Aluminum Hydroxide (Al(OH)$_3$) as defluoridating agent in drinking water soil pots (vessels of earthenware)

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Abstract: Water generally being the principal source of fluoride. Presence of fluoride in drinking water above (and some times even below) permissible limits (1.5 ppm accordingly to WHO) leads to fluorosis (WHO, 1984). Men and nature both are responsible for this disease. It is a worldwide health problem and is affecting both the developing and developed countries. In the whole world, about 25 countries have high fluoride concentration in ground water. Rajasthan is the worst affected state in India. As per a report of WHO, 20% of fluoride-affected village in the whole world are in India. Aluminum salts are commonly used as coagulants in water treatments. Aluminum fluoride is less toxic than other fluorides. In this study Al(OH)$_3$ was used as defluoridating agent in drinking water earthenware. Al(OH)$_3$ was incorporated in different amounts in soil. Some soil pots were prepared by the mixture. It was noted that these soil pots had a remarkably decreased concentration of fluoride in drinking water. The concentration of fluoride was determined by the fluoride ion selective electrode method.

Keywords: Adsorption, Aluminum Hydroxide, Defluoridating, Fluoride, Fluorosis.

INTRODUCTION

The terms "Fluoride and Fluorine" are used interchangeably in the literature as generic terms. Fluorine has a relative atomic mass of 19; at room temperature it is a pale yellow-green gas and extremely poisonous. It is the most electronegative and reactive relative to all elements (Vogel's, 1989;Alexeyev; Lee, 1996). Thus, in nature, it is rarely found in its elemental state. Fluorine combines directly at ordinary or elevated temperature with all elements other than oxygen and nitrogen. Fluoride ions have a strong tendency to form complex with heavy metal ions in aqueous solution e.g., FeF_6^{3-}, AlF_6^{3-}, MnF_5^{2-} ,MnF^{3-}, ZnF_6^{2-} and ThF_6^{3-}. The toxic potential of inorganic fluoride is mainly associated with their behaviour and the formation of insoluble fluorides (WHO, 1970,1984).

Fluorine reacts with metallic elements to form compound that are usually ionic, both in the crystalline state and in solution. Most of these fluorides are readily soluble in water. However, Lithium, Aluminum, Strontium, Barium, Lead, Magnesium, Calcium and Manganese fluorides are insoluble or sparingly soluble in water (Alexeyev; Vogel's, 1989;Balsu, 1984). Fluoride content present in drinking water causes various health problems when the concentration of fluoride is greater than 1.5ppm (According to WHO). The prolonged intake of water containing excess of fluoride causes the crippling disease called fluorosis (Skeletal and Dental fluorosis)(Fig.1). The first case of endemic fluorosis in India was reported from Andhra Pradesh in 1937(RGNDMW, 1993; Chandrawat, 2005).

According to WHO 20% villages out of total fluoride affected village in the world are found in India and out of total affected villages in India 52% are in Rajasthan (Yadav, 2006) (Fig.2). It is to be noted that India is not only the country but several other nations in the world are severely affected by the problem of fluorosis. Apart from India, high concentration of

fluoride has been detected in the ground water in several countries including Argentina, Algeria, Australia, several African Nations, Bangladesh, and China etc (RGNDMW, 1993).
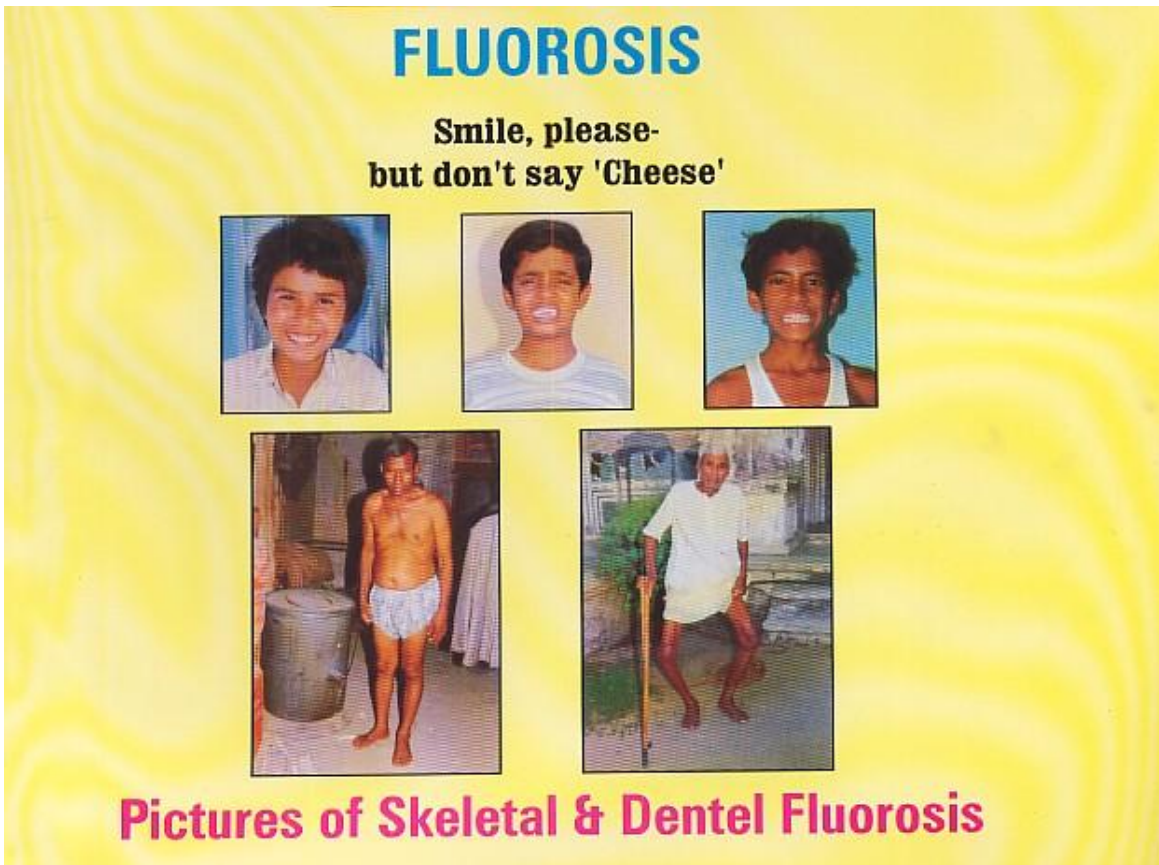

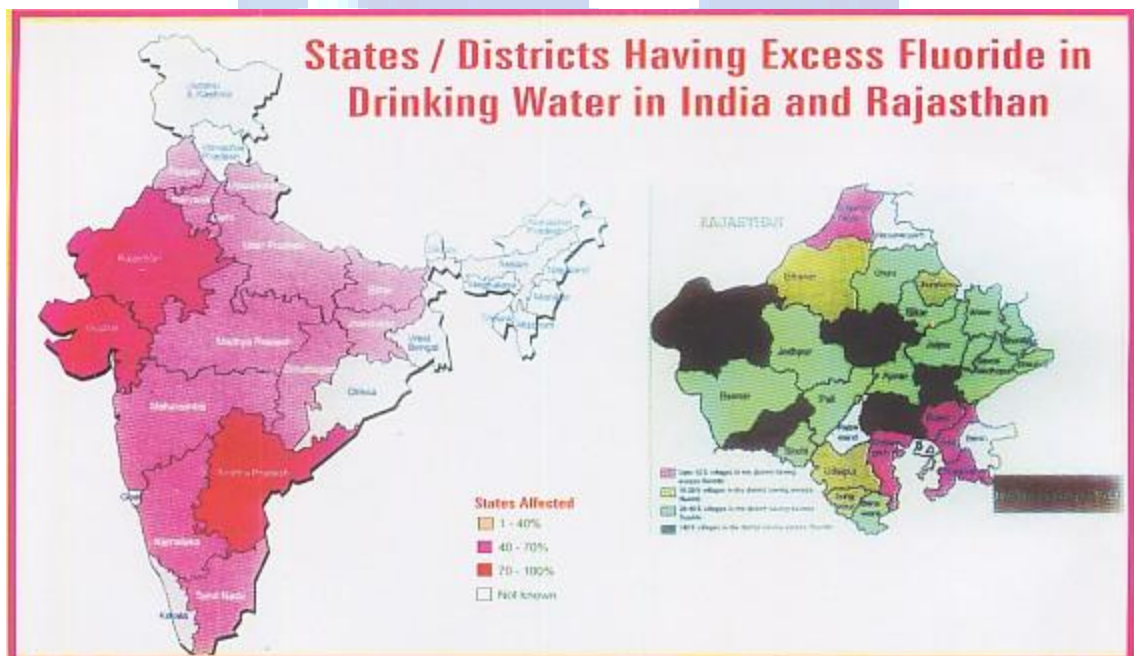**Figure 1 Pictures showing Fluorosis in human beings.**

Figure 2 Picture showing States/Districts having excess fluoride in drinking water in India and Rajasthan

A comparative study of degree of toxicity of NaF, NaSiF$_6$, CaF$_2$, CaSiF$_6$, MgF$_2$, ZnF$_2$, AlF$_3$ and CuF$_2$ showed that calcium and Aluminum fluoride work less toxic than other fluoride (WHO, 1970;Balsu, 1984;Yadav, 2006). Although several methods, such as lime, treatment Alum Coagulation, Nalgonda technique (NEERI, 1987), ion exchange resin, activated alumina, membrane or electrolysis, Electrocoagulation, Flotation, Adsorption etc.have been identified as promising technique for removal of fluoride from drinking water but these existing methods for defluoridation of drinking water involve expansive and high technology or are slow, inefficient and or unhygienic. It is found out that fluoride from semiconductor wastewater can be removed by electrocogulation-flotation process (Ching-yao Hu et al, 2005). Electro coagulation-flotation (ECF) process can be used for removal of fluoride from semiconductor wastewater (Ching-yao Hu et al, 2005). Treatment method of high fluoride content wastewater by continuous electro coagulation-flotation system with bipolar aluminum electrode is found out by Ching-yao Hu, 2007.Laterite soil, the geometrical is used as adsorbent for the removal of fluoride from drinking water by Mitali sarkar et.al (2006).

The conventional methods for the removal of fluoride from drinking water are adsorption, coagulation, ion exchange and membrane procedures. But to operational difficulties, these methods have limited application. Adsorbents such as latersite, activated alumina, tamarenal seed etc. have been used but with limited success. Thus, the attention has shifted to prepared incorporated soil pots of aluminum hydroxide, which have large area and a high degree of surface activity. Therefore, in present paper authors were used aluminum hydroxide as defluoridating agents in soil pots of drinking water and developed a new defluoridation method.

Experimental Methods:

The soil was collected from rural area of Alwar city, Rajasthan, India and sieved to remove the unwanted materials. This soil was chemically analyzed and then four pots were prepared after uniform incorporation of aluminum hydroxide, 2gm, 4gm, 6gm and 8gm.per kg in soil respectively (Fig.3). After some time, 10ppm fluoride standard solution was taken in each soil pots and then determined their fluoride concentration after 3hrs, 24hrs, 48hrs,and 120hrs time interval by Orion 720 A$^+$ ion meter using fluoride ion selective electrode. Result shown in Table-1.
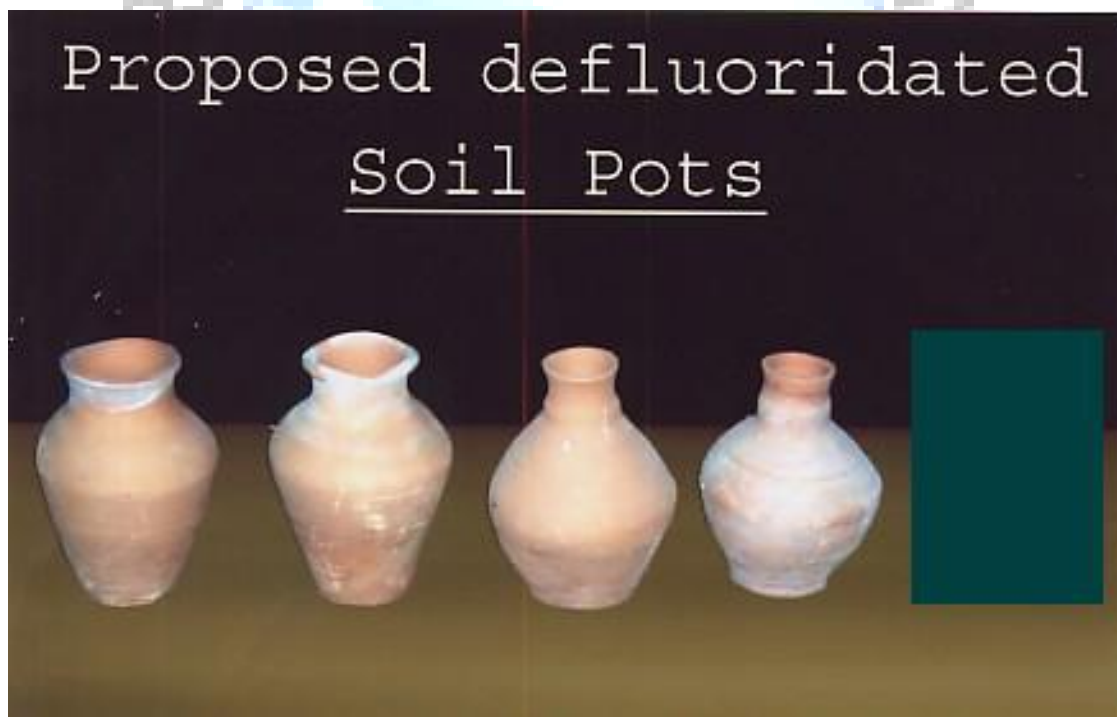

Figure 3 Defluoridated Soil Pots

RESULTS AND DISCUSSION

Table-1 revels that the fluoride concentration of drinking water sample (10ppm) decreases in the all soil pots with increasing amounts of aluminum hydroxide and with time periods. It was found that soil pot No-1 (having 2gm Al(OH)$_3$), decreases the fluoride concentration of the water sample about 40%but incase of soil pot No-4 (having 8gm Al(OH)$_3$), the

concentration of fluoride decreases about 60% in 120 hrs. This can be explained on the basis of surface chemistry. It is a general phenomena of surface chemistry that more the surface area of adsorbent more the adsorbate are adsorbed on the surface of adsorbent upto form a unimolecular layer (Langmuir isotherm limitation) of adsorbent during chemsorption process. Result shows that a certain amount of aluminum hydroxide reduces the fluoride concentration in water sample.

Table 1 Effect of aluminum hydroxide in soil pots as defluoridating agents.

Soil pots No.	$Al(OH)_3$ in soil pots (gm/kg soil)	Initial conn of F^- in water sample	Fluoride concentration (mg/l)			
			After 3 hours (c_e)	After 24 hours (c_e)	After 48 hours (c_e)	After 120 hours (c_e)
1	2 gm	10mg/1	9.09	7.30	6.33	5.28
2	4 gm	10mg/1	8.99	7.33	6.45	4.94
3	6 gm	10mg/1	8.92	7.06	6.28	5.10
4	8 gm	10mg/1	8.73	7.14	6.23	4.72

(**Temp**: 20 ± 5^0C, pH: $7\pm.0.5$)

The removal of fluoride from water sample (10ppm) is expected due to the formation of polyhydroxide aluminum complex (e.g. $[Al(H_2O)_3(OH)_3][Al(H_2O)_2(OH)_2]$etc) with fluorides and adsorption/absorption of fluoride on polymeric aluminum hydroxide
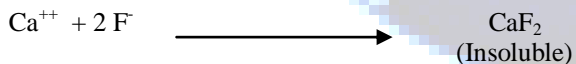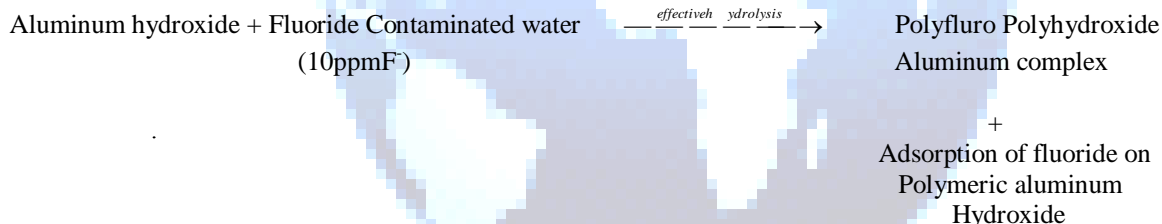Following reaction are proceeds in soil pots:

$$Al(OH)_3 + H_2O \longrightarrow Al^{+3} + 4OH^- + H^+$$

$$Al^{+3} + 3F^- \rightarrow AlF_3 \text{ (Adsorption and insoluble Fluoride)}$$

Aluminum hydroxide + Fluoride Contaminated water $\xrightarrow{\text{effectiveh ydrolysis}}$ Polyfluro Polyhydroxide
(10ppmF⁻) Aluminum complex

\+
Adsorption of fluoride on
Polymeric aluminum
Hydroxide

$$Ca^{++} + 2F^- \longrightarrow CaF_2 \text{ (Insoluble)}$$

Table 2 Adsorption of fluoride in different soil pots.

Soil pots No.	$Al(OH)_3$ in soil pots (gm/kg soil)	Initial conn of F^- in water sample	Fluoride adsorbed (mg/l)			
			After 3 hours (x)	After 24 hours (x)	After 48 hours (x)	After 120 hours (x)
1	2 gm	10mg/1	0.91	2.70	3.67	4.72
2	4 gm	10mg/1	1.01	2.67	3.55	5.06
3	6 gm	10mg/1	1.08	2.94	3.72	4.90
4	8 gm	10mg/1	1.27	2.86	3.77	5.28

(**Temp**: 20 ± 5^0C, pH: 7 ± 0.5)

Adsorption Isotherm Study: -

The adsorption isotherm of fluoride ions from water sample at pH 6.5-7.5 on surface of different soil pots with time are presented in Fig: 5. In order to investigate the maximum adsorption capacity of aluminum hydroxide towards fluoride, Langmuir and Freundlich isotherm studies were conducted. The adsorbent dose was varied in the range of 2gm to 8gm per kg soil. The initial concentration of fluoride was 10 mg/l at pH 6.0-7.0 and tested at the interval of 3 hrs, 24 hrs, 48 hrs and 120 hrs at temperature $20^{\circ} + 5^{0}$c.

The adsorption isotherm data may be described by the classical Langmuir equation

$$x / x_m = K C_e / 1 + K C_e$$

Where x is the amount adsorbed at equilibrium concentration C_e and x_m is the maximum amount adsorbed K is the Langmuir equation constant. The relation between the amount of adsorbate adsorbed by an adsorbent and the equilibrium concentration (C_e) of the adsorbate can be expressed by the linearized Langmuir adsorption isotherm as:

$$C_e / x = 1 / K x_m + C / x_m$$

The linear Langmuir plots between C_e/x and C_e are shown in Figure 5 and the Langmuir equation constant K and x_m calculated from the linear plots are recorded in Table –5.

The linear form of the Freundlich equation can be written as:

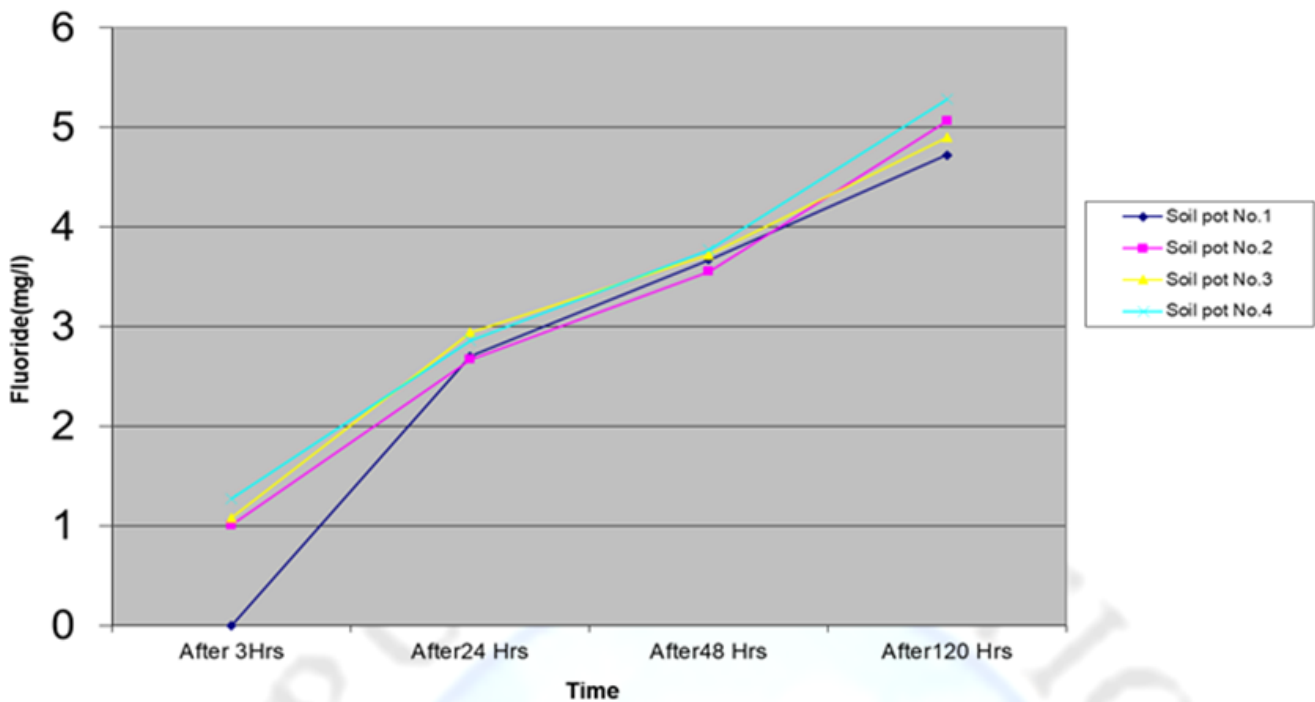$$\text{Log } x = \log k_f + n \log c_e$$

Fig. 4: Adsorption of Fluoride by different soli post as a function of time

Where n is a parameter characterizing quasi-Gaussian energetic heterogeneity of the adsorbent surface (adsorption intensity) and K_f adsorption capacity (Freundlich equation constant) in mg/g n and K_f are depend on the nature of the adsorbent and adsorbate.

The constant values of the both isotherm for each soil pot are given in Table-5, it is observed from both the curves and correlation coefficient data the adsorption follows neither Langmuir isotherm nor Freundlich isotherm in a perfect way. However, it follows Langmuir isotherm in a better way. It is seen that the value of n is always less then unity, which indicates that, none of the soil pots have completely energetically homogeneous surface. This can be explained that all the four soil pots are associated with certain amounts of aluminum hydroxide at certain specific sites associated with different

activation energy .The adsorption involves attractive electrostatic interaction between the negative sites created by the ionization of the sodium fluoride and the positively charged Al^{+3} cations.The adsorption take place on certain specific sites on the soil pots surface and only a fraction of the BET surface area is π occupied by the fluoride ions. The adsorption data obeys both the Langmuir and Freundlich isotherm equation.

Table 3 Characteristics of water sample

Parameters	Quantitative Value
PH	7.88
Turbidity (NTU)	0.7
Hardness (mg/l)	400
Fluoride (ppm)	10.0
T.D.S (mg/l)	1198
Al (ppm)	0.1727

Table 4 Characteristics and Composition of Soil

Properties	Quantitative Value
Geometric mean size (mm)	0.154
Bulk density (g/cm^3)	2.1
Surface area (m^2/g)	13.265
Pore Value (cm^3/g)	0.011
Al (ppm)	0.011
Fe (ppm)	19.6
Zn (ppm)	0.9
Cu (ppm)	1.80
pH	7.9
Biological Carbon (%)	0.22
Available Phosphorus (kg/hector)	90
Potash (kg/hector)	≥337
Electric Conductivity (E.C.) (mM/cm)	0.38

Table 5 Langmuir and Freundlich equation constants for adsorption of fluoride ions on different soil pots.

Quantity of Al(OH)$_3$ in soil pot	Langmuir equation constants		Freundlich equation constants	
	x$_m$(mg/g)	k	n	k$_f$
2 gm	0.83	-1.23	-2.8425	9494.00
4 gm	0.84	-0.66	-6.7332	609.03
6 gm	0.93	-0.80	-2.5888	735.15
8 gm	1.22	-2.86	-2.3834	1635.84

CONCLUSION

Adsorption isotherm of fluoride ions follows the mixed model of the Langmuir and Freundlich isotherm. The adsorption does not depend on the BET surface area of the pots and takes place on certain specific site. Result shows that aluminum hydroxide can be used as defluoridating agent in soil pots. This defluoridation method is beneficial for society especially for the people which intakes fluoride-contaminated drinking water.

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