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FLUORIDE CONTAMINATION IN DRINKING WATER: A HEALTH RISK

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Abstract: - Today fluoride contamination is endemic in many parts of the world. Fluoride is essential for building teeth & bones up to a small level. Long term exposure of high fluoride content in drinking water has serious health effects viz. dental, skeletal and non-skeletal fluorosis. Defluoridation of drinking water has an environmental application as it is the most feasible method. This review paper describes occurrence and sources of fluoride, its clinical manifestations and its mitigation strategies. The paper also reviews more than 80 references covering the wide scale of defluoridation techniques and provides precise information regarding different fluoride removal techniques investigated by various researches. Recent developments in the field of water defluoridation have also been discussed.

Keywords: Adsorption, Defluoridation, Electro dialysis, Fluorosis, Membrane Process, Reverse Osmosis

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INTRODUCTION

Water is referred to as free gift of nature which is essential for sustaining life on earth. It is well known that about 70% of the earth's surface is covered with water. About 2.5% of it is fresh water. Fresh water occurs as surface water, groundwater and 2/3rd of it is frozen in ice caps and glaciers. Moreover only 0.01% of the total water on earth is accessible for consumption. Our needs are met preferably by groundwater. It contains variety of substances in different concentrations,[1,2] as it has ability to dissolve almost all substances. Fluoride is one of them. People using groundwater with high content of fluoride is affected by fluorosis and become crippled. This has become an alarming situation in India. So we need to have an idea of fluoridated sources, its manifestations and mitigating strategies. This paper comprises a review on fluoride, its effect -fluorosis and its removal techniques.

FLUORIDE AND ITS STANDARDS

Fluorine is the 13th most abundant element in the earth's crust with atomic weight 18.998 and atomic no. 9.[3] It has high affinity to combine with other elements as it is most electronegative and highly reactive.[4,5] Fluoride can be determined qualitatively by SPANDNS (sodium-2-parasulphophenylazo-1,8-dihydroxy-3,6-naphthalenedisulphonate) method and quantitatively by ion meter using F^- ion selective electrode.

Presentation of water quality standards was first made by USPHS in 1914. In 1964 USPHS suggested 0.7- 1.2 mg/L as permissible limit of F^- ion.[6] According to ICMR the highest desirable limit of F^- in drinking water is 1.0 mg/L.[7] However, WHO has fixed the maximum permissible F^- ion concentration in drinking water to 1.5 mg/L.[8,9] The same was suggested by Bureau of Indian Standards (BIS) in 1997.[10] But this doesn't mean that it is safe. Whether F^- level in drinking water is hazardous depends on many other factors also viz. nutrition, temperature etc. Fluoride is an essential microelement which is considered beneficial for human health,[11] however its higher concentration is harmful. Thus water having F^- beyond desirable range (below or above) causes detrimental effects.

OCCURRENCE

Fluorosis is wide spread in the world. Algeria,[12] Morocco, Argentina, Thailand, Kenya,[13] Turkey,[14,15] China, Senegal, USA, Japan, Iran,[16] Iraq, Tanzania,[17] Australia, Egypt, Saudi Arabia,[18] Syria, Jordan, South Africa, New Zealand, Persian Gulf, India etc. are the nations where fluorosis is prevalent. Fluorosis is one of the serious health problems that are endemic in India. Andhra Pradesh, Bihar, Gujarat, Karnataka, Madhya Pradesh, Maharashtra, Punjab &

Haryana, Rajasthan, Tamil Nadu, Uttar Pradesh etc. are the different parts of the country which have been reported having fluoride contaminated water.

As per WHO report, 20% of the fluoride affected villages in the whole world are in India. Out of 33,211 fluoride affected villages in the country Rajasthan has 16560 villages, which is more than 51%. That means nearly 10% of the F^- affected habitations in the world is in the Rajasthan alone.[19] Fluorosis is wide spread in these villages.[20,21] According to state profile, groundwater scenario of Rajasthan given by groundwater department Ajmer, Alwar, Banswara, Barmer, Bharatpur, Bhilwara, Bikaner, Bundi, Chittorgarh, Churu, Dausa, Dhaulpur, Dungarpur, Ganganagar, Hanumangarh, Jaipur, Jaiselmer, Jalore, Jhunjhunu, Jodhpur, Karauli, Kota, Nagaur, Pali, Rajasamand, Sirohi, Sikar, Sawaimadhopur, Tonk and Udaipur are the districts having f^- > 1.5mg/L in the groundwater. In the state 90% of the drinking water supply source is groundwater.[22] Ajmer – Mewar was first reported as endemic region by Shourie.[23] Gopal et al studied physicochemical characteristics of 1300 ground water samples collected from four arid districts Barmer, Jaiselmer, Bikaner and Jodhpur. Fluoride range of the samples is shown in the table 2.[24,25]

District	Barmer	Jaiselmer	Bikaner	Jodhpur
F^-(mg/L)	0.2 - 10.9	Traces - 8.0	Traces - 20.0	Traces - 11.2

Hussain et al examined 44 groundwater samples from Nawa block of Nagaur district. About 56% samples were having F^- more than 1.0 mg/L.[26] All districts of Rajasthan are known to be endemic for fluoride and having fluoride concentration range from 0.2 to 37.0 mg/L.[27] Geologically there is a belt underneath Aravali range that is rich in fluorspar, cryolite and fluoroapetite.[23] Many other workers stated that groundwater is contaminated with high fluoride content in Rajasthan.[28-31] In a survey conducted in 18 districts of the state highest no. of non-skeletal cases were found in Jodhpur (2262), Churu (1325) and Jaipur (1068). Out of 2,76 lac people on which the tests were conducted by the health department, 90122, 17,160 and 4850 people were found as suspected cases of dental fluorosis, skeletal fluorosis and non-skeletal fluorosis respectively.

SOURCES OF FLUORIDE:

The safe limit of F^- in drinking water is 1.0 mg/L. Drinking water having high F^- content is the major source of fluoride which causes deleterious health effects. We need to have an alternate

source of water if our water supply is having fluoride concentration beyond desirable limit. Although drinking water is the major source of fluoride intake but it is not the only one. There are other sources too viz. cosmetics, drugs, food etc. through which fluoride is ingested into the body. Some such food materials are summarized in the table below.

Table: Fluoride concentration in some food materials[32]

Food item	fluoride concentration (mg/kg)	Food item	fluoride concentration (mg/kg)
Wheat	4.6	Mango	3.7
Rice	5.9	Apple	5.7
Pulses legumes	5.6	Guava	5.1
Green gram dal	2.5	Almond	4.0
Red gram dal	3.7	Coconut	4.4
Soya bean	4.0	Mustard seeds	5.7
Cabbage	3.3	Groundnut	5.1
Tomato	3.4	Tea	60-112
Cucumber	4.1	Coriander	2.3
Lady finger	4.0	Garlic	5.0
Spinach	2.0	Turmeric	3.3
Lettuce	5.7	Rock salts	200-250
Mint	4.8	Areca but (supari)	3.8-12
Potato	2.8	Beetle leaf (pan)	7.8-12
Carrot	4.1	Tobacco	3.2-38

Drugs which are used in the treatment of rheumatoid arthritis, osteoporosis cause adverse effects on patients due to presence of fluoride in them. Use of phosphate containing fertilizers increases fluoride content in soil and thereby in crops also.[33] It also increases fluoride content in groundwater and surface water indirectly through agricultural runoff.

IMPACTS ON HEALTH: FLUOROSIS

The clinical manifestations of excess fluoride intake are known as Fluorosis in consolidated form. It may be of three kinds – Dental, skeletal and non- skeletal. The incidence of mottled enamel was first reported in 1930 by Anderson and Stevenson in China.[34] Vishwanathan reported similar disease in India very first in 1933.[35] However the disease was identified as fluorosis by Schortt.[36] Fluoride reacts with hydroxyapatite which is major constituent of tooth enamel,[37] displaces OH^- ion and forms fluoroapetite thereby increasing tooth strength and resistance.[38,39] Moreover on prolonged consumption of fluoride contaminated water it leads to dental fluorosis.[40] It starts as shine loss, yellow discoloration and turns into brown horizontal steaks to black tooth.[41] Eventually tooth becomes brittle. This is endemic among children in developing tooth stage.

Fig. various stages dental fluorosis

Fig: skeletal fluorosis

Fluoride also gets deposited in joints of bones leading to skeletal fluorosis. Pain and stiffness in joints are the most common and primary symptoms of the disease. Later calcification occurs which gradually reduces movement. The spine vertebrae stick together and patient is left crippled. Unfortunately it is not easy to recognize it in early stage. Besides teeth and bones excessive fluoride intake may also badly affect other body parts and systems. Non skeletal effects may be gastrointestinal, neurological, may be related to respiratory system, blood circulation system etc. Swollen joints, systematic rigidity, muscular tenderness etc are some symptoms of non-skeletal fluorosis. Chauhan et.al reported that even semen quality is reduced due to over exposure to fluoride.[42] It doesn't affect human only, animal may also be a victim of this non skeletal fluorosis.[43,44]

MITIGATION:

We have to have an alternate source of water with low fluoride concentration. Rain water harvesting is the best option for this. Nutritious food is another preventive measure to the problem, as it is observed that mal nutrition is a factor that makes people susceptible to fluorosis. Calcium and Vitamin C rich food is useful in preventing form fluorosis. Besides this, creating awareness among people regarding this disease thereby avoiding use of fluoride rich food, cosmetics, beverages etc. is an essential step. The most feasible mitigating measure to solve the problem is defluoridation of drinking water. Several methods are there which have been reported for fluoride removal viz. precipitation, ion exchange, adsorption, reverse osmosis, electrodialysis etc.

Adsorption is the most common and widely used method. Numerous adsorbents have been derived for fluoride adsorption. Alumina was studies as an adsorbent by many researchers.[45] Maximum fluoride removal was found between pH 5-6 at 25°C.[46] Ghorai and Pant investigated activated alumina column performance and found that on regeneration fluoride removal efficiency is increased upto 85%.[47] Modified alumina was also used by some researchers for defluoridation of water.[48,49] Calcium salts, iron and other metal based adsorbents have also been studied for fluoride removal. Researchers have also been explored various carbon based materials.[50-52] Modifications with activated charcoal have been done to make it a better adsorbent for fluoride removal. It was found that ZIAC (Zirconium impregnated activated charcoal) is better than Activated charcoal for the same purpose.

Various types of clay,[53-55] rice husk[56] and zeolites[57] have also been used for removal of fluoride. Many researchers examined chitosan beads for fluoride removal.[58-60] It was observed that 20% La incorporated chitosan was more efficient in fluoride removal than simple chitosan

and chitin. Fluoride removal was found to be observed 98% with 10% La incorporation.[61] Alagumuthu et al derived activated carbon form Cynodon dactylon and examined it for defluoridation. 83.77% fluoride was found to be removed at neutral pH.[62] Polyaniline/Chitosan was found less efficient for defluoridation when it was compared to Polypyrrole/Chitosan composite.[63] Numerous nanosorbents have been investigated as fluoride removing agent.[64-66] They are found evidently good for this purpose.

In Ion Exchange process, a column containing ion exchange resin (having quaternary ammonium functional groups) is used for fluoride removal. Fluoride ion in water replaces Cl^- ion from the resin on passing water through the column. To regenerate column, it is backwashed with sodium chloride rich water. Many researchers studied fluoride removal using ion exchange resins.[67-70] Resins are expensive and disposal of backwash is also a problem.

Coagulation-precipitation is another method which has been studied for defluoridation. In this method coagulant such as lime is used to coagulate fluoride as fluorite. Alum is also used in this process. Nalgonda technique which is developed in NEERI Nagpur (India) is based on this principle. Aluminium toxicity is a serious drawback of this technique.

Membrane process is an advanced technique which has drawn attention of researchers in recent years. Defluoridation using membrane techniques has been investigated by many workers.[71-75] It comprises reverse osmosis (RO), nano filtration (NF), donnan dialysis (DD) and electrodialysis (ED). Reverse osmosis is reverse of natural osmosis in which pressure is applied to the concentrated side of the membrane and water is purified through a semipermeable membrane. The difference between RO and NF is that in NF the membrane has slight larger pore size than in RO membranes. Consequently in NF less pressure, less energy, less effort is required for removal of solutes thereby decreasing cost of the treatment. A review was compiled in 1999 on use of nanofilteration membranes.[76] Tahaikt et al performed fluoride reduction experiments using NF pilot plant and compared the performances of two commercial membranes NF400 and NF90.[77] It was found that water with satisfactory quality was produced from NF400, while mineralization was required for the water produced from NF90. Performances of NF and LPRO (low pressure reverse osmosis) for fluoride and salinity removal from brackish water using a pilot plant were also studied by Diawara et al.[78] For water with fluoride and salinity far beyond the recommended limits LPRO was found to be effective than NF.

In dialysis process separation occurs via transportation of solute through a membrane while in RO and NF water (solvent) passes through it. Dialysis can be done either by donnan effect or by

applying an electric field. Durmatz et al studied fluoride removal using Neosepta AHA anion exchange membrane and effect of various parameters was observed. On comparison it was found that AFN has better transport efficiency than AHA membrane.[79] Tor reported that ACM has less transport efficiency than that if AFN and AHA membranes.[80] Recently Boubakri et al studied fluoride removal by DD using 2^4 full factorial design.[81] In Electrodialysis direct potential is applied to purify water. Tahaikt et al studied fluoride removal from ground water using electrodialysis with pilot plant having capacity of $1m^3/h$.[82] Several other researchers have also studied electrodialysis for defluoridation.[83-86] Recently Elazhar et al studied comparison of performance and investment & operating costs between NF and ED using two different adopted models.[87] Their performances were found to be comparable while operating & capital costs were much higher for NF than for ED. Membrane processes are costly in comparison with conventional methods. Secondly RO removes all the ions though some ions are essential ions. Despite of all these drawbacks membrane process is highly efficient in fluoride removal. Researchers are trying to make it cost effective by doing modifications and improving its materials.

CONCLUSION:

Fluoride contamination in groundwater has become a worldwide issue now. Rajasthan is known as the most affected state in India where fluorosis is endemic. Small amount intake of fluoride is known to be beneficial but long term consumption mitigates itself in dental, skeletal and other disorders. Hence some cost effective technique is required to reduce fluoride content in drinking water. Researchers are making efforts in this field to innovate a method which can be assumed as the best one. Government should also undertake programs for creating people awareness and developing fluoride removal technologies.

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REFERENCES:

1. Day AK (1987) Environmental Chemistry, 2nd edn. Wiley, New Delhi.
2. Hussain I, Arif M, Hussain J (2012) Fluoride contamination in drinking water in rural habitations of central Rajasthan India. Environ Monit Assess 184:5151-5158.
3. Weinstein LH, Davison A (2003) Fluoride in the Environment. CABI.
4. Greenwood NN, Earnshaw A (1984) Chemistry of the Elements. Pergamon Press, Toronto.
5. Gillespie RJ, Humphries DA, Baird NC, Robinson EA (1989) Chemistry, 2nd edn. Allyn & Bacon, Boston.
6. Gopal R, Ghosh PK (1985) Fluoride in Drinking Water .Its Effects and Removal . Def Sci J 35:71-88.
7. ICMR (1975) Manual of Standards of Quality of Drinking Water Supplies, Special Report Series. No. 44.
8. WHO (1984) Guidelines for drinking water quality, Health Criteria and other Supporting information, 2nd edn. Vol 2 World Health Organization, Geneva.
9. WHO (1993) Guidelines for drinking water quality, World Health Organization, Geneva.
10. BIS (1992) Indian standard specifications for drinking water, IS: 10500.
11. Bell MC, Ludwig TG The supply of fluoride to man: ingestion from water, Fluorides and Human Health, WHO monograph Series 59, World Health Organization, Geneva, 1970.
12. Messaitfa A (2008) Fluoride contents in groundwaters and the main consumed foods (dates and tea) in Southern Algeria region, Special Issue: Groundwater Flow - selected papers from XXXIII IAH Congress, Zacatecas, Mexico, Environmental Geology 55(2):377-383.
13. Gaciri SJ, Davies TC (1993) The occurrence and geochemistry of fluoride in some natural waters of Kenya. Journal of Hydrology 143:395-412.
14. Oruc N (2008) Occurrence and problems of high fluoride waters in Turkey: An overview. From the issue entitled "Medical Geology in Developing Countries, Part 2". Environmental Geochemistry and Health 30(4):315-323.
15. Davraz A, Sene E, Sener S (2008) Temporal variations of fluoride concentration in Isparta public water system and health impact assessment (SW-Turkey). Environmental Geology 56:159-170.
16. Moghaddam AA, Fijani E (2008) Distribution of fluoride in groundwater of Maku area, northwest of Iran. Environmental Geology 56:281–287.
17. Nanyaro JT, Aswathanarayana U, Mungure J S, Laiiermo PW (1984) A geochemical model for the abnormal fluoride concentrations in waters in parts of northern Tanzania. Journal of African Earth Sciences 2(2):129-140.

18. Alabduláaly AI (1997) Fluoride content in drinking water supplies of Riyadh, Saudi Arabia. Environ Monit Assess 48:261–272.
19. Singh P, Rani B, Singh U, Maheshwari R (2011) Fluoride Contamination in Groundwater of Rajasthan and its Mitigation Strategies. J Pharmaceu Biomed Sci 6(9):1-12.
20. Thergaonkar. V. P. &Bhargava R. K., Indian J. of Env. Health 16 (1974):168-80.
21. Kathuria, A. K., et al. Indian, J. Env. Heabh, 16 (1974).222-32.
22. Batheja K, Sinha AK, Seth G (2008) Nitrate and Fluoride contaminations in groundwater of Churu block, Rajasthan. J IWWA 45-49.
23. Rani B, Bagaria PS, Mohan L, Verma N, Maheshwari RK (2013) Hazardous Fluoride ion in Groundwater of Rajasthan: Its irrefutable manifestations, precautionary measures and attenuation methodologies. Bulletin on Geological Sciences 9(1):33-52.
24. Gopal, R., et a1 Trans. Isdt. &Ucds.,8 (1983), 10-12.
25. Gopai, R., et a1 Anals. of Arid Zone, 22 (1983), 87-93.
26. Hussain I, Arif M, Hussain J (2012) Fluoride contamination in drinking water in rural habitations of central Rajasthan, India. Environ Monit Assess 184:5151-5158.
27. Meenakshi , Maheshwari RC (2006) Fluoride in drinking water and its removal. J Hazardous Mat B137:456–463.
28. Suthar S, Garg VK, Jangir S, Kaur S, Goswami N, Singh S (2008) Fluoride contamination in drinking water in rural habitations of Northern Rajasthan, India. Environmental Monitoring and Assessment 145:1-6.
29. Yadav AK, Khan P, Saxena U (2009) Geochemical Observation of Fluoride in Ground Water of Tonk (Rajasthan). Rasayan J Chem 2(4):994-1000.
30. Choubisa SL (2001) Endemic Fluorosis in Southern Rajasthan, India. Fluoride 34(1):61-70.
31. Gautam R, Bhardwaj N, Saini Y (2011) Study of Fluoride Content in Groundwater of Nawa Tehsil in Nagaur, Rajasthan. Journal of Environmental Biology 32(1):85-89.
32. Sengupta SR, Pal B (1971) Iodine and fluoride content of foodstuffs. Indian J. Nutr. Dicter. 8:66–71.
33. Yadav RK, Sharma S, Bansal M, Singh A, Panday V, Maheshwari R (2012) Effects of Fluoride Accumulation on Growth of Vegetables and Crops in Dausa District, Rajasthan, India. Advances in Bioresearch 3(4):14-16.
34. Anderson BG, Stevenson PH (1930) The occurrence of mottled enamel among the Chinese. Journal of Dental Research 10:233-238.
35. Vishwanathan GR (1935) Annual Report Madras, Indian Council of Agricultural Research, New Delhi. Quoted from Indian Institute of Science 33A, 1. 1951.
36. Shortt WE (1937) Indian Medical Gazette, 72:396.

37. Brudevold F, Soremark R (1967) Structural and Chemical Organization of Teeth, edited by A. G. W. Miles Academic Press, New York and London 2: 247.
38. Russel AL, Elvove E (1951) Pub Health Rep. 66:1389.
39. Patel B (1982) Science Service. 1.
40. Peckham S, Awofeso N (2014) Water Fluoridation: A Critical Review of the Physiological Effects of Ingested Fluoride as a Public Health Intervention. The Scientific World Journal Article ID 293019.
41. Dean HT (1942) The investigation of physiological effects by the epidemiological method. Am Asso adv sci 19:23-33.
42. Chauhan DS, Singh VP, Tripathi S, Tomar A, Tiwari M, Tomar S, Kumar S, Mahdi AA (2013) Fluoride reduces semen quality at risk level in high fluoride affected regions. Int J Biol Med Res 4(3):3410-3413.
43. Tripathi N, Bajpai S, Tripathi M (2009) Genotoxic alterations induced by fluoride in Asian catfish, Clariasbatrachus (Linn.). Fluoride 42(4):292–296.
44. Choubisa SL, Modasiya V, Bahura CK, Sheikh Z (2012) toxicity of fluoride in cattle of the indian thar desert, Rajasthan, India. Fluoride 45(4):371–376.
45. Fletcher HR, Smith DW, Pivonka P (2003) Modeling the sorption of fluoride onto alumina. J Environ Eng 132:229–246.
46. Bahena JLR, Cabrera AR, Valdivieso AL, Urbina RH (2002) Fluoride adsorption onto Al_2O_3 and its effect on the zeta potential at the alumina-aqueous electrolyte interface. Sep Sci Technol 37:1973–1987.
47. Ghorai S, Pant KK (2004) Investigations on the column performance of fluoride adsorption by activated alumina in a fixed-bed. Chem Eng J 98:165–173.
48. Bansiwal A, Pillewan P, Biniwale RB, Rayalu SS (2010) Copper oxide incorporated mesoporous alumina for defluoridation of drinking water. Microporous Mesoporous Mater 129:54–61.
49. Teng SX, Wang SG, Gong WX, Liu XW, Gao BY (2009) Removal of fluoride by hydrous manganese oxide-coated alumina: Performance and mechanism. J Hazard Mater 168:1004–1011.
50. Cui H, Qian Y, An H, Sun C, Zhai J, Li Q (2012) Electrochemical removal of fluoride from water by PAOA modified carbon felt electrodes in a continuous flow reactor. Water Res 46:3943–3950.
51. Montoya VH, Montoya LAR, Petriciolet AB, Morán MAM (2012) Optimizing the removal of fluoride from water using new carbons obtained by modification of nut shell with a calcium solution from egg shell. Biochem Eng J 62:1–7.

52. Sivasankar V, Murugesh S, Rajkumar S, Darchen A (2013) Cerium dispersed in carbon (CeDC) and its adsorption behavior: A first example of tailored adsorbent for fluoride removal from drinking water. Chem Eng J 214:45–54.
53. Ramdani A, Taleb S, Benghalem A, Ghaffour N (2010) Removal of excess fluoride ions from Saharan brackish water by adsorption on natural materials. Desalination 250:408–413.
54. Thakre D, Rayalu S, Kawade R, Meshram S, Subrt J, Labhsetwar N (2010) Magnesium incorporated bentonite clay for defluoridation of drinking water. J Hazard Mater 180:122–130.
55. Maiti A, Basu JK, De S (2011) Chemical treated laterite as promising fluoride adsorbent for aqueous system and kinetic modeling. Desalination 265:28–36.
56. Ganvir V, Das K (2011) Removal of fluoride from drinking water using aluminum hydroxide coated rice husk ash J hazard mater 185:1287-1294.
57. Sun Y, Fang Q, Dong J, Cheng X, Xu J (2011) Removal of fluoride from drinking water by natural stilbite zeolite modified with Fe (III). Desalination 277:121-127.
58. Viswanathan N, Sundaram CS, Meenakshi S (2009) Development of multifunctional chitosan beads for fluoride removal. J Hazard Mater 167:325–331.
59. Viswanathan N, Sundaram CS, Meenakshi S (2009) Removal of fluoride from aqueous solution using protonated chitosan beads. J Hazard Mater 161:423–430.
60. Viswanathan N, Meenakshi S (2009) Synthesis of Zr(IV) entrapped chitosan polymeric matrix for selective fluoride sorption. Colloids Surf B: Biointerfaces 72:88–93.
61. Bansiwal A, Thakre D, Labhshetwar N, Meshram S, Rayalu S (2009) Fluoride removal using lanthanum incorporated chitosan beads. Colloids Surf B: Biointerfaces 74:216–224.
62. Alagumuthu G, Veeraputhiran V, Venkataraman R (2011) Fluoride sorption using Cynodon dactylon- based activated carbon. Hem Ind. 65(1):23–35.
63. Karthikeyan M, Kumar KKS, Elango KP (2011) Batch sorption studies on the removal of fluoride ions from water using eco-friendly conductingpolymer/bio-polymer composites. Desalination 267:49–56.
64. Wang Y, Chen N, Wei W, Cui J, Wei Z (2011) Enhanced adsorption of fluoride from aqueous solution onto nanosized hydroxyapatite by lowmolecular-weight organic acids. Desalination 276:161–168.
65. Zhang D, Luo H, Zheng L, Wang K, Li H, Wang Y, Feng H (2012) Utilization of waste phosphogypsum to prepare hydroxyapatite nanoparticles and itsapplication towards removal of fluoride from aqueous solution. J Hazard Mater 241:418–426.
66. Yu X, Tong S, Ge M, Zuo J (2013) Removal of fluoride from drinking water by cellulose@ hydroxyapatite nanocomposites**.** Carbohydrate polymers 92:269-275.
67. Meenakshi S, Viswanathan N (2007) Identification of selective ion-exchange resin for fluoride sorption. Journal of Colloid and Interface Science 308:438–450.

68. Wasay SA, Haron MJ, Tokunaga S (1996) Adsorption of fluoride, phosphate and arsenate ion on lanthanum impregnated silica gel. Water Environ. Res. 68:295-300.
69. Wasay SA, Tokunaga S, Park W (1996) Sep. Sci. Technol. 31:1501.
70. Okabayashi Y, Oh R, Nakagawa T, Tanaka H, Chikuma M (1998) Analyst 113: 829.
71. Arora M, Maheshwari RC, Jain SK, Gupta A (2004) Use of Membrane Technology for potable water production. Desalination 170:105-112.
72. Ndiaye PI, Moulin P, Dominguez L, Millet JC, Charbit F (2005) Removal of fluoride from electronic industrial effluent by RO membrane separation. Desalination 173:25–32.
73. Amor Z, Bariou B, Mameri N, Taky M, Nicolas S, Elmidaoui A (2001) Desalination, 133:215.
74. Hichour M, Persin F, Sandeaux J, Gavach G (2000) Sep Purif Technol 18:1.
75. Pontié M, Buisson H, Diawara CK, Essis-Tome H (2003) Desalination, 157:127.
76. Drioli E, Lagana F, Crlscuoh A, Barbieri G (1999) Integrated membrane operations in desalination processes. Desalination 122:141-145.
77. Tahaikt M, El Habbani R, Ait Haddou A, Achary I, Amor Z, Taky M, Alami A, Boughriba A, Hafsi M, Elmidaoui A (2007) Fluoride removal from groundwater by nanofilteration. Desalination 212:46-53.
78. Diawara CK, Diop SN, Diallo MA, Farcy M, Deratani A (2011) Performance of Nanofiltration (NF) and Low Pressure Reverse Osmosis (LPRO) Membranes in the Removal of Fluorine and Salinity from Brackish Drinking Water. Journal of Water Resource and Protection 3:912-917.
79. Durmaz F, Kara H, Cengeloglu Y, Ersoz M (2005) Fluoride removal by Donnan dialysis with anion exchange membranes. Desalination 177:51–57.
80. Tor A (2007) Removal of fluoride from water using anion-exchange membrane under Donnan dialysis condition. J Hazard Mater 141:814–818.
81. Boubakri A, Helali N, Tlili M, Amor MB (2014) Fluoride removal from diluted solutions by Donnan dialysis using full factorial design. Korean J Chem Eng 31:461-466.
82. Tahaikt M, Achary I, Menkouchi Sahli MA, Amor Z, Taky M, Alami A, Boughriba A, Hafsi M, Elmidaoui A (2004) Defluoridation of Moroccan ground water by electrodialysis: continuous operation. Desalination 167:357.
83. Tahaikt M, El Habbania R, Ait Haddoua A, Acharya I, Amora Z, Takya M, Alamib A, Boughribab A, Hafsib M, Elmidaouia A (2007) Fluoride removal from groundwater by nanofilteration. Desalination 212:46–53.
84. Sahli MA, Annouar A, Tahaikt S, Mountadar M, Soufiane A, Elmidaoui A (2007) Fluoride removal for underground brackish water by adsorption on the natural chitosan and by electrodialysis. Desalination 212:37–45.

85. Kabay N, Ara O, Samatya S, Yu ksel U, Yu ksela M (2008) Separation of fluoride from aqueous solution by electrodialysis: effect of process parameters and other ionic species. J Hazard Mater 153:107–113.
86. Lahnid S, Tahaikt M, Elaroui K, Idrissi I, Hafsi M, Laaziz I, Amor Z, Tiyal F, Elmidaoui A (2008) Economic evaluation of fluoride removal by electrodialysis. Desalination 230:213–219.
87. Elazhar F, Tahaikt M, Zouahri A, Taky M, Hafsi M, Elmidaoui A (2013) Defluoridation of Moroccan Groundwater by Nanofiltration and Electrodialysis: Performances and Cost Comparison. World Applied Sciences Journal 22:844-850.