RESEARCH ARTICLE OPEN ACCESS

Impact and remedial strategy of Fluoride in Ground Water – A Review

Bhagwan yadav*Abha Garg**
*Research Scholar in Dr.K.N.Modi University, Newai, Distt. Tonk, Rajasthan - 304021 (India)
**Professor in Department of chemistry, Dr.K.N.Modi University, Newai, Distt.Tonk, Raj. - 304021

Abstract
According to WHO report 20% of the fluoride-affected villages in the whole world are in India, viz 33,231 villages are affected by fluoride in the country. Drinking water with excessive concentration of fluoride causes fluorosis which progresses gradually and becomes a crippling malady in the long run. It affects people of all age group, rich, rural, and urban population. It has attained a very alarming dimension. Rajasthan suffers both the problems of quantity and quality of water. In most part of the state groundwater is either saline or having high nitrates and fluoride content. Obviously, groundwater is the major source of drinking water and over 94% of the drinking water demand is met by groundwater. Fluoride concentrations beyond the standards cause dental and skeletal fluorosis. Fluoride toxicity can also cause non-skeletal diseases like aches and pain in the joints, non-ulcer dyspepsia, Polyurea and polydipsia, muscle weakness, fatigue, anemia with very low hemoglobin levels, etc besides other reasons. Many researchers have used various types of inexpensive and effective adsorption medium like clays, solid industrial wastes such as red mud, spent bleaching earths, spent catalysts and fly ash, activated alumina, carbonaceous materials, bone charcoal, natural and synthetic zeolites, etc. for the treatment of fluoride contamination. This paper presents a review, which focuses on the sources of fluoride in ground water, its impacts on health and different control measures.
Keywords : Groundwater, Fluoride, Dental Fluorosis, Skeletal Fluorosis.

I. INTRODUCTION

Water is the major medium of fluoride intake by humans [1]. Fluoride in drinking water can be either beneficial or detrimental to health, depending on its concentration [2]. The presence of fluoride in drinking water within permissible limits is beneficial in the calcification of dental enamel. According to the World Health Organization (WHO), the maximum acceptable concentration of fluoride is 1.5 mg/l[3], while India's permissible limit of fluoride in drinking water is 1 mg/l[4] .Concentrations beyond these standards have shown dental and skeletal fluorosis, and lesions of the endocrine glands, thyroid and liver[4],[5], [6]. Fluoride stimulates bone formation [7] and small concentrations have beneficial effects on the teeth by hardening the enamel and reducing the incidence of caries [8]. McDonagh et al.[9] described in great detail the role of fluoride in the prevention of dental fluorosis. At low levels (<2 ppm) soluble fluoride in the drinking water may cause mottled enamel during the formation of the teeth, but at higher levels other toxic effects may be observed[10],[11],[12]. Severe symptoms lead to death when fluoride doses reach 250–450 ppm [13]. It is found that the IQ of the children in the high fluoride areas (drinking water fluoride 3.15 ppm) is significantly low [14]. Fluorides enter the human body mainly through the intake of water and, to a lesser extent, foods.

Among the foods rich in fluorides are fish, tea, and certain drugs [15]. Ingested fluorides are quickly absorbed in the gastrointestinal tract, 35–48% is retained by the body, mostly in skeletal and calcified tissues, and the balance is excreted largely in the urine. Chronic ingestion of fluoride-rich fodder and water in endemic areas leads to development of fluorosis in animal's e.g. dental discoloration, difficulty in mastication, bony lesions, lameness, debility and mortality [16]. Besides the health effects, dental fluorosis may have social and psychological consequences. There has been an escalation in daily fluoride intake via the total human food and beverage chain, with the likelihood that this escalation will continue in the future [17]. Carbonated soft drinks have considerable amounts of fluorides [18]. Beers brewed in locations with high fluoride water levels may contribute significantly to the daily fluoride intake [19], and sweetened iced teas contain significant amounts of fluoride [20]. Children's ingestion of fluoride from juices and juice-flavoured drinks can be substantial and a factor in the development of fluorosis [21]. Borah and Dey[22] reported that a large population in India is very severely affected by fluorosis. More than 15 states are affected by endemic fluorosis in India [23, 24, 25, 26]. This paper states that different fluoride concentrations influence the human health. Various sources of fluoride and treatment methods have also been explained in this paper.

II. SOURCES OF FLUORIDE

The world's fluoride stores in the ground are estimated to 85 million tons. Out of which nearly 12 million tons are located in India. The most common fluorine-bearing minerals, which constitute natural source for fluoride in drinking water, are fluorite, apatite, rock phosphate and topaz. The low calcium and magnesium hardness and high alkalinity are characteristic in the majority of the drinking water samples. With increasing concentrations of fluoride in drinking water, calcium and magnesium hardness decreases and the alkalinity increases [27]. According to epidemiological surveys on endemic skeletal fluorosis, the toxic effects of fluoride on bones and teeth are more pronounced and severe in individuals who are drinking water of higher alkalinity and lower calcium and magnesium hardness (soft water). Calcium and magnesium hardness in water appear to inhibit fluoride toxicity. Naturally occurring fluorides in groundwater are a result of the dissolution of fluoride-containing rock minerals by water [28] while artificially high soil F levels can occur through contamination by application of phosphate fertilizers or sewage sludges, or from pesticides [15]. The F compounds added to soils by pollution are usually readily soluble. Fluorine is a typical lithophile element under terrestrial conditions, and there are not many stable F minerals; the most common are topaz (Al_2 (F, OH) 2Sio4) and fluorite (CaF_2). F reveals an affinity to replace hydroxyl groups in minerals, and these reactions have resulted in fluoroapatite (Ca10 $(PO_4)_6F_2$), the most common F mineral, and have also been responsible for increased amounts of F in amphiboles and micaceous minerals [28]. The mobility of F in soils is complex and the predominant factors controlling the level of this ion in the soil solution are the amount of clay minerals, the soil pH, and the concentration of Ca and P in soils. The greatest adsorption of F by soil mineral components is at about pH 6 to 7. The range for most normal soils seems to be from 150 to 400 ppm [29], but the overall variation is much broader, and in some heavy soils F levels above 1,000 ppm has been found [28]. Much higher levels of F in uncontaminated soils are reported for provinces of endemic fluorosis. Endemic fluorosis remains a challenging and extensively studied national health problem in India. In 1991, 13 of India's 32 states and territories were reported to have naturally high concentrations of fluoride in water [30], but this had risen to 17 by 1999[31]. The most seriously affected areas are Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh [32, 33]. The highest concentration observed to date in India is 48 mg/l in Rewari District of Haryana [31].

Milk typically contains low levels of fluoride, e.g. 0.02 mg/l in human breast milk and 0.02–0.05 mg/l in cow's milk [34]. Thus milk is usually responsible for only a small fraction of total fluoride exposure. Tea leaves contain high levels of fluoride (up to 400 mg/kg dry weight). Fluoride exposure due to the ingestion of tea has been reported to range from 0.04 mg to 2.7 mg per person per day [34]. However, some Tibetans have been observed to ingest large amounts of fluoride (e.g. 14 mg per day) due to the consumption of brick tea as a beverage [35]. For a given individual, water consumption increases with temperature, humidity, exercise and state of health, and is modified by other factors including diet. Roughly, the closer to the Equator, the higher the water consumption [34] and hence increase in level of fluoride. The variation of fluoride is dependent on a variety of factors such as amount of soluble and insoluble fluoride in source rocks, the duration of contact of water with rocks and soil temperature, rainfall, oxidation- reduction process [36]. Naturally, groundwater contains mineral ions. These ions slowly dissolve from soil particles, sediments, and rocks as the water travels along mineral surfaces in the pores or fractures of the unsaturated zone and the aquifer. A major and widespread cause of groundwater quality deterioration is heavy pumping, which may cause the migration of more highly mineralized water from surrounding strata to the well. Intensive and long-term irrigation causes weathering and leaching of F from the soils/weathered rocks [37]. Easy accessibility of circulating water to the weathered products during irrigation dissolves and leaches the minerals, including fluorine, contributing F to the surface water and groundwater [38]. Weathering of alkali, silicate, igneous and sedimentary rocks contribute a major portion of fluorides to groundwater. Occurrence of alkaline soil around the fluoride contaminated water sources is the outstanding feature of the fluoride-affected areas [37].

III. HEALTH EFFECTS OF FLUORIDE

Dental fluorosis, which is characterized by discolored, blackened, mottled or chalky white teeth, is a clear indication of overexposure to fluoride during childhood when the teeth were developing. These effects are not apparent if the teeth were already fully grown prior to the fluoride overexposure; therefore, the fact that an adult may show no signs of dental fluorosis does not necessarily mean that his or her fluoride intake is within the safety limit [40]. When the tea is heavily consumed as sweet and strong and is consumed from a very young age when it is put in nursing bottles cause dental fluorosis [39]. Chronic intake of excessive fluoride can lead to the severe and permanent bone and joint deformations termed as skeletal fluorosis. Early symptoms include sporadic pain and stiffness of joints: headache, stomach-ache and muscle weakness can also be warning signs. The next stage is osteosclerosis (hardening and calcifying of the bones), and finally the spine, major joints, muscles and nervous system are damaged. Whether dental or skeletal, fluorosis is irreversible and no treatment exists. The only remedy is prevention, by keeping fluoride intake within safe limits [41]. Research of several investigators during the last 5–6 years has proven that life-long impact and accumulation of fluorides causes not only human skeletal and teeth damage, but also changes in the DNA-structure, paralysis of volition, cancer, etc[42].

In India, about 62 million people including 6 million children suffer from fluorosis because of fluoride contaminated water[43]. The chronic fluoride toxicity depends upon the actual amount of fluoride ingested per day and the duration of exposure to high fluoride intake through drinking water since the amount of fluoride taken through food appears to be relatively small.[27]. The daily intake of fluoride depends upon (a) concentration of fluoride in drinking water, (b) total amount of water ingested per day. The amount of water ingested is itself dependent upon a number of variables such as body size, food habits, environmental temperature and extent of physical activity. During the hot summer season, agricultural laborers may drink up to 8 liters of water a day. In addition, Indian diets contain large amounts of water and practically all staples are cooked in water. Large numbers of villagers of Patan district of Gujarat, India are suffering from skeletal/dental fluorosis. They also observed that people living in higher concentration zone of fluoride having body pain, knee pain and back pain [37]. A large population of Karbi Anglong and Nowgaon districts of Assam, India is affected by fluorosis. The presence of fluoride in drinking water up to 6.88 mg/L in different parts of capital city of Guwahati, Assam, India has been reported [22]. Fluoride concentration in drinking water had ranged from 0.6 to 13.4 mg/L in the Gulbarga district of Karnataka, India. The 89% children had dental fluorosis and 39% skeletal fluorosis [23]. Susheela[43] reported that fluoride contamination problems like aches and pain in the joints, viz. neck, back, hip, shoulder and knee without visible signs of fluid accumulation; non-ulcer dyspepsia, viz. nausea, vomiting, pain in the stomach, bloated feeling/gas formation in the stomach, constipation followed by diarrhea; Polyurea (tendency to urinate more frequently) and polydipsia (excessive thrust), if detected, may be due to fluoride toxicity manifestations besides diabetes and/or other diseases; muscle weakness, fatigue, anemia with very low hemoglobin levels; complaint of repeated abortions/stillbirth; complaints of male infertility with abnormality in sperm morphology, oligospemia (deficiency of spermatozoa in the semen), azoospermia (absence of spermatozoa in the semen) and low testosterone levels. Discolouration of the enamel surface in front row of teeth of the patient (central and lateral incisors of the upper and lower jaw) may be due to dental fluorosis. These problems may be due to fluoride toxicity besides other reasons. Czarnowski et al.[6] has explained that increase in fluoride intake affects the fluoride levels in urine and hair and also has an impact on bone density.

Enamel mottling at 0.5 ppm and 0.9-1.0 ppm fluoride levels has been reported [44, 45]. At 6.0 ppm, 100% prevalence of dental fluorosis has been reported [43]. Choubisa et al.[47] have observed a prevalence of 25.6% and 84.4% of grade II dental fluorosis in children at fluoride levels of 1.4 ppm and 6.04 ppm, respectively. Shivashankara et al.[23] found dental fluorosis among the children of Kheru Thanda, 89%. An overall prevalence of skeletal fluorosis with severe symptoms among 18 (39%) of the children at a mean fluoride level of 5.98 ppm was observed. The prevalence of skeletal fluorosis was marginally higher in males. They also found the prevalence of fluoride toxicity and associated deformities were restricted to the children. None of the adults have visible symptoms of skeletal toxic effects. However, a few of them complained of vague back pain and stiffness. Teotia [48] found that fluoride toxicity affects children more severely and after shorter exposure to fluoride than adults, owing to the greater and faster accumulation of fluoride in the metabolically more active growing bones of children.

IV. REMEDIAL MEASURES OF FLUORIDE

The popular technologies for the removal of fluoride from water include: coagulation followed by precipitation, membrane processes, ion exchange and adsorption [49, 50, 51, 52, 53]. In coagulation, trace amounts of fluoride ions tend to remain in solution due to solubility restriction. Other shortcomings include the resulting high pH of the treated water and the generation of large amount of wet bulky sludge [54, 55]. The Nalgonda technique, based on precipitation processes, is also a common defluoridation technique. The limitations of the process are: daily addition of chemicals, large amount of sludge production, and low effectiveness for water having high total dissolved solids and hardness. Further, increase in residual aluminum in the treated water has been reported [56]. This may endanger human health as concentrations of aluminum, a neurotoxin, as low as 8.0 × 10−2 mg/l in drinking water have been associated with Alzheimer's disease [57, 58]. Membrane processes, though effective in fluoride removal, demineralise water completely, besides the high initial and maintenance costs. Ion exchange methods are efficient for fluoride removal, but a tedious and difficult process of preparation of resins as well as the high cost necessitates a search for an alternative technique. Adsorption techniques have been quite popular in recent years due to their simplicity, as well as the availability of wide range of adsorbents. Research has focused on various types of inexpensive and effective adsorption media, such as different clays [13, 59, 60], solid industrial wastes like red mud, spent bleaching earths, spent catalysts and fly ash[61, 62, 63, 64, 65], activated alumina, carbonaceous materials[66, 67, 68], bone charcoal[69], natural and synthetic zeolites and other low-cost adsorbents, with various degrees of success[70]. Murutu et al.[2] conducted study for the removal of fluoride ions from water using phosphoric acid treated lime.

Considerable work on defluoridation has been done all over the world. The most economical adsorbent for fluoride removal from drinking water is activated alumina [71],[72]. Literature survey on studies for fluoride removal from aqueous solutions has revealed that zeolites and cross-linked polystyrene based ion exchange resins are effective for the removal of fluoride ion from contaminated drinking water. In the last few years, layered double oxides such as Mg–Al oxides [73]. Borah and Dey[22] has reported other adsorbents like fly ash, silica gel, soil, water hyacinth, bone charcoal, zeolites, bentonite, etc which controls the fluoride contamination. They also carried out pilot scale study for the treatment of fluoride using coal particles as adsorbent materials. The amount, contact time and particle size of the adsorbent influenced the treatment efficiencies of fluoride. For the removal of fluoride, Chidambaram et al.[74] used natural materials such as red soil, charcoal, brick, fly-ash and serpentine. Each material was set up in a column for a known volume and the defluoridation capacities of these materials were studied with respect to time. According to the maximum defluoridation capacity these materials were added proportionately to the vertical column. Ten mg/l of fluoride was passed through the column and the variation of fluoride removal for a known rate of flow was studied. They found that red soil has good fluoride removal capacity followed by brick, fly-ash, serpentine and charcoal. The main factors in red soil the dominance of very fine clays, organic matter and rich in iron aluminum oxide in composition and have good anion exchange capacity. In general, aluminum compounds are found to be good fluoride removers because of the reaction between Al and F molecules. The magnesite, apophyllite, natrolite, stilbite, clinoptilolite, gibbsite, goethite, kaolinite, halloysite, bentonite, vermiculite, zeolite(s), serpentine, alkaline soil, acidic clay, kaolinitic clay, China clay, aiken soil, Fuller's earth, diatomaceous earth and Ando soil are among the numerous naturally occurring minerals which have been studied and confirmed to adsorb fluoride from water[75,76,77]. . A novel bimetallic oxide adsorbent was synthesized by the co-precipitation of Fe (II) and Ti (IV) sulphate solution using ammonia titration at room temperature for fluoride removal from water [78]. Mg-doped nano ferrihydrite powder [79], Fe (III) modified montmorillonite [80], iron rich laterite [81], Awareness generation and emphasis on importance of consuming calcium, vitamin C, E and antioxidant-rich diet can be made for minimizing the adverse effects of fluoride [43].

V. CONCLUDING REMARKS

Rock minerals and waste disposal contributes fluoride contamination in groundwater. Researchers have observed different concentrations of fluoride for the different diseases. To mitigate fluoride contamination for an affected area, the provision of safe, low fluoride water from alternative sources should be investigated as the first option otherwise various methods, which have been developed for the defluoridation of water can be used to prevent fluoride contamination. Groundwater of a particular area should be thoroughly studied before its use for domestic purposes and accordingly a suitable method can be chosen for its treatment.

REFERENCES

[1] WHO, Environmental Health Criteria for Fluorine and Fluorides., Geneva, 1984,1-136.
[2] Murutu, C., Onyango, M.S., Ochieng, A. and Otieno, F.A., Fluoride removal performance of phosphoric acid treated lime: Breakthrough analysis and point-of-use system performance, Water SA, 2012,38 (2), 279-286.
[3] WHO (World Health Organization), Guidelines for Drinking-Water Quality: Incorporating First Addendum to Third

Edition. World Health Organization, Geneva. 2006,375 p.

[4] Misra, A.K. and Mishra, A., Study of quaternary aquifers in Ganga Plain, India: Focus on groundwater salinity, fluoride and fluorosis. J. Hazardous Mater. 2007,144, 438-448.

[5] Meenakshi, R.C., Garg, V.K., Kavita, Renuka and Malik, A., Groundwater quality in some villages of Haryana, India: focus on fluoride and fluorosis. J. Hazardous Mater. 2004,106, 85-97.

[6] Czarnowski, W., Krechniak, J., Urbańska, B., Stolarska, K., Taraszewska-Czarnowska, M. and Muraszko-Klaude, A., The impact of waterborne fluoride on bone density. Fluoride, 1999,32 (2), 91–95.

[7] Richards, A., Moskilder, L. and Sogaard, C.H., Normal age-related changes in fluoride content of vertebral trabecular bone—relation to bone quality. Bone, 1994, 6, 15–21.

[8] Fung, K., Zhang, Z., Wong, J. and Wong, M., Fluoride contents in tea and soil from tea plantations and the release of fluoride into tea liquor during infusion. Environ. Pollut., 1999, 104, 197–205.

[9] McDonagh, M.S., Whiting, P.F., Wilson, P.M., Sutton, A.J., Chestnutt, I., Cooper, J., Misso, K., Bradley, M., Treasure, E. and Kleihnen, J., Systematic review of water fluoridation., Brit. Med. 2000, J., 321, 855–859.

[10] Weast, R.C. and Lide, D.R., Handbook of Chemistry and Physics., 70th Edition 1989–1990, CRC Press, Boca Raton, Florida, 1990, B-17.

[11] K.K. Satpathy, R.K.Padhi, M. Sowmya., Fluoride in ground water: a comment on “fluoride contamination in groundwater: a major challenge”. 2013, DOl: 10.1007/s10661-013-3525-4.

[12] Shashank Shekhar, Pandey Ac., Evaluation of fluoride contamination in groundwater sources in hard rock terrainin Gahwa district, Jharkhand, India. 2013, DOI:10.6088/ijes.2012030133010.

[13] Luther, S.M., Poulsen, L., Dudas, M.J. and Rutherford, P.M., Fluoride sorption and mineral stability in an Alberta soil interacting with phosphogypsum leachate., Can. J. Soil Sci., 1996,76, 83–91.

[14] Lu, Y., Sun, Z.R., Wu, L.N., Wang, X., Lu, W. and Liu, S.S., Effect of high-fluoride water on intelligence in children. Fluoride, 2000,33(2), 74–78.

[15] EPA, Public Health Global for Fluoride in Drinking Water, Pesticide and Environmental Toxicology, Section Office of Environmental Health Hazard Assessment, California Environmental Protection Agency, December. 1997.

[16] Patra, R.C., Dwivedi, S.K., Bhardwaj, B. and Swarup, D., Industrial fluorosis in cattle and buffalo around Udaipur, India. Sci. Tot. Environ. 2000,253, 145–150.

[17] Marier, J.R., Some current aspects of environmental fluoride, Sci. Tot. Environ. 1977, 8, 253–265.

[18] Heilman, J.R., Assessing fluoride levels of carbonated soft drinks. J. Am. Dent. Assoc., 1999, 130, 1593–1599.

[19] Warnakulasuriya, S., Harris, C., Gelbier, S., Keating, J. and Peters, T., Fluoride content of alcoholic beverages. Clin. Chim. Acta. 2002,320 (1–2), 1–4.

[20] Behrendt, A., Oberste, V. and Wetzel, W.E., Fluoride concentration and pH of iced tea products, Caries Res., 2002,36, 405–410.

[21] Kiritsy, M.C., Levy, S.M., Warren J.J., Guha-Chowdhury, N., Heilman, J.R. and Marshall, T., Assessing fluoride concentrations of juices and juice-flavored drinks. J. Am. Dent. Assoc., 1996, 127, 895–902.

[22] Borah, L. and Dey, N.C., Removal of fluoride from low TDS water using low grade coal., Indian J. Chem. Technol., 2009,16, 361-363.

[23] Shivashankara, A.R., Shankara, Y.M.S., Rao, S.H. and Bhat, P.G., A clinical and biochemical study of chronic fluoride toxicity in children of Kheru Thanda of Gulbarga district, Karnataka, India, Fluoride, 2000, 33 (2), 66-73.

[24] Punita parikh,Rahul parikh., Current status of fluoride contamination in ground water of kheralu block of mehasana district,Gujrat. 2013. DOI:10.6088/ijes.2013030600035.

[25] Arif M, Hussain I, Hussain J, Sharma S, Kumar S., Fluoride in the Drinking Water of Nagaur Tehsil of Nagaur District, Rajasthan, India. Bull Environ Contam Toxicol,2012,DOI 10.1007/s00128-012-0572-4.

[26] Arif M, Hussain J, Hussain I, Neyol S., Fluoride Contamination of Ground Water of Merta Block in Nagaur District, Rajasthan, India. In The conference of advance in Environmental chemistry (AEC), Aizwal, Mizoram, 2011, pp-146-148.

[27] Teotia, S.P.S., Teotia, M. and Singh R.K., Hydro-geochemical aspects of endemic skeletal fluorosis in India - An epidemiologic study. Fluoride, 1981,14 (2), 69-74.

[28] Kabata Pendias, A. and Pendias, H., Trace Elements in Soil and Plants., CRC Press, Boca Raton, Florida, 1984,33431.

[29] Turekian, K. and Wedepohl, K.H., Distribution of elements in some major units of the earth's crust. Bull. Geol. Soc. Am., 1961,175–192.

[30] Mangla, B., India's dentists squeeze fluoride warnings off tubes., New Scientist, 1991,131, 16.

[31] UNICEF, State of the art report on the extent of fluoride in drinking water and the resulting endemicity in India., 1999, Report by Fluorosis Research & Rural Development Foundation for UNICEF, New Delhi.

[32] Kumaran, P., Bhargava, G.N. and Bhakuni, T.S., Fluorides in groundwater and endemic fluorosis in Raajasthan. Indian J. Environ. Health, 1971,13, 316–324.

[33] Teotia, S.P.S., Teotia, M., Singh, D.P., Rathour, R.S., Singh, C.V., Tomar, N.P.S., Nath, M. and Singh, N.P., Endemic Fluorosis: change to deeper bore wells as a practical community-acceptable approach to its eradication. Fluoride, 1984,17, 48–52.

[34] Murray J.J., (Ed.), Appropriate Use of Fluorides for Human Health., 1986, World Health Organization, Geneva.

[35] Cao, J., Bai, X., Zhao, Y., Zhou, D., Fang,S., Jia, M. and Wu, J., Brick tea consumption as the cause of dental fluorosis among children from Mongol, Kazak and Yugu populations in China., Food Chem. Toxicol., 1997,35(8), 827–833.

[36] Mahapatra M.K., Mishra A. and Das B.P., Fluorosis first reported in Naupada district of Orissa India., Ecology Environment and Conservation, 2005, 11(2), 277-280.

[37] Paya, P. and Bhatt, S.A., Fluoride contamination in groundwater of Patan District, Gujarat, India., International Journal of Engineering Studies, 2010,2 (2), 171–177.

[38] Rao, N.S. and Rao A.T., Fluoride in ground waters in a developing area of Guntur district, Andhra Pradesh, India, J. Appl. Geochem., 2003,5, 94–100.

[39] Shomar, B., Mu¨ ller, G., Yahya, A., Askar, S. and Sansur, R., Fluorides in groundwater, soil and infused black tea and the occurrence of dental fluorosis among school children of the Gaza Strip, J Water Health, 2004, 23-35.

[40] Chaturvedi, A.K., Yadava, K.P, Pathak, K.C. and Singh, V.N., Defluoridation of water by adsorption on fly ash., Water, Air, and Soil Pollut., 1990, 49, 51-60.

[41] Fluorine and Fluorides, 1984, Environmental health criteria, International Program on Chemical Safety.

[42] Johnston, R. and Heijnen, H., Safe water technology for arsenic removal. 2002, Report World Health Organization.

[43] Susheela, A.K., Fluorosis management programme in India. Curr. Sci., 1999,77(10), 1250-1255.

[44] Venkateswarulu, P., Rao, D.N., Rao, and K.R., Studies in endemic fluorosis, Vishakapatnam and suburban areas., Indian J Med Res, 1952,40, 353-62.

[45] Ray, S.K., Ghosh, S., Nagchauduri, J., Tiwari, I.C. and Kaur, P., Prevalence of fluorosis in rural community near Varanasi, India. Fluoride, 1981,14(2), 86-90.

[46] Leone, N.C., Martin, A.E., Minoguchi, G., Schlesinger, E.R., Siddiqui, A.H., Fluorides and general health., In: Fluorides and human health., Geneva: WHO, 1970,273-320.

[47] Choubisa, S.L., Choubisa, D.K., Joshi, S.C., Choubisa, L., Fluorosis in some tribal villages of Dungarpur district of Rajasthan, India., Fluoride, 1997,30(4), 223-8.

[48] Teotia, S.P.S., Teotia, M., Singh, D.P., Fluoride and calcium interactions, syndromes of bone disease and deformities (Human studies)., Proceedings of the International Symposium: Disorders of bone and mineral metabolism., Henry Ford Hospital, Michigan, USA, 1983,502-3.

[49] Bhatnagar, A., Kumar, E. and Sillanpää, M., Fluoride removal from water by adsorption – A review. Chem. Eng. J., 2011, 171, 811-840.

[50] Huo, Y., Ding, W., Huang, X., Xu, J. and Zhao, M., Fluoride removal by lanthanum alginate bead: Adsorbent characterization and adsorption mechanism. Chin. J. Chem. Eng., 2011,19(3), 365-370.

[51] Meenakshi, R.C. and Maheshwari, Fluoride in drinking water and its removal., J. Hazardous Mater., 2006, 137, 456-463.

[52] Ndiaye, P.I., Moulin, P., Dominguez, L., Millet, J.C. and Charbit, F., Removal of fluoride from electronic industrial effluent by RO membrane separation., Desalination, 2005, 173, 25-32.

[53] Mohapatra, M., Anand, S., Mishra, B.K., Giles, D.E. and Singh, P., Review of fluoride removal from drinking water. J. Environ. Manage, 2009,91, 67-77.
[54] Gong, W., Qu, J., Liu, R. and Lan, H., Effect of aluminum fluoride complexation on fluoride removal by coagulation. Colloids Surf. A, 2012, 395, 88-93.
[55] Pinon-Miramontes, M., Bautista-Margulis, R.G. and Perez-Hernadez, A., Removal of arsenic and fluoride from drinking water with cake alum and a polymeric anionic flocculent., Fluoride, 2003, 36**,** 122-128.
[56] Gupta, S.K., A Process for defluoridation of water by a filter bed using indigenous material. Indian J. Environ. Sci., 1997, 1 (2), 149-156.
[57] Simate, G.S., Iyuke, S.E., Ndlovu, S., Heydenrych, M. and Walubita, L.F., Human health effects of residual carbon nanotubes and traditional water treatment chemicals, Surendra Roy *et al.*: Fluoride Contamination in Drinking Water – A Review in drinking water. Environ. Int., 2012, 39, 38-49.
[58] Yadav, A.K., Kaushik, C.P., Haritash, A.K., Kansal, A. and Rani, N., Defluoridation of groundwater using brick powder as an adsorbent., J. Hazardous Mater., 2006, 128, 289-293.
[59] Ramdani, A., Taleb, R., Benghalem, A. and Ghaffour, N., Removal of excess fluoride ions from Saharan brackish water by adsorption on natural materials. Desalination, 2010, 250, 408-413.
[60] Zevenbergen, C., Van Reeuwijk, L.P., Frapporti, G., Louws, R.J. and Schuiling, R.D., A simple method for defluoridation of drinking water at village level by adsorption on Ando soils in Kenya., Sci. Total Environ., 1996, 188 (2), 225-232.
[61] Chaturvedi, A.K., Yadava, K.P., Pathak, K.C. and Singh, V.N., Defluoridation of water by adsorption on fly ash. Water Air Soil Pollut., 1990, 49**,** 51-60.
[62] Cengeloglu, Y., Kir, E. and Ersoz, M., Removal of fluoride from aqueous solution by using red mud, Sep. Purif. Technol., 2002, 28, 81-86.
[63] Lai, Y.D. and Liu, J.C., Fluoride removal from water with spent catalyst. Sep. Sci. Technol., 1996, 31, 2791-2803.
[64] Piekos, R. and Paslawaska, S., Fluoride uptake characteristic of fly ash, Fluoride, 1999, 32, 14-19.
[65] Xu, X., Li, Q., Hao, C., Pang, J., Sun, L., Hao, A. and Zhai, J., Adsorption of fluoride from aqueous solution on magnesia-loaded fly ash cenospheres., Desalination, 2011, 272, 233-239.
[66] Abe, I., Iwasaki, S., Tokimoto, T., Kawasaki, N., Nakamura, T. and Tanada, S., Adsorption of fluoride ions onto carbonaceous materials. J. Colloid Interface Sci., 2004, 275, 35-39.
[67] Li, Y.H., Wang, S., Zhang, X., Wei, J., Xu, C., Luan, Z. and Wu, D., Adsorption of fluoride from water by aligned carbon nanotubes. Mater. Res., 2003a, 38**,** 469-476.
[68] Li, Y.H., Wang, S., Zhang, X., Wei, J., Xu, C., Luan, Z., Wu, D. and Wei B., Removal of fluoride from water by carbon nanotube supported alumina., Environ. Technol., 2003b, 24, 391-398.
[69] Mjengera, H. and Mkongo, G., Appropriate defluoridation technology for use in fluorotic areas in Tanzania., 3rd Water Net Symposium Water Demand Management for Sustainable Development, 2002, 30-31 October, Dares Salaam.
[70] Onyango, M.S., Kojima, Y., Kumar, A., Mitsuhiro, K. and Matsuda, H., Uptake of fluoride by Al3+ pretreated low-silica synthetic zeolites: Adsorption equilibrium and rate studies. Separ. Sci. Technol., 2006, 41 (4)**,** 683-704.
[71] Rubel, J.F., Fluoride Effects on Vegetation, Animals and Humans. Paragon Press, Salt Lake City, 1983.
[72] C.A. Babu, D. Sujish, A comprehensive treatment method for defluoridation of drinking water, Ind. J. Chem. Technol. 18, 2011, 314–318.
[73] J.H. Kim, C.G. Lee, J.A. Park, J.K. Kang, S.Y. Yoon, S.B. Kim, Fluoride removal using calcined Mg/Al layered double hydroxides at high fluoride concentrations, Water Sci. Tech. Water Supply 13,2013,249–256.
[74] Chidambaram, S. Ramanathan, A.L. and Vasudevan, S., Fluoride removal studies in water using natural materials, Water SA., 2003, 29 (3), 339-343,
[75] Bower, C.A. and Hatcher, J.T., Adsorption of fluoride by soils and minerals., Soil Sci., 1967, 103 (3), 151–154.
[76] Björvatn, K. and Bårdsen, A., Use of activated clay for defluoridation of water. In: Proceedings of the First International Workshop on Fluorosis and Defluoridation of Water, 18–22 October 1995, Tanzania, The International Society for Fluoride Research, Auckland, 1997,40–45.

[77] Singano, J.J., Mashauri, D.A., Dahi, E. and Mtalo, F.W., Effect of pH on defluoridation of water by magnesite. In: Proceedings of the First International Workshop on Fluorosis and Defluoridation of Water. 18–22 October 1995, Tanzania, the International Society for Fluoride Research, Auckland, 1997, 30–34.

[78] Chen L, He BY, He S, Wang TJ, Su CL, Jin Y: Fe-Ti oxide nano-adsorbent synthesized by co-precipitation for fluoride removal from drinking water and its adsorption mechanism. *Powder Technol* 2012, 227:3-8.

[79] Mohapatra M, Hariprasad D, Mohapatra L, Anand S, Mishra BK: Mg-doped nano ferrihydrite - A new adsorbent for fluoride removal from aqueous solutions. *Appl Surf Sci* 2012, 258:4228-4236.

[80] Bia G, Pauli CPD, Borgnino L: The role of Fe(III) modified montmorillonite on fluoride mobility: Adsorption experiments and competition with phosphate. *J Environ Manage* 2012, 100:1-9.

[81] Vithanagea M, Jayarathnaa L, Rajapakshaa AU, Dissanayakea CB, Bootharajub MS, Pradeep T: Modeling sorption of fluoride on to iron rich laterite Colloids and Surfaces A. *Physicochem Eng Aspects* 2012, 398:69-75.