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Archives of Applied Science Research, 2010, 2 (3): 11-22

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ISSN 0975-508X

CODEN (USA) AASRC9

Study of the Aluminum Ammonium Sulphate as defluoridated Agent in Drinking Water Earthenware

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ABSTRACT

Fluorosis is the 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. Aluminum salts are commonly used as coagulants in water treatments. Aluminum fluoride is less toxic than other fluorides. In this study Aluminum Ammonium Sulphate has been used as defluoridating agent in drinking water earthenware and noted that these earthenware decrease the concentration of fluoride in drinking water. Langumir and Frenlich study had carried out with these earthenware.

Key words : fluorosis, defluoridating agent, earthenware

INTRODUCTION

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 [1,11,27]. 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^{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 [5,27]. 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 [1,3,16-19]. 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[4,15].

Fluorosis problem is not only health problem but now it has become a social problem too. 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 [31].

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 [15].

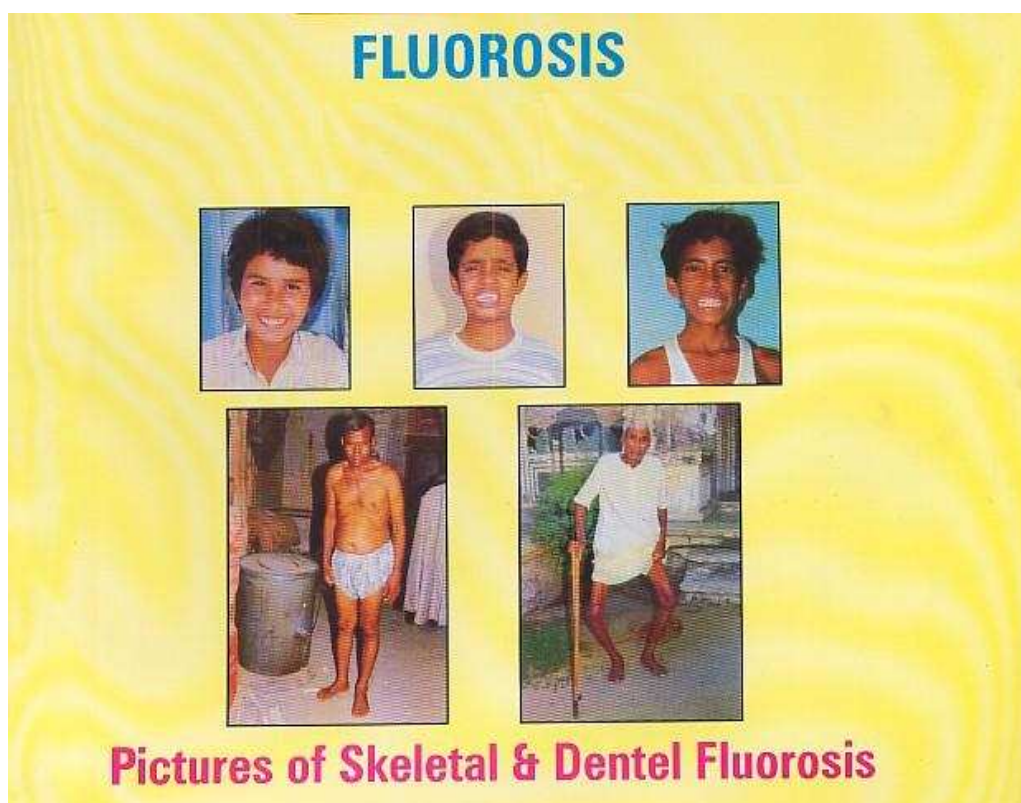


Figure 1. Pictures showing Fluorosis in human beings.

A comparative study of degree of toxicity of NaF, NaSiF₆, CaF₂, CaSiF₆, MgF₂, ZnF₂, AlF₃ and CuF₂ showed that calcium and Aluminum fluoride work less toxic than other fluoride [2,28,31]. Although several methods, such as lime treatment, Alum Coagulation, Nalgonda technique, ion exchange resin, activated alumina, membrane or electrolysis, Electro coagulation-Flotation, Adsorption etc. have been identified as promising technique for removal of fluoride from drinking water [6-10,13,14]. Adsorbents such as laterite, activated alumina, tamarind seed etc. also have been used to remove 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 and have limited application [21-26,28-31].

Hence, the present investigation was undertaken to minimize the fluoride content in drinking water by use of aluminum ammonium sulphate as defluoridation agent in earthenware (soil pots) and developed a new defluoridation method.

Fig 4 Adsorption of Fluoride by different Soil pots as a function of time

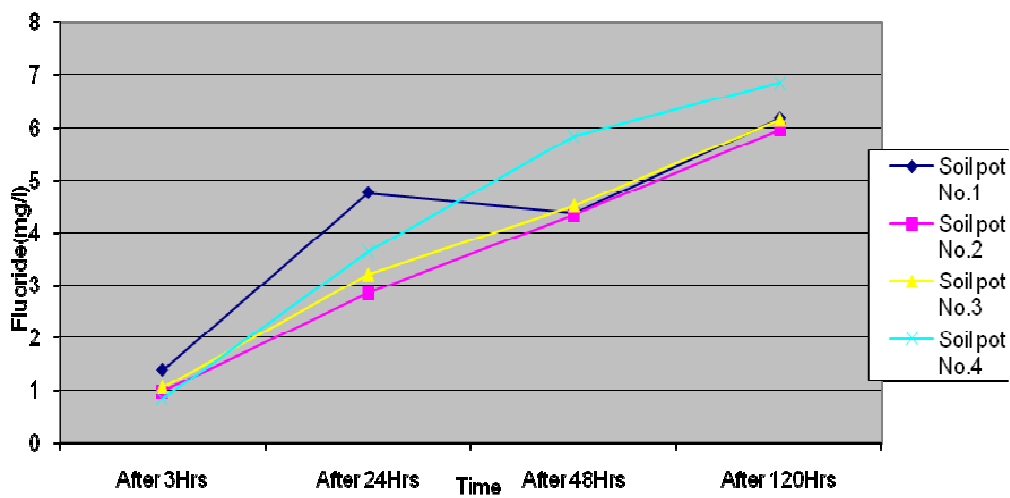


Fig 5 Linear Langmuir plot of fluoride ions on soil pot no 1.

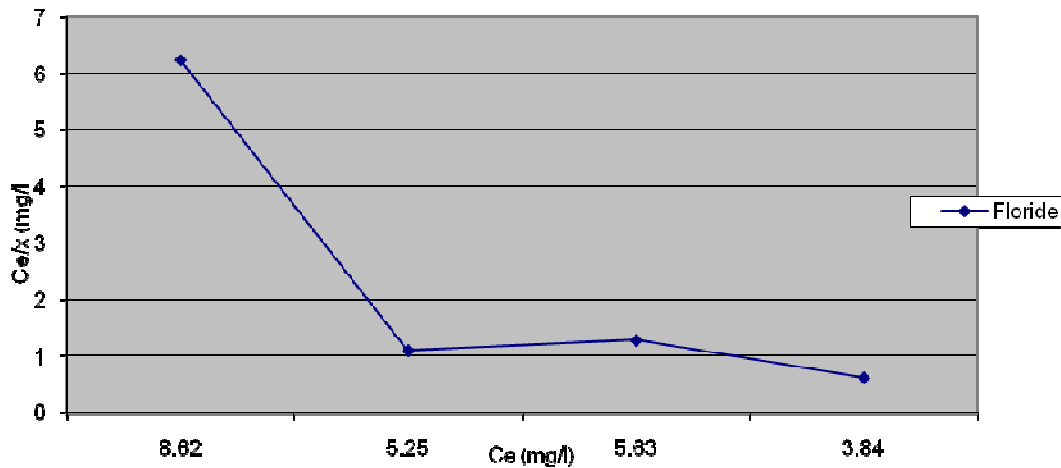


Fig 6 Linear Langmuir plot of fluoride ions on soil pot no 2.

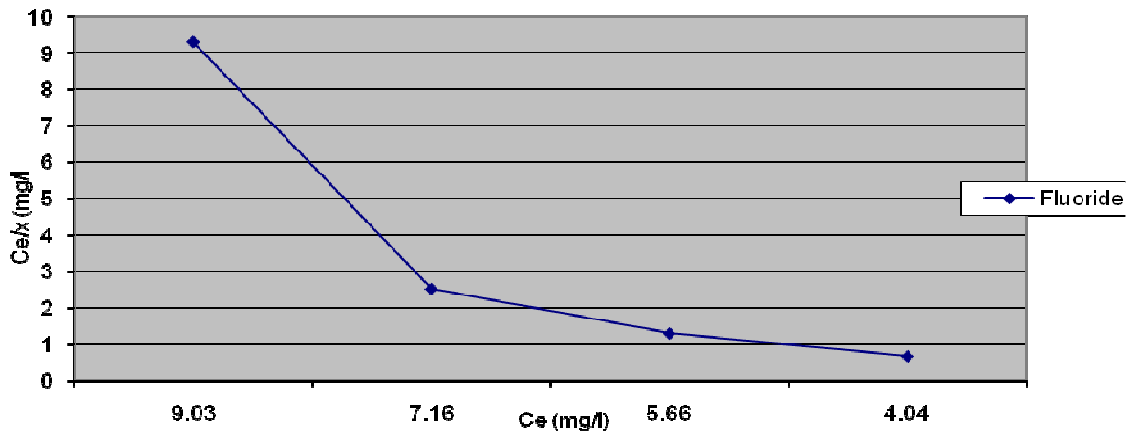


Fig 7 Linear Langmuir plot of fluoride ions on soil pot no 3.

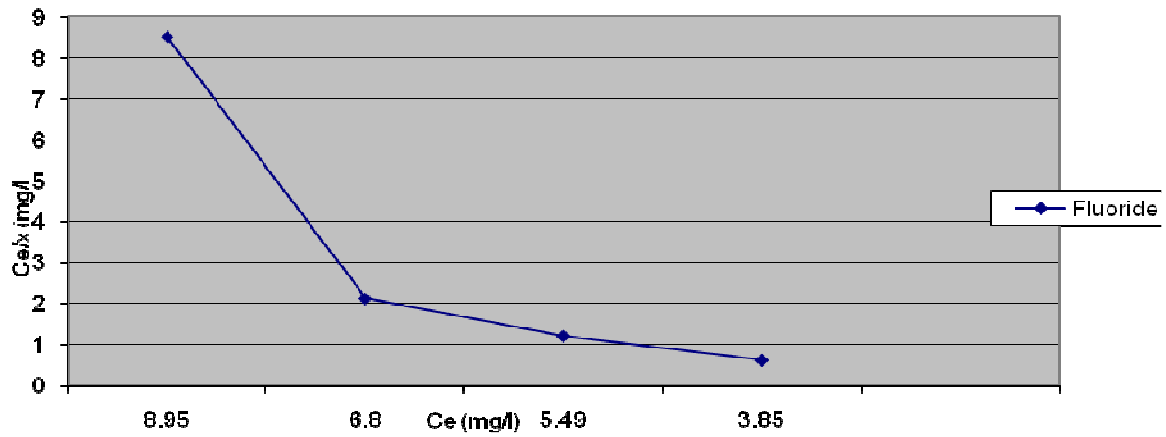


Fig 9 Linear Freundlich plot of fluoride ions on soil pot no 1.



Fig 10 Linear Freundlich plot of fluoride ions on soil pot no 2.

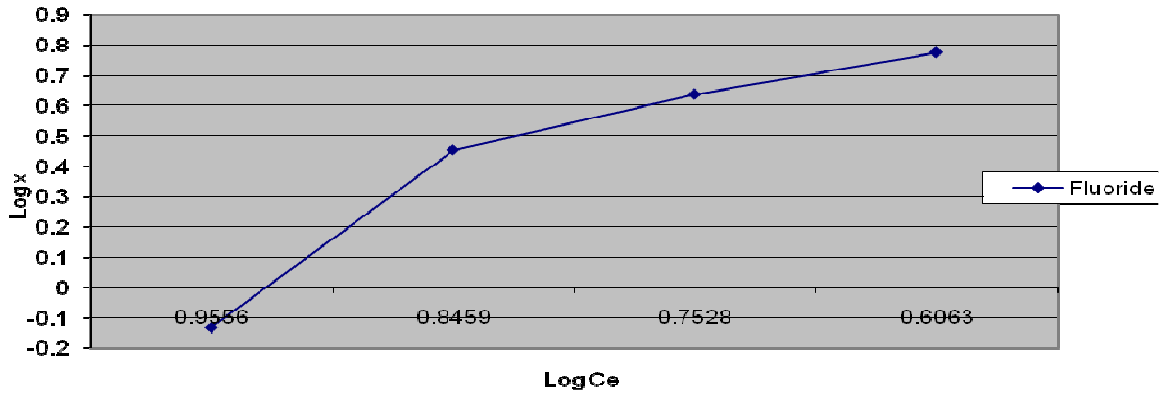


Fig 11 Linear Freundlich plot of fluoride ions on soil pot no 3.

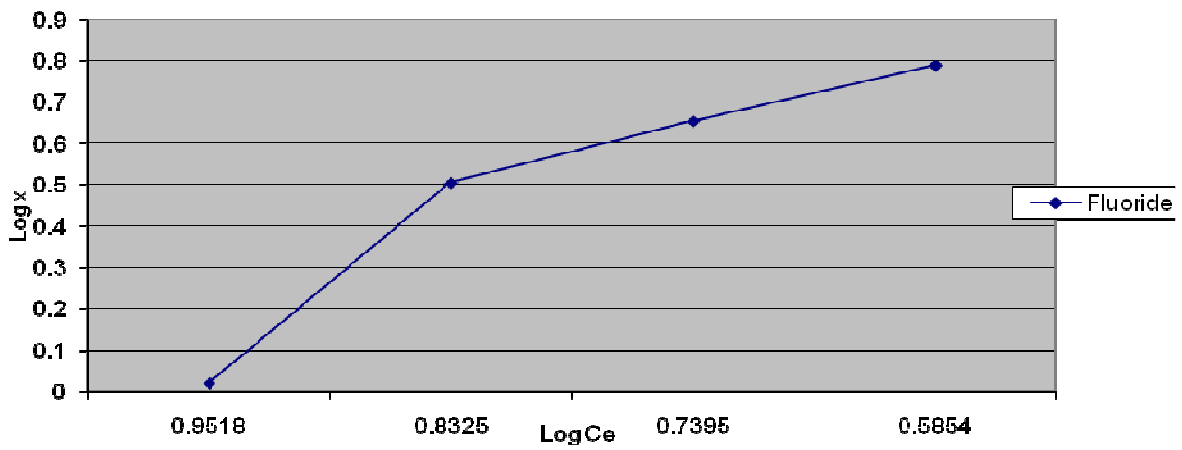
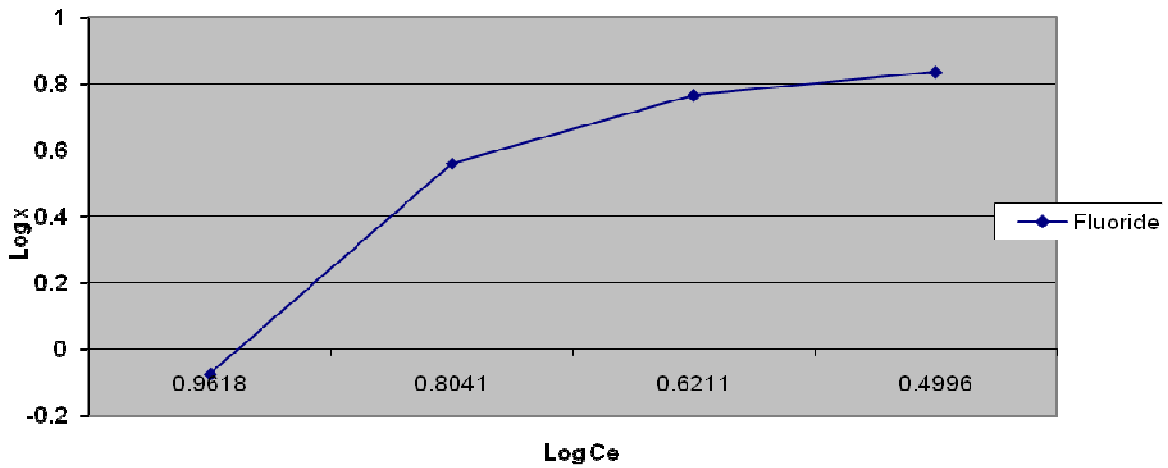


Fig 12 Linear Freundlich plot of fluoride ions on soil pot no 4.



MATERIALS AND METHODS

Following materials and methods were used in this research work.

Soil : Geometric mean size 0.154 (mm); Bulk density 2.1 (g/cm³); Surface area 13.265 (m²/g); Pore Value 0.011 (cm³/g); Al 0.011 (ppm); Fe 19.6 (ppm); Zn 0.9 (ppm); Cu 1.80 (ppm) ; pH 7.9; Biological Carbon 0.22 (%); Available Phosphorus 90 (kg/hector); Potash \geq 337 (kg/hector); Electric Conductivity (E.C.) 0.38 (mM/cm).

Stock fluoride solution: - Orion 940907 fluoride stock solution was used.

Standard fluoride solution: - Dilute 100 ml stock solution to 1000 ml with distilled water
1000 ml: 10 ppm F⁻.

TISAB - III (Total ionic strength adjustment buffer): - Orion 940911 TISAB III (concentrate with CDTA) was used.

Sodium Fluoride: A.R. sodium fluoride is used for preparation for standard fluoride solution.

Aluminum Ammonium Sulphate: - A.R Aluminum Ammonium Sulphate was used to prepare soil pots.

Ion Meter: - Orion 720A⁺ ion meter was used to determine the concentration of fluoride[20].

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 ammonium sulphate, 2gm, 4gm, 6gm and 8gm.per kg in soil respectively (Fig.2). After some time, 10ppm fluoride standard solution was taken in each soil pots and then determined theirs 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.Flow chart of adsorbent (soil pots) preparation and fluoride adsorption onto soil pots shown in Fig-3.

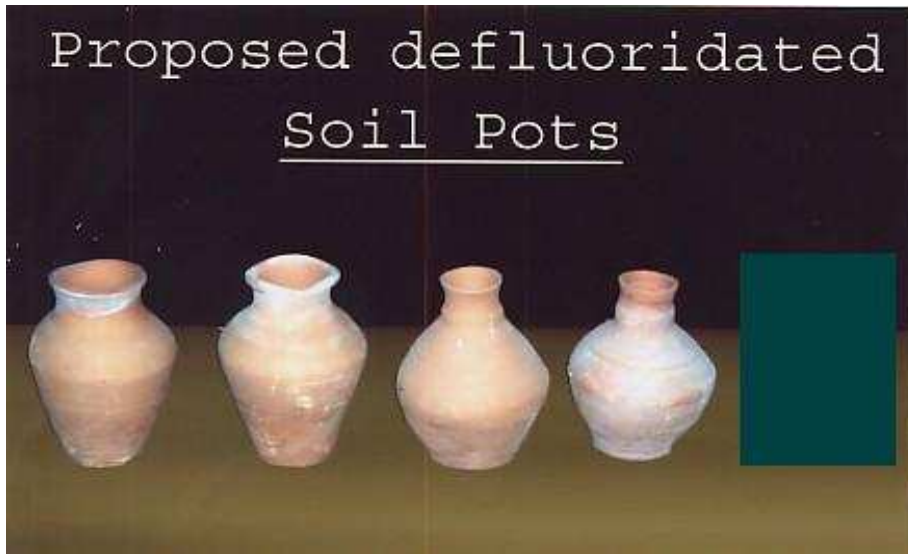


Figure 2. Proposed Soil Pots

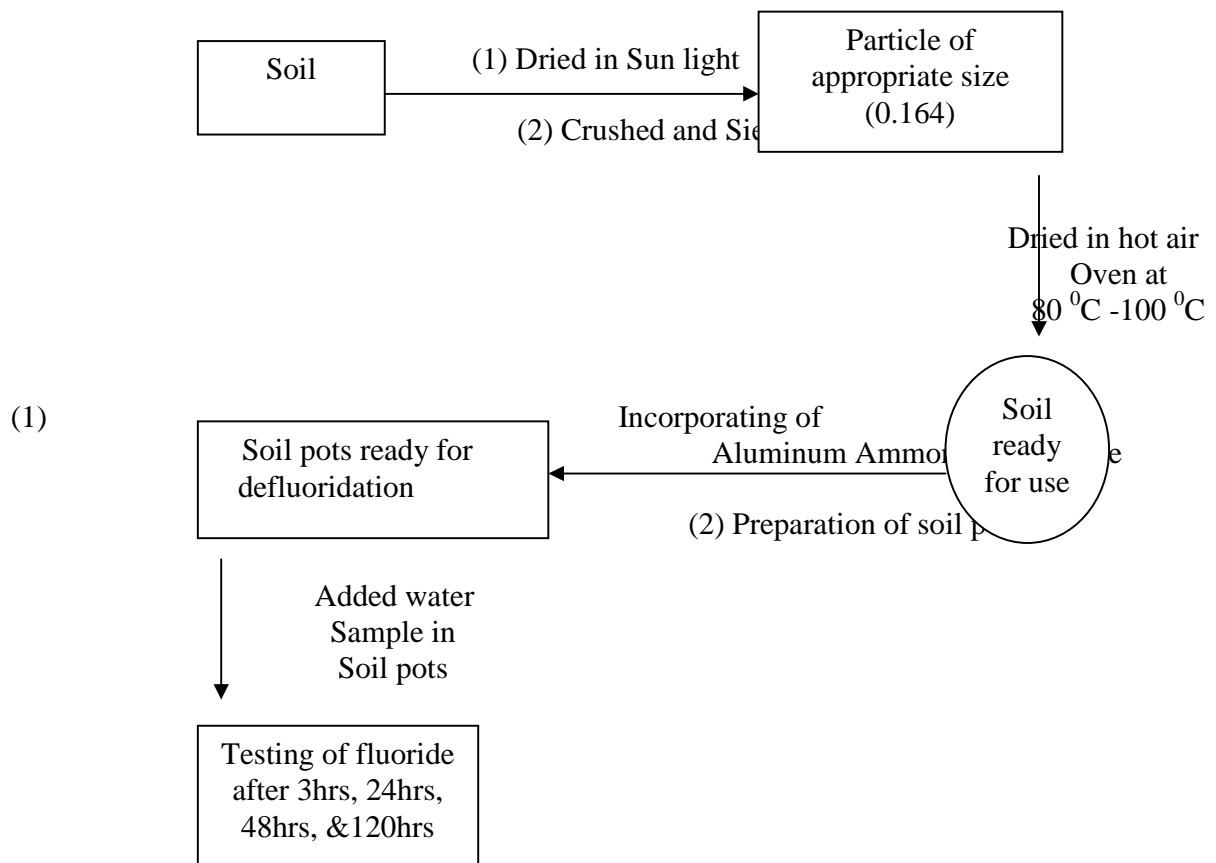


Figure 3. Flow chart of Adsorbent (Soil pots) preparation and Fluoride Adsorption onto soil pots.

RESULTS AND DISCUSSION

Table-1 reveals that the fluoride concentration of drinking water sample (10ppm) decreases in the all soil pots with increasing amounts of aluminum ammonium sulphate with time. It was found that soil pot No-1 (having 2gm Aluminum Ammonium Sulphate), decrease the fluoride concentration of the water sample about 61% but in case of soil pot No-4 (having 8gm Aluminum Ammonium Sulphate), the concentration of fluoride decrease about 68% 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 up to form a unimolecular layer (Langmuir isotherm limitation) of adsorbent during chemisorption process. Result shows that a certain amount of Aluminum Ammonium Sulphate reduces the fluoride concentration in water sample.

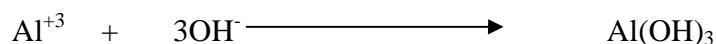
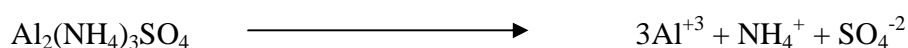
Table 1 Aluminum Ammonium Sulphate in soil pots as defluoridating agents.

Soil pots No.	Aluminum Ammonium Sulphate in soil pots (gm/kg soil)	Initial con ⁿ 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/l	8.62	5.25	5.63	3.84
2	4 gm	10mg/l	9.03	7.16	5.66	4.04
3	6 gm	10mg/l	8.95	6.80	5.49	3.85
4	8 gm	10mg/l	9.16	6.37	4.18	3.16

(Temp: 20±5⁰C, pH: 7.0±0.5)

The removal of fluoride from water sample (10ppm) is expected due to the formation of polyhydroxide aluminum complex (e.g. [Al(H₂O)₃(OH)₃][Al(H₂O)₂(OH)₄]etc) with fluorides and adsorption/absorption of fluoride on polymeric Aluminum Ammonium Sulphate.

Following reaction are proceeds in soil pots:



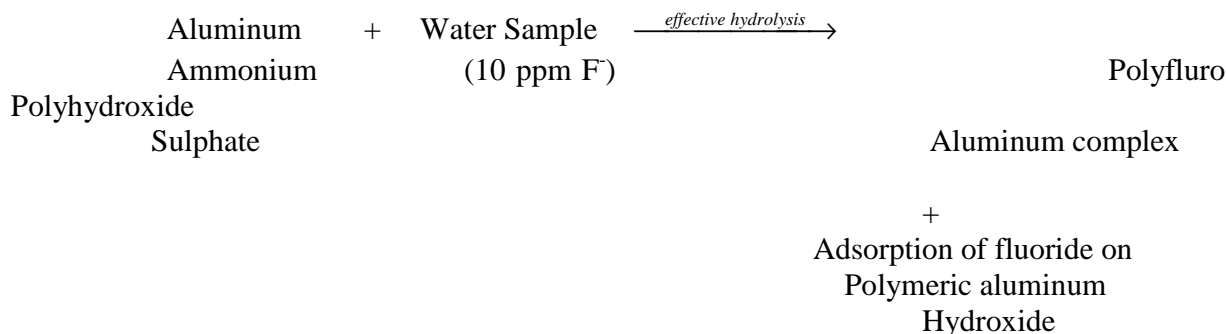


Table 2 Adsorption of fluoride in different soil pots

Soil pots No.	Aluminum Ammonium Sulphate in soil pots (gm/kg soil)	Initial con ⁿ 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/l	1.38	4.75	4.37	6.16
2	4 gm	10mg/l	0.97	2.84	4.34	5.96
3	6 gm	10mg/l	1.05	3.20	4.51	6.15
4	8 gm	10mg/l	0.84	3.63	5.82	6.84

(Temp: 20±5⁰C, pH: 7.0± 0.5)

Adsorption Isotherm Study

The adsorption isotherm of fluoride ions from water sample at pH 7.0± 0.5 on surface of different soil pots with time are presented in Fig: 4. In order to investigate the maximum adsorption capacity of Aluminum Ammonium Sulphate 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 7.0± 0.5 and tested at the interval of 3 hrs, 24 hrs, 48 hrs and 120 hrs at temperature 20 ± 5⁰c.

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 Fig- (5-8) and the Langmuir equation constant K and x_m calculated from the linear plots are recorded in Table-4

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

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

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 Linear Freundlich isotherm model are shown in Fig- (9-12) by plotting $\text{log } x / \text{log } C_e$. The constant values of the both isotherm for each soil pot are given in Table-4. 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 Ammonium Sulphate 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 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 Langmuir and Freundlich equation constants for adsorption of fluoride ions on different soil pots

Quantity of Aluminum Ammonium Sulphate in soil pot	Langmuir equation constants	Freundlich equation constants
	$x_m(\text{mg/g})$ k	n k_f
2 gm	1.6469 0.3380	-1.6611 152.11
4 gm	1.1270 0.2741	-2.3560 4557.50
6 gm	1.2733 0.2957	-2.1263 1428.77
8 gm	1.7142 0.3744	-1.8447 1107.67

CONCLUSION

Isotherm of fluoride ions follows the mixed model of the Langmuir as well Freundlich isotherm. The adsorption takes place on certain specific site in soil pot. Result shows that Aluminum Ammonium Sulphate may be used in earthenware (soil pots) to reduce the fluoride concentration in the potable water.

Acknowledgement

Authors thank University Grants Commission, Govt. of India for the financial help under its project no. 32-295/2006(SR) and to the Department of Chemistry, R.R.Govt. (P.G.) College, Alwar for academic facilities during this work. The authors are also thankful to Dr.M.P.S. chandrawat. Sh.K.C pande, Dr.V.S.Yadav, Rajesh Yadav, Sh.M.S.Aswal for their cooperation during the progress of this work.

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