

Defluorination of Drinking Water

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ABSTRACT

It is generally accepted that a low level of fluorine in mains water (0.4 to 1 mg • L⁻¹ depending on the climate of the country concerned) promotes the formation of tooth enamel and protects teeth from decay. On the other hand, too much fluorine will destroy this enamel and cause a range of endemic type disorders that are generally called “fluoroses”: malformed teeth, staining of the enamel, decalcification, tendon mineralisation, digestive and nervous disorders, etc. These problems can appear in individuals for widely variable quantities of the product. Water must be discharged or treated as soon as it contains more than 1 to 1.5 mg • L⁻¹ of F⁻. Some natural waters contain more than 10 mg • L⁻¹ of fluorine. This concentration has to be reduced to approximately 1 mg • L⁻¹ (the acceptable concentration falling as the average annual temperature rises); the European standard has set 1.5 mg • L⁻¹.

Many studies have been carried out to address the issue however little success has been reported up to date. Layered double hydroxides (LDHs) which readily undergo anion exchange reactions have been used as a suitable candidate for defluorination. Also there is regeneration of the material after removal of fluoride ions without releasing fluoride ions back in to the water cycle. F⁻ elimination using a nanofiltration (NF) operation will solve problems for-large-scale pilot plants in the future.

Many defluorination projects have significant effectiveness on the prevention of endemic fluorosis. The concentrations of water fluoride were below 1 mg/L. Advanced on-site methods, such as under sink reserve osmosis units, can remove fluoride but are too expensive for developing areas. Calcium carbonate as a cost effective sorbent for an onsite defluorination drinking water system. Batch and column experiments have been performed to characterize F⁻ removal properties. The present review discusses various techniques of defluorination of water.

INTRODUCTION

Fluoride is often described as a „double-edged sword“ as inadequate ingestion is associated with dental caries, where as excessive intake leads to dental, skeletal and soft tissue fluorosis- which has no cure. In fact, the famous „McKay“s discovery“ of the connection between excessive content of fluoride in water and endemic mottling of the enamel was one of the main starting points of research into fluorides related hard-tissue physiology and pathology[1].

Fluoride removal may be due to the precipitation of fluoro-compounds. It was claimed, that the presence of some ions in the treated water samples, was decreasing the fluoride removal since it compete the fluoride ions on occupying the available adsorption sites, However, phosphate and silicate ions from its sodium slats were used to investigate the correctness of this claim, but it was found that these ions enhanced the fluoride removal percentage, hence, precipitation of calcium-fluoro compounds of these ions can be suggested[2].

In a study fluoride-resistant bacteria have been isolated from fluoride-contaminated groundwater and soil samples for their potential use in defluorination. Out of a total of 53 bacterial isolates that were recovered and screened for fluoride resistance, three highly fluoride-resistant isolates DWC1, DWC2 and DWB5, resistant to up to 9200 mg L⁻¹, 7200 mg L⁻¹ and 5200 mg L⁻¹ fluoride respectively, were characterized and identified as *Aeromonas* sp., *Brevibacterium* sp. and *Paenibacillus* sp.

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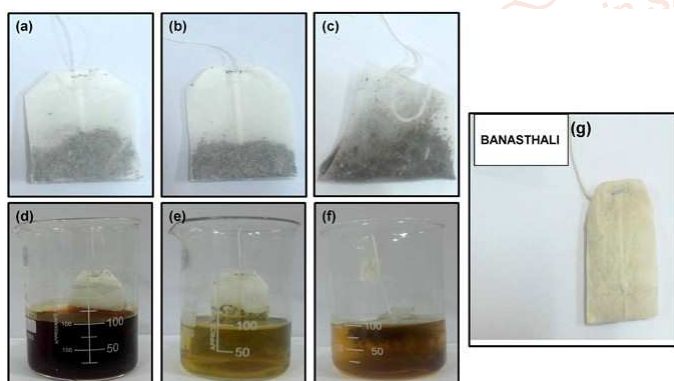


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respectively. The fluoride removal capacity of isolates DWC1, DWC2, DWB5 and a consortium of all the three isolates was found to be 68.7%, 73.4%, 76.7 % and 70.1% respectively on nutrient broth supplemented with NaF (2000 mg L⁻¹) after 8 days of incubation. Defluorination by the strain showing the best result was *Paenibacillus* sp. [3]

Development of a cost-effective, portable, environment and user-friendly defluorination technique is imperative. In another study, development of a green and cost-effective method utilizing Fe₃O₄ and Al₂O₃ nanoparticles (NPs) that were synthesized using jojoba defatted meal. These NPs were impregnated on to polyurethane foam (PUF) and made into tea infusion bags. The Al₂O₃ NPs-PUF displayed a higher water defluorination [4] capacity of 43.47 mg g⁻¹ of F as compared to 34.48 mg g⁻¹ of F with Fe₃O₄ NPs-PUF. The synthesized Al₂O₃-PUF infusion bags removed the F that was under the permissible limit of 1.5 mg L⁻¹. [5]



Al₂O₃-PUF infusion bags

This was found beneficial for researchers working towards further improvement in water purification technologies.[6]

Further one more experiment was that octacalcium phosphate (OCP), a mineralogical precursor of bioapatite, was tested as a fluoride remover. A new two-step method for the synthesis of OCP was proposed:

1. Synthesis of brushite from calcium carbonate and phosphoric acid;
2. Subsequent hydrolysis of brushite. [7]

Defluorination experiments were performed in batch-mode using different initial concentrations of fluoride (from 40 to 140 mg/L) and reaction times. Most of fluoride was removed within the first 2 h of all experiments, and the drinkable limit of 1.5 mg/L had reached within a minimum of 3 h for an initial fluoride concentration of 40 mg/L. [8] The experimental fluoride removal capacity of OCP was 25.7 mg/g, and 4 g of OCP could effectively treat 1 L of water with fluoride concentration up to 50 times higher than the drinking limit of 1.5 mg/L. The

chemical characterization of the solid phases, before and after the removal experiments, indicated that OCP transformed into fluorapatite (FAP) up taking fluoride from solution.[9]

OBSERVATIONS AND DISCUSSION

Low dental caries incidence rates demonstrate that fluoride concentrations of up to 1.0 mg/l in potable water are beneficial to the oral health of children and, to a lesser extent, adults. In several developed countries fluoridation of water supplies is practiced [10] if the natural concentration is below the desired level. Recently, however, fluoridation of drinking water has been questioned and many countries have expressed concerns over this practice due to the adverse health effects of fluoride. Dental fluorosis, also called “mottled enamel”, occurs when the fluoride level in drinking water is marginally above 1.0 mg/l. [11]

A relationship between fluoride concentration in potable water and mottled enamel was first established in 1931. Typical manifestations of dental fluorosis are loss of shining and development of horizontal yellow streaks on teeth. [12] Since this is caused by high fluoride in or adjacent to developing enamel, dental fluorosis develops in children born and brought up in endemic areas of fluorosis. Once formed, the changes in the enamel are permanent. When the above manifestations are seen in an adult, they clearly indicate that the person has been exposed to high fluoride levels during her or his childhood. [13]



Dental fluorosis

Skeletal fluorosis affects both adults and children and is generally manifested after consumption of water with fluoride levels exceeding 3 mg/l. Typical symptoms of skeletal fluorosis are pain in the joints and backbone.[14] In severe cases this can result in crippling the patient. Recent studies have shown that excess intake of fluoride can also have certain non-skeletal health impacts such as gastro-intestinal

problems, allergies, anaemia and urinary tract problems. Nutritional deficiencies can enhance the undesirable effects of fluoride.[15]



Skeletal fluorosis

In an experiment, a column was set up using mixture of red soil and sand with a ratio by weight of 4:1. It is noted that the red soil is fine grained substance with clay size particles and, with good ion exchange capacity but lesser permeability, hence it was mixed with sand to increase the permeability.[16] The removal rate of fluoride was tested using 250 gm of mixture soil (200 g of red soil and 50 g of sand). The fluoride concentration in the samples was measured by using an Orion, model 2100 expandable ion analyzer EA 940 and the fluoride ion selective electrode BN 9609 (Orion, Thermo Fisher Scientific, USA).[17] The standard solution of 10 mg/l fluoride was prepared from 100 mg/l⁻¹ standard (Thermo Orion) by using DDW (Doubled Distilled Water). The samples were collected at definite intervals. [18]

Eleven different Batch experiments were conducted by passing Fluoride standard of 10 mg/l⁻¹. 10 ml of sample was collected after the treatment and analyzed. A total of about 62 samples were collected in different batches during the entire experimental period.[19] Out of these samples collected, different parameters were observed along with F concentration. Rate of flow of water through the column, their variation in pH, Percentage of fluoride adsorption, adsorption capacity, bicarbonate concentration and EC were also observed.[20] pH and EC were analyzed by ion sensitive electrodes, HCO₃ was estimated by titrimetry method using standard procedures (APHA 1998).[21]

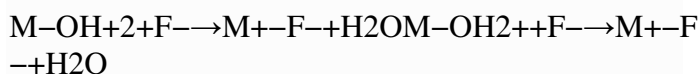
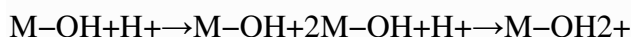
The adsorption capacity was calculated by using the formula,

$$q_e(\text{mmol/g}) = (C_o - C_e) \times V / W \times 1,000$$

C_e is equilibrium adsorbate (fluoride) concentration (mmol/l). C_o is initial adsorbate (fluoride) concentration (mmol/l). q_e amount of fluoride adsorbed per unit gram of the adsorbant at

equilibrium (mmol/g). V is volume of solution (l). W is weight of adsorbant (g).

F⁻ sorption via ligand exchange may also explain F⁻ removal at pH <6.5, in accordance with following equations:



Where, M represents metal ions like Al³⁺, Fe³⁺. The supported iron and aluminum oxides form the aqua complex with water and form the surface charges through amphoteric dissociation. At acidic pH, more positively charged surface sites developed which attract the negatively charged fluoride ions by electrostatic attraction resulting in the enhanced fluoride removal at acidic pH[22]



The ligand-exchange interaction occurred between fluoride and hydroxyl ions at neutral pH.

RESULTS

Plant materials have been reported to accumulate fluoride and hence application as defluorinating agents has been suggested. The use of medicinal plant materials for the fluoride removal was investigated. The study investigated defluorination capacities of the following plant materials-Ramacham (*Vetiveria zizanioides*), Tamarind seed (*Tamarindus indica*), Clove (*Eugenia carryophyllata*), Neem (*Azadirachta indica*), Acacia (*Acacia catechu* willd), Nutmeg (*Myristica fragarns*), and coffee husk (*Coffea arabica*). [23] All the plant materials were washed well with tap water and then with distilled water, dried in an air oven at 110°C for 5 hour, micronized in a flour mill and sieved to get particles of sizes 0.1, 0.2 0.3, 0.5 mm. A synthetic solution of fluoride was prepared from analytical reagent sodium fluoride and stored in polythene bottles. [24]The pH of the solution was adjusted to the required level, using HCl (0.1 mol/l) and NaOH (0.1 mol/l) solutions. Activation of Vetiver root was carried out by giving heat treatment (at 600°C - 800°C) and with the use of phosphoric acid in the ratio 1:4. The activated product is washed with water and dried.[25]

Freundlich and Langmuir equations were used to find the patterns of adsorption by adsorbent activated Vetiver root for fluoride removal. The sorption isotherm studies are conducted by varying the initial concentration of fluoride from 1 to 5 mg/L and maintaining the adsorbent dosage of 0.5 g.[26]

Freundlich Adsorption Isotherm

The non-linear form of Freundlich equation is:

$$X/m = K C_e^{1/n}$$

where X/m = Amount adsorbed per unit weight of adsorbent (mg/g) or adsorption capacity and is calculated as follows.

$$X/m = (C_i - C_e) \times V \times \text{eq.wt.}/1000 \times m.$$

C_i = Initial concentration of solution in mg/L.

C_e = Equilibrium concentration of the solution in mg/L.

V = volume of the solution in mL.

K = Constant of the system depending on temperature and is known as Freundlich adsorption coefficient. It represents the adsorption capacity.

n = Freundlich constant, which should be between 1 and 10 for favorable adsorption. Values of “ n ” greater than unity suggest that adsorption is relatively more efficient at low concentration.

This equation is conveniently used in the linear form by taking the log on both sides as,

$$\text{Log}(X/m) = \text{log } K + (1/n) \text{log } C_e$$

A plot of $\text{log}(X/m)$ against $\text{log } p$ or $\text{log } C_e$, yield a straight line. The constants K and n are determined from the intercept and slope respectively.

Langmuir equation is based on the assumption of a monolayer of adsorbate molecules. It is of the form,

$$(X/m) = (a V_m C_e) / (1 + a C_e)$$

where a = adsorption bond energy;

V_m = maximum adsorption density (corresponding to monolayer formation on the adsorbent).

Linear form of the equation is,

$$C_e / (X/m) = 1 / (a V_m) + (1/V_m) C_e$$

A plot of $C_e / (X/m)$ against C_e , yield a straight line. The Langmuir constants a and V_m were calculated from intercept and slope respectively.[27]

The order of removal of fluoride is: Vetiver root (*Vetiveria zizanioides*, 80%), Tamarind seed (*Tamarindus indica*, 75%), Clove (*Eugenia carryophyllata*, 70%), Neem (*Azadirachta indica* 52%), Acacia (*Acacia catechu* willd, 47%), Nutmeg (*Myristica fragarns*, 45%), and Cofee husk (*Coffea arabica*, 38%).[28]

Vetiver root was found to be promising for the removal of fluoride. In its activated powdered form, Vetiver root has the potential to be an efficient defluoridating agent. The sorption process of fluoride ion on activated Vetiver root was influenced by many

experimental conditions. The equilibrium data obtained fitted well with Langmuir and Freundlich isotherms.[29]

CONCLUSION

Various studies have been reviled that major of the kidney diseases have a great inclination of toxicity of fluoride and a high dose and short term exposure of fluoride can exterminate the kidney function. [30] Several research groups reported that fluoride can interfere with the function of pineal gland as well as brain. Pineal gland is one of the major fluoride accrued site in body with high concentration of teeth and bones. The high concentration of fluoride diagnosed bladder cancer.[31]

In the given review, among various methods used for defluorination of water, adsorption method is relatively simple, economical, and appropriate for drinking water treatment, especially for small communities.[32] Biological mode of defluorination using plants, seeds etc is the best, non contaminating, ecofriendly and low cost method. [33]

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