Int. J. Chem. Sci.: 7(2), 2009, 760-774

DEFLUORIDATION OF THE POTABLE WATER BY ALUMINUM SULPHATE

R. N. YADAV* **and RAJDEEP YADAV**

Centre for Applied Research, Deptt. of Chemistry, R. R. Govt. (P. G.) Autonomous College,
ALWAR -301001 (Raj.) INDIA

ABSTRACT

Presence of fluoride in drinking water above (and some times even below) permissible limits (1.5 ppm accordingly to WHO) leads to fluorosis. Aluminum fluoride is less toxic than other fluorides. In this study, $Al_2(SO_4)_3$, was incorporated in different amounts in soil and prepared soil pots by the mixture. It was noted that these soil pots had remarkably decreased the concentration of fluoride in drinking water. Aluminum sulphate may be used as a defluoridating agent in drinking water earthenware (soil pots). Langmuir and Freundlich isotherm study were also carried out.

Key words : Adsorption, Aluminum sulphate, Defluoridating, Fluoride, Fluorosis, Earthenware.

INTRODUCTION

The first case of endemic fluorosis in India was reported from Andhra Pradesh in 1937[1, 2]. 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[3, 4]. Fluorine reacts with metallic elements to form compounds 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[5-7]. Fluoride content present in drinking water causes various health problems when the concentration of fluoride is greater than 1.5 ppm (According to WHO). The prolonged intake of water containing excess of fluoride causes the crippling disease called fluorosis (Skeletal and dental fluorosis).

---

* Author for correspondence; E-mail: yadav_rama62@yahoo.co.in;
E-mail: rajdeep.yadav@rediffmail.com

At least 17 Indian states including Rajasthan have been identified as having excess fluoride in drinking water. All the 33 districts in Rajasthan are endemic for fluorosis. 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[8] (Fig. 1). 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. A part 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.[2]

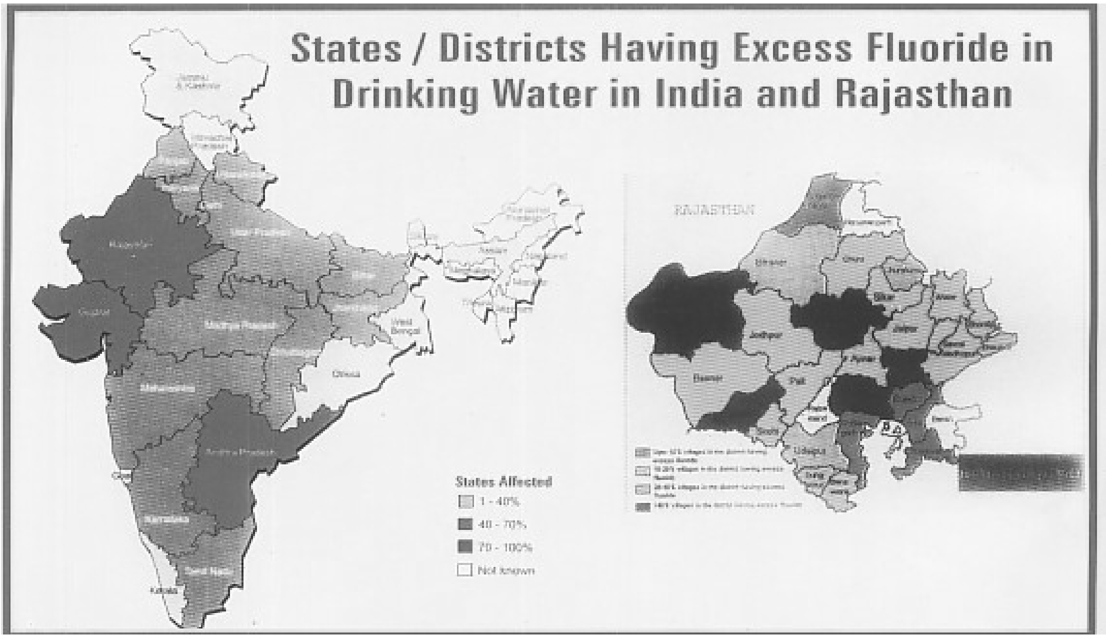

Fig. 1: Picture showing states/districts having excess fluoride in drinking water in India and Rajasthan

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[2,4,8]. Although several methods, such as lime treatment, alum coagulation, Nalgonda technique, 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 electro coagulation-flotation process[10]. Treatment method of high fluoride content wastewater by continuous electro coagulation-flotation system with bipolar aluminum electrode is found out[10]. Laterite soil, the geometrical is used as adsorbent for the removal of fluoride from drinking water by Sarkar et al.[11].

Thus, the attention has shifted to prepare soil pots after uniform incorporation of aluminum sulphate, which has large surface area and a high degree of surface activity. Therefore, in present paper, authors have used aluminum sulphate as defluoridating agents in soil pots of drinking water and developed a new defluoridation method.

EXPERIMENTAL

Materials and methods

Characteristics and composition of soil

Following characterized soil was used : Geometric mean size 0.154 mm; Bulk density 2.1 g/cm^3; Surface area 13.265 m^2/g; Pore value 0.011 cm^3/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 ≥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 sulphate : A. R Aluminum sulphate was used to prepare soil pots.

Characteristics of aluminum sulphate

Molecular formula - $Al_2(SO_4)_3 \cdot 16H_2O$; Molar mass - 342.15 g/mol as anhydrous salt; Appearance - white crystalline solid; Density - 2.672 g/cm^3, solid; Melting point - 770ºC decomp.; Solubility in water- 870 g/L.

Ion meter : Orion 720A$^+$ ion meter was used to determine the concentration of fluoride.

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 sulphate, 2 g, 4 g, 6 g and 8 g. per kg in soil respectively (Fig. 2).

Fig. 2 : Proposed defluoridated soil pots

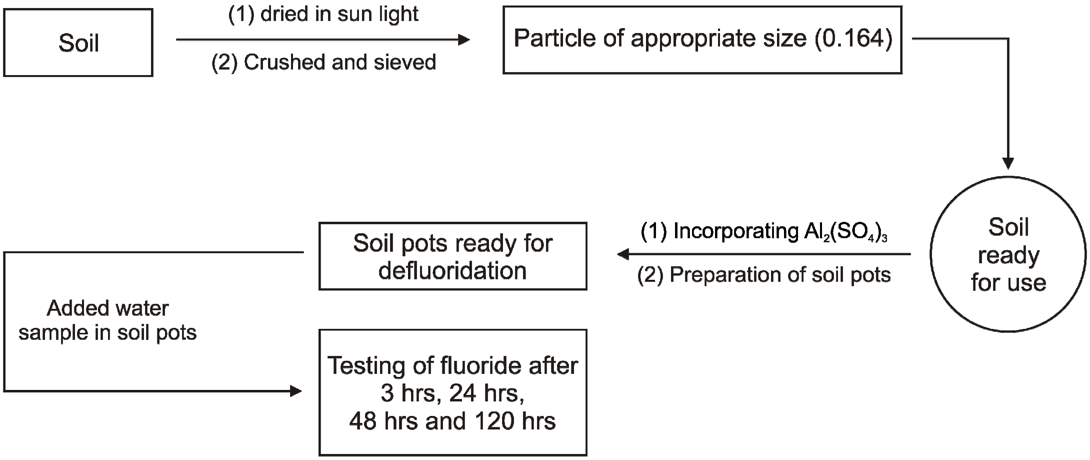

Fig. 3: Flow chart of absorbent (soil pots) preparation and fluoride adsorption onto soil pots

After some time, 10 ppm fluoride standard solution was taken in each soil pots and then their fluoride concentration was determined after 3 hrs, 24 hrs, 48 hrs and 120 hrs time interval by Orion 720 A^+ ion meter using fluoride ion selective electrode. Results are shown in Table 1. Flow chart of adsorbent (soil pots) preparation and fluoride adsorption onto soil pots shown in Fig. 3.

RESULTS AND DISCUSSION

Table 1 reveals that the fluoride concentration of drinking water sample (10 ppm) decreases in the all soil pots with increasing amounts of aluminum sulphate and with time periods. The soil pot No. 4 (having 8 g $Al_2(SO_4)_3$), reduces the concentration of fluoride about 40% in 120 hrs and soil pot No. 1 reduces the fluoride concentration about 2.68%. According to surface chemistry that more is 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. Results show that a certain amount of aluminum sulphate reduces the fluoride concentration in water sample.

Table 1. Effect of aluminum sulphate in soil pots as defluoridating agents (Temp : 20 ± 5^0C, pH : 7.0 ± 0.5)

Soil pot No.	$Al_2(SO_4)_3$ in soil pots (g/kg soil)	Initial conc. of F^- in water sample (mg/L)	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 g	10	9.39	8.53	8.04	7.32
2	4 g	10	8.99	8.19	7.59	6.77
3	6 g	10	8.5	7.86	7.39	6.59
4	8 g	10	8.1	7.56	7.2	6.45

The removal of fluoride from water sample (10 ppm) is expected due to the formation of polyhydroxide aluminum complex (e. g. $[Al(H_2O)_3(OH)_3]$ $[Al (H_2O)_2(OH)_4]$ etc.) with fluorides and adsorption/absorption of fluoride on polymeric aluminum sulphate.

Following reactions proceed in soil pots :

$$Al_2(SO_4)_3 + H_2O \longrightarrow 2\,Al^{3+} + OH^- + H^+ + 3\,SO_4^{2-} \qquad ...(1)$$

$$Al^{+3} + 3F^- \longrightarrow AlF_3 \text{ (Adsorption and insoluble fluoride)} \qquad ...(2)$$

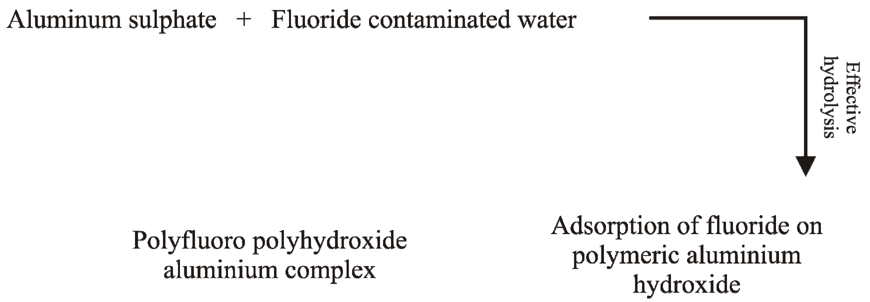

Table 2. Adsorption of fluoride in different soil pots

Soil pot No.	$Al_2(SO_4)_3$ in soil pots (g/kg soil)	Initial Conc. of F^- in water sample (mg/L)	Fluoride adsorbed (mg/L)			
			After 3 hours (x)	After 24 hours (x)	After 48 hours (x)	After 120 hours (x)
1	2	10	0.61	1.47	1.96	2.68
2	4	10	1.01	1.81	2.41	3.23
3	6	10	1.5	2.14	2.61	3.41
4	8	10	1.9	2.44	2.8	3.55

(**Temp** : 20 ± 5°C, pH : 7.0 ± 0.5)

Table 3. Characteristics of water sample

Parameters	Quantitative value
pH	7.88
Turbidity (NTU)	0.7
Hardness (mg/L)	400
Fluoride (ppm)	10
T. D. S (mg/L)	1198
Al (ppm)	0.1727

Study of Langumir and Frendlich isotherms

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 sulphate towards fluoride, Langmuir and

Freundlich isotherm studies were conducted. The adsorbent dose was varied in the range of 2 g to 8 g 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 ± 5ºC.

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

$$x / x_m = K\, C_e / 1 + K\, C_e \qquad \ldots(3)$$

Where x is the amount adsorbed at equilibrium concentration, C_e and x_m is the maximum amount adsorbed and 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:

$$C_e / x = 1 / K\, x_m + C / x_m \qquad \ldots(4)$$

The linear Langmuir plots between C_e/x and C_e are shown in Figs. (5-8) and the Langmuir equation constant K and x_m calculated from the linear plots are recorded in Table 4.

Table 4. Langmuir and Freundlich equation constants for adsorption of fluoride ions on different soil pots

Quantity of $Al_2(SO_4)_3$ in soil pot	Langmuir equation constants		Freundlich equation constants	
	x_m(mg/g)	k	n	k_f
2 g	0.2634	-0.1464	-5.7915	84294913.05
4 g	0.4252	-0.1636	-2.5862	27010.48
6 g	0.5396	-0.1728	-3.1651	5782.15
8 g	0.7022	-0.1881	-2.8367	1251.30

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

$$\log x = \log\ k_f + n \log c_e \qquad \ldots(5)$$

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 depend on the nature of the adsorbent and adsorbate.

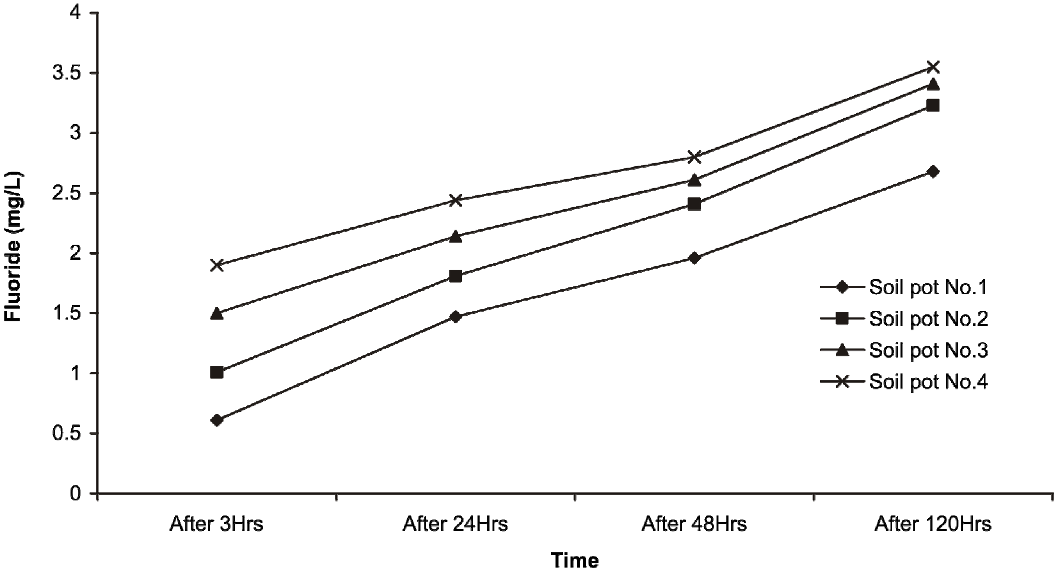

Fig. 4: Adsorption of fluoride by different soil pots as function of time

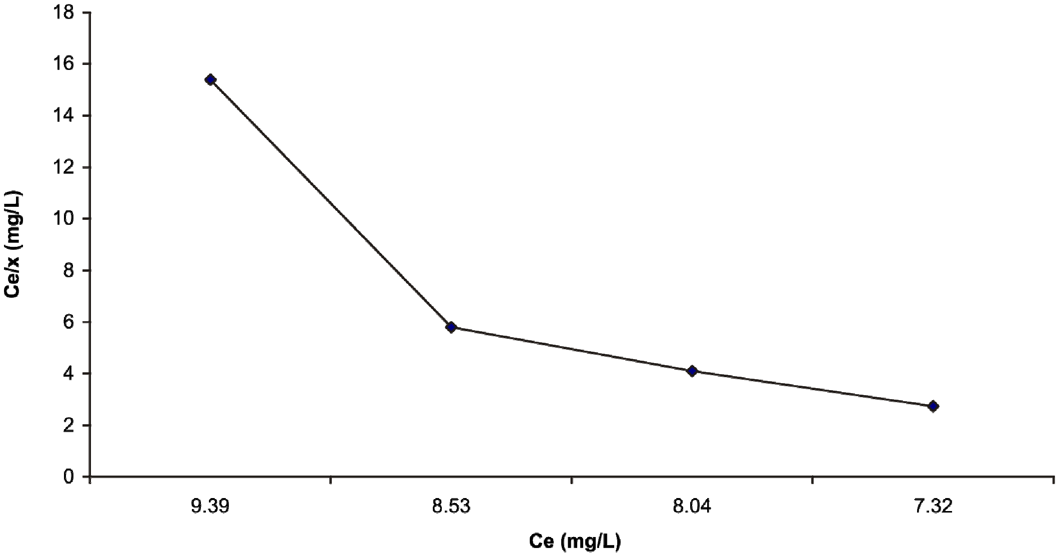

Fig. 5: Linear Langmuir plot of fluoride ions on soil pot No. 1

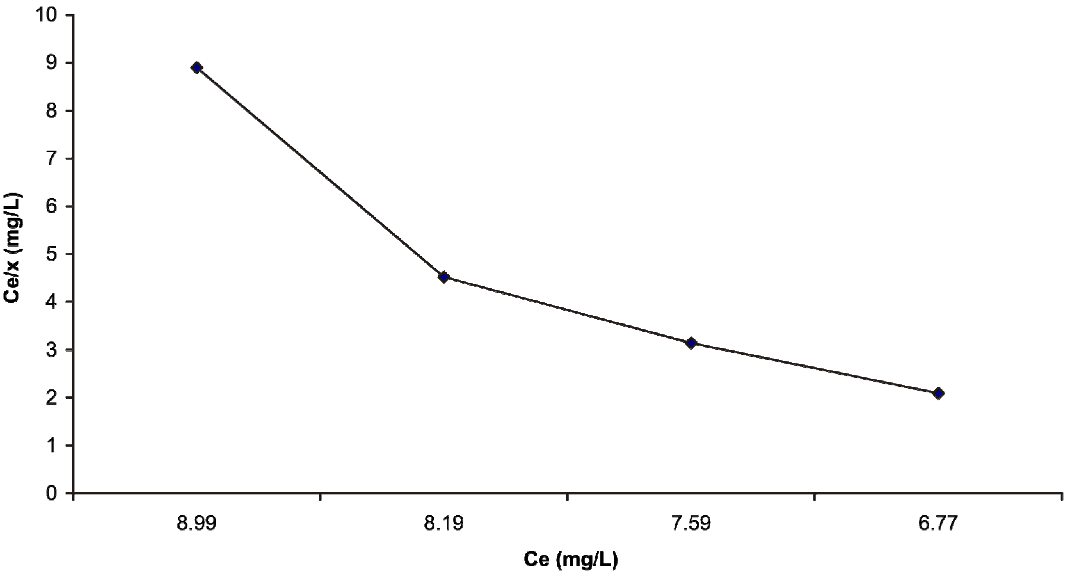

Fig. 6: Linear Langmuir plot of fluoride ions on soil pot No. 2

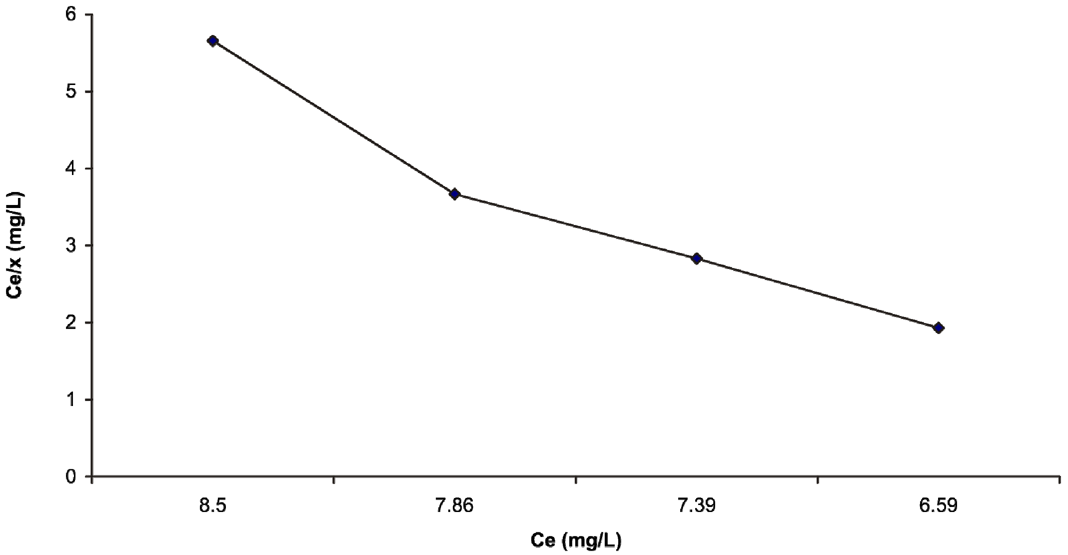

Fig. 7: Linear Langmuir plot of fluoride ions on soil pot No. 3

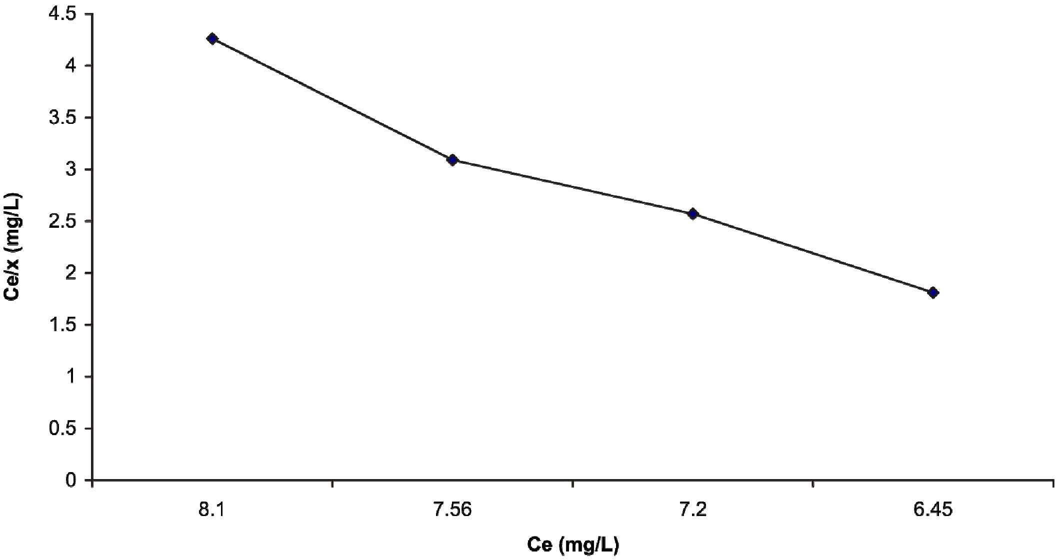

Fig. 8: Linear Langmuir plot of fluoride ions on soil pot No. 4

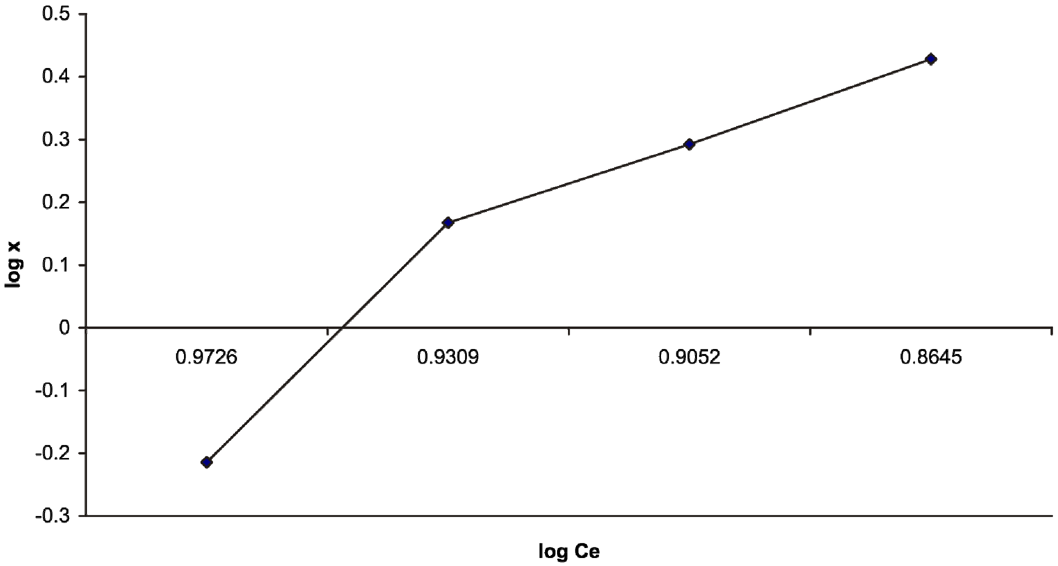

Fig. 9: Linear Freundlich plot of fluoride ions on soil pot No. 1

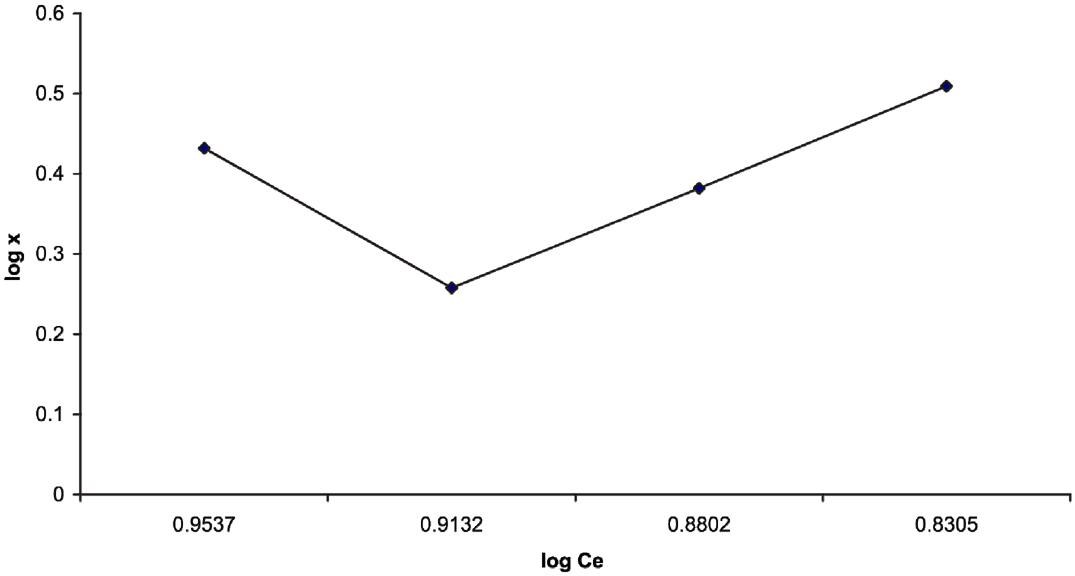

Fig. 10: Linear Freundlich plot of fluoride ions on soil pot No. 2

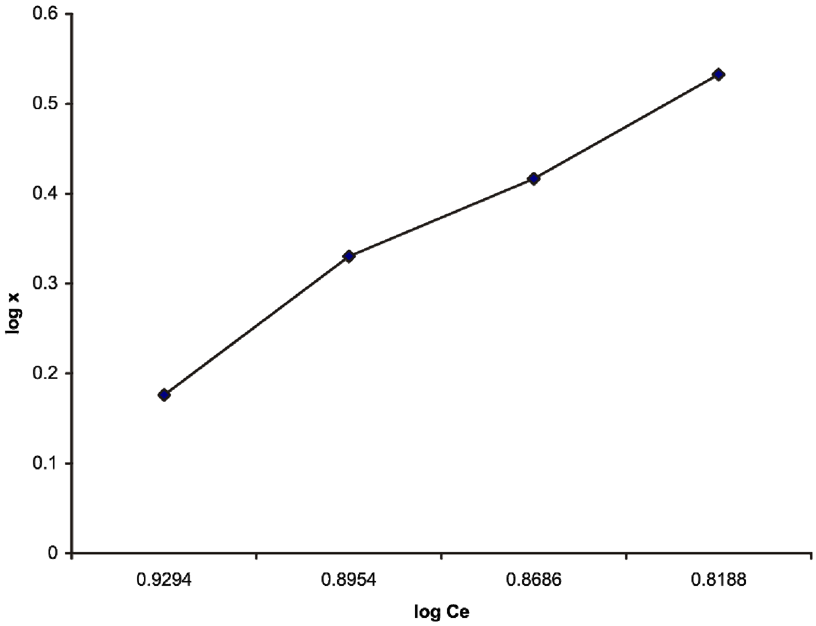

Fig. 11: Linear Freundlich plot of fluoride ions on soil pot No. 3

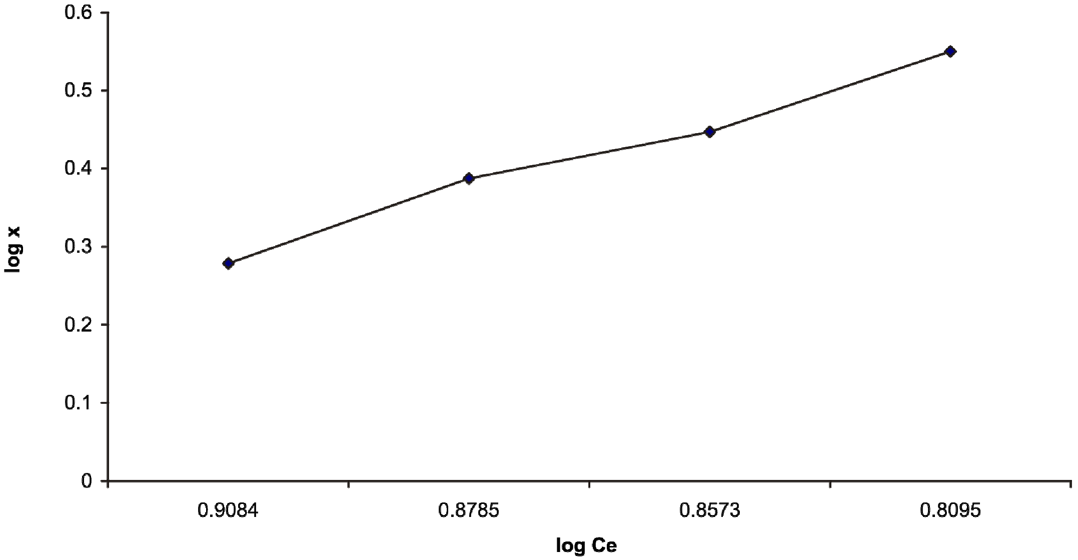

Fig. 12: Linear Freundlich plot of fluoride ions on soil pot No. 4

The linear Freundlich isotherm model are shown in Figs. 9-12 by plotting log x / log Ce. The constant values of the both isotherms for each soil pot are given in Table 4. It is observed from both the curves and correlation coefficient data that 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 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 takes 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 equations.

CONCLUSIONS

Adsorption isotherm of fluoride ions follows the mixed model of the Langmuir and Freundlich isotherms. The adsorption does not depend on the BET surface area of the pots and takes place on certain specific sites. Results shows that aluminum sulphate 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.

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. O. P. Singh, Dr. V. S. Yadav, Rajesh Yadav and Dr. Upendra Singh for their cooperation during the progress of this work.

REFERENCES

1. M. P. S. Chandrawat, S. Karwasara and R. N. Yadav, Fluoride, **38(3)**, 258 (2005).
2. Rajiv Gandhi National Drinking Water Mission, Prevention and Control of Fluorosis in India, Ministry of Rural Development, New Delhi, **I,** 24-40 (1993).
3. Fluoride and Fluorides Environmental Health Criteria 36 WHO Report, Geneva, 21-23, 63 (1984).
4. W. H. O., Fluoride and Human Health, W. H. O. Monograph Series No. 59, Geneva (1970).
5. V. N. Alexeyev, Qualitative Chemical Semimicro Analysis, P. K. Agasyan (Ed.), Mir Publishers, Moscow, USSR, 129820 Moscow, (1973) p. 110.
6. K. R. Balusu, Defluoridation of Water Using Combination of Aluminum Sulphate, J. Institution of Engineers, India, EVN. Engg, **65**, 25-29. (1984).
7. Vogel's Qualitative Inorganic Analysis, 6th Ed. Revised, Orient Longmann Ltd., (1989) p. 180.
8. R. N. Yadav, Fluoride and its Impact on Human Beings - A Report Proceeding of State Seminar on Excess Fluoride in Potable Water and its Associated Health Hazards (4-5 August, 2006).
9. National Environmental Engineering Research Institute, Defluoridation, Nagpur, (1987) 5, 9.
10. C. Y. Hu, S. L. Lo, W. H. Kuan and Y. D. Lee, Removal of Fluoride from Semiconductor Waste Water by Electro Coagulation-Flotation, Water Research, **31** (5), 895-901 (2005).
11. Mitali Sarkar, Aparna Banerjee, Partha Pratim Pramanick and Asit Ranjan Sarkar, Design and Operation of Fixed Bed Laterite Colum for the Removal of Fluoride from Water, Chem. Engg. J., **131** (1-3), 329-335 (2007).

12. E. D. B. Douglas and M. H. Dari, Concepts and Model of Inorganic Chemistry, **3rd** Ind. Reprint**,** Gulab Pirmlani, Oxford and IBH Publishing CO. Park Hotel Building, 17, Park Street Calcutta 700016, 225 (1976).

13. R. K. Gangal, The Level and Distribution of Fluoride in the Water Resources of Four States of India and its Removal by Nanofilatration, Fluoride, **40** (4), 259-292 (2007).

14. R. K. Gangal, Fluoride, **38 (**3), 241 (2005).

15. G. Ya-Ming, N. Rui-Yan, W. Chun-Xiang, S. Zi-Long and W. Jun-Dong, Effects of Fluoride and Related Factors on the Nervous System, Fluoride, **40** (4), 259-292 (2007).

16. M. Goyal and R. Amutha, Adsorption of Hg (II) Ions from Water by Activated Carbons, Res. J. Chem. Environ, **12** (1), 76-83 (2008).

17. J. D. Lee, Concise Inorganic Chemistry, 5th Edition ELBS, (1996) p. 587.

18. M. H. Trivedi, R. J. Verma, N. J. Chinoy, R. S. Patel and N. G. Sathawara, Effect of High Fluoride Water on Intelligence of School Children in India, Fluoride, **40** (3), 178-183 (2007),

19. M. Murugan and E. Subramanian Studies on Defluoridation of Water by Tamarind Seed, An Unconventional Biosorbent, J. Water Health, **04,** 453-461 (2006).

20. Sanjoy Kumar Maji, Anjali Pal and Tarasankar Pal, Arsenic Removal Household Filter for Small Community, Res. J. Chem. Environ, **12** (1), 23-32 (2008).

21. V. Raman, Endowment Lecture by A. K. Susheela in the 38th Annual Convention of Ind. Water Works Association (IWWA), Jaipur (2006).

22. J. D. Sharma, Fluoride, **38** (3), 249 (2005).

23. J. L. Sharma and P. L. Buldini, A Dictionary of Pollution, CBS Publishers and Distributors (P) Ltd., New Delhi (1994).

24. Standard Methods for the Examination of Water and Waste Water, 17th Edition, American Public Health Association, Apha, New York, U. S. A. (1989).

25. A. K. Susheela, IAHS, Publisher, 233, 123-134 (1995).

26. A. K. Susheela, Treatise on Fluorosis Published by Fluorosis Research and Rural Development Foundation, 3rd Revised Edition, Delhi. (2006).

27. A. K. Susheela, Doctor's Handbook on Fluorosis, **1st** Edition, (2005).

28. A. K. Susheela, M. Bhatnagar, K. Vig and N. K. Mondal, Excess Fluoride Ingestion and Thyroid Hormone Derangements in Children Living in Delhi, India, Fluoride, **38** (2), 98-108 (2005).

29. M. Tripathi, Everyman's Science, **XLI,** 340 (Dec. 06 - Jan. 07).

30. Frank Welcher I and B. Hahnn Richard, Semimicro Qualitative Analysis, East-West Edition, 2nd Reprint. Affiliated East - West Press Pvt. Ltd., New Delhi, (1969) p. 317.

31. R. N. Yadav and Rajdeep Yadav, Assessment of Fluoride Content, pH and T. D. S. in Potable Water of Alwar City (Raj), Research J. Chem. Environ. (Communicated)

Accepted : 12.01.2009