isotherm [63]. It was found that the sufficient time for the adsorption equilibrium of fluoride ion was approximately 1 hour [64]. The removal of fluoride ions was reported to be maximum at the adsorbent dosage of 50 mg/50 ml and the adsorption was maximum at 60 min [65]. The presence of interfering ions such as nitrate and carbonate showed a positive effect while sulphate and chloride showed little negative effect and phosphate showed a high negative effect for the adsorbent [64]. The results obtained from the present study satisfy the drinking water standards. The defluoridization capacity of raw vermiculite, as well as the mixture, is presented as Tables 1 and 2 respectively.

Table 1: Defluoridization capacity of raw vermiculite (80 mesh size)

Initial concentration of fluoride (Co) mg/l	Final concentration of fluoride (C) mg/l	Amount of Fluoride adsorbed (X) mg/l	Percent defluoridization
3	1.2	1.8	60
4	1.3	2.7	67.5
5	1.4	3.6	72

The Percentage of defluoridization is evaluated making use of the equation

$$X= \frac{C_0 - C}{C_0} \times 100$$

C_0-Initial concentration of fluoride
C-Final concentration of fluoride
X-C_0-C (Amount of fluoride adsorbed)

Table 2: Defluoridization capacity of raw vermiculite and powdered *Strychnos potatorum linn.* seeds mixed in the ratio of 70:30 w/w

Initial concentration of fluoride (Co) mg/l	Final concentration of fluoride (C) mg/l	Amount of Fluoride adsorbed (X) mg/l	Percent defluoridization
3	0.8	2.2	73
4	0.9	3.1	77.5
5	0.9	4.1	82

The Percentage of defluoridization is evaluated making use of the equation

$$X= \frac{C_0 - C}{C_0} \times 100$$

C_0-Initial concentration of fluoride
C-Final concentration of fluoride
X-C_0-C (Amount of fluoride adsorbed)

From the data obtained, it is evidenced that the mixture containing raw vermiculite at a mesh size of 80 and powdered *S. potatorum* seeds possess significant defluoridization capacity when compared to raw vermiculite. The treatment with mixture significantly improves the taste, odour and turbidity. The seeds of *S. potatorum* are reported to have effective coagulant properties which in turn due to the presence of alkaloids containing the –COOH and free –OH surface groups. The specific coagulation mechanism associated with *S. potatorum* seeds is due to the presence of the copious amount of –OH groups along the chains of galactomannan and galactan provide weakly but abundant adsorption sites that ultimately lead to the aforesaid coagulant inter particle bridging effect.

Table 3: Effect of pH on the removal of fluoride in the mixture containing raw vermiculite and *Strychnos potatorum linn.* seeds mixed in the ratio of 70: 30 w/w with Initial fluoride concentration (F–) 0 = 5 ppm

pH	Final Concentration of Fluoride (C) mg/l	Amount of fluoride adsorbed	Percent defluoridization (X) mg/l
4	1.7	3.3	66
5	1.9	3.1	62
6	2.1	2.9	60
7	2.2	2.8	58
8	2.3	2.7	54
9	2.3	2.7	54

The Percentage of defluoridization is evaluated making use of the equation

$$X= \frac{C_0 - C}{C_0} \times 100$$

C_0-Initial concentration of fluoride
C-Final concentration of fluoride
X-C_0-C (Amount of fluoride adsorbed)

Table 3 shows the effect of pH on the defluoridization capacity of the mixture containing raw vermiculite and *S. potatorum* linn. seeds mixed in the ratio of 70: 30 w/w. From the results obtained, the effective pH was found to be in the range of 4 to 6. Higher defluoridization of vermiculite at acidic pH is expected since the acidic dissociation of surface hydroxyl groups leads to the production of cationic surfaces, facilitating the adsorption of anionic fluoride [66]. However, the optimum pH values for *S. potatorum* seeds were reported to be ranging from 6.6 to 8.5 which are within the desirable limits (6.0 to 8.0) [57].

CONCLUSION

Based on the results obtained, it is concluded that the mixture containing raw vermiculite and *S. potatorum* seeds seems to be a conventional, economical and efficient method for defluoridization of drinking water. Further detailed studies are in progress to determine the effect of different particle size, contact time, adsorbent dose, adsorption kinetics and the effect of co-existing anions present in the water samples and the regeneration of the adsorbents used.

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