

Full Length Research Paper

Fluoride removal from water by zirconium (IV) doped chitosan bio-composite

R. Dongre^{1*}, D. N. Ghugal¹, J. S. Meshram¹ and D. S. Ramteke²

¹P. G.T.D. of Chemistry, R. T. M. Nagpur University, Nagpur-440022, (M.S.) India.

²National Environmental Engineering Research Institute, Nagpur, (M.S.) India.

Accepted 6 February 2012

Water containing fluoride above 1.5 mg/L leads to health and environmental harms that creates skeletal and dental fluorosis. Adsorption technique prominently removes fluoride from water and its competence is reliant on development of recyclable, environmentally benign adsorbents. Many reported sorbents for defluoridation below stringent level 1.5 mg/L, displayed low to moderate adsorption capacity at varied concentrations and pH. Besides, viable defluoridation techniques are usually unsuccessful in developing countries. In this novel, cheap and efficient porous chelating resin, chitosan doped 20% zirconium (IV) with control morphologies were synthesized for defluoridation. This bio-composite was at par with commercial alumina to mitigate water fluoride limit up to 1 to 1.5 mg/L. Effect of parameters namely pH, adsorbent dose, contact time and initial fluoride concentration were studied in batch scale. Kinetic data showed a rapid adsorption, indicated practicable operations in packed column. Findings encourage blending with other polymers as an effective option for defluoridation on a large scale.

Key words: Fluorosis, chitosan, zirconium, bio-composite, defluoridation, water.

INTRODUCTION

Unanimously water is accepted as main source of our nourishment, ultimately an elixir to us. United Nations has declared 2005 to 2015 as "decade of water for life". Globally, about two billion citizens are facing with the problem of scarcity of drinking water. In India it is particularly an acute crisis as millions of people currently lack access to clean and safe water and so some drink unsafe/contaminated water (Giridharadas, 2005). As regards 21% of transmissible diseases in India, some are related to consumption of unsafe drinking water (UNICEF, 2002; Arjunan et al., 2009). Since water owes inherent ion dissolving capacity so, picks up fluoride anion from minerals and salts in earth crust during runoff/percolation. Environmental fluoride contagion can occur via natural degradation of fluoride bearing minerals like fluor spar (CaF_2), cryolite (NaAlF_6), topaz ($\text{Al}_2\text{F}_2\text{SiO}_4$), amblygonite ($\text{Li}(\text{F}, \text{OH}) \text{AlPO}_4$), fluoroapatite

($\text{Ca}_5\text{F}(\text{PO}_4)_3$) and apophyllite ($\text{KFCa}_4(\text{Si}_8\text{O}_{20}) 8\text{H}_2\text{O}$). Most of the fluorides bearing minerals are associated with the rocks of either igneous or metamorphic origin. Fluoroapatite is associated with the rocks of sedimentary origin (Fawell et al., 2006) and apophyllite is found in the inner lining of cavities of the amygdules in basaltic rocks (Biswas et al., 2007; Singh and Maheshwari, 2001). As well as by anthropogenic sources as fluorine is often encountered in minerals, geochemical deposits which may pollute subsoil water sources due to discharge in natural water percolation. Effluents from industries like chemical processing, aluminum making, electroplating also act as contributing source. The polluted water then seeps in underground and contaminates groundwater sources. The fluoride affected areas of India relates to groundwater-fluoride contamination which affects about 66 million people as depicted in Figure 1 (Teotia et al., 1984 and UNICEF Report, 1999).

Another perspective is that fluoride is recognized as essential element in human diet system since its balance level is helpful as dissolved fluoride concentrations up to

*Corresponding author E-mail: rsdongre@hotmail.com.

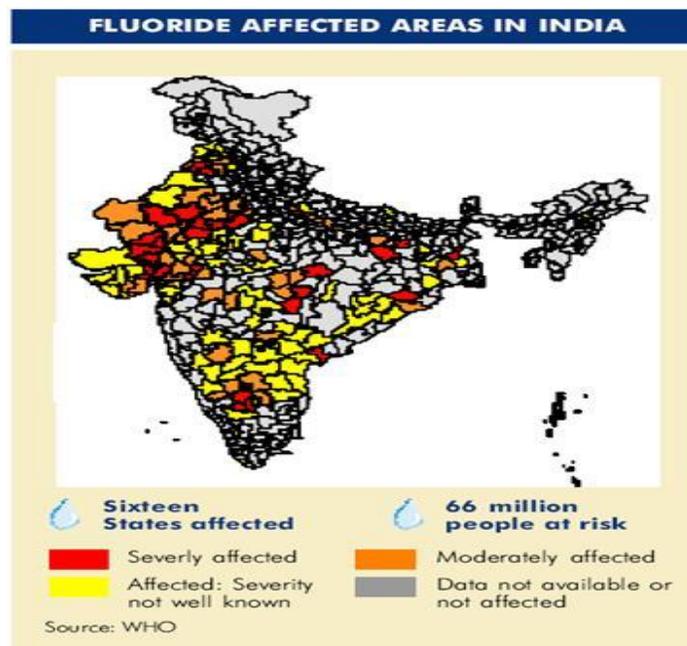


Figure 1. Fluoride content/affected regions in India.

Table 1. Biological effects of excess fluoride via water air and food.

S/No	Fluoride concentration in mg/L	Intrude media	Side effect of excess fluoride
1.	0.002	Air	Injury to vegetation/plants
2.	1	Water	Dental caries reduce
3.	2 or More	Water	Mottled dental enamel
4.	8	Water	10% Osteosclerosis/ bones and muscles
5.	50	Foods and water	Thyroid changes
6.	100	Foods and water	Growth retardation/ defective development
7.	120	Foods ad water	Kidney function changes/damages.

0.8-1.0 mg/L helps in development and strengthening of bones (Chinoy et al., 1992) and in preventing dental caries (Wood, 1974) and beneficial for calcification of dental enamel especially for children below 8 years of age. Due to consumption of excess fluoride containing drinking water in long durations, in Mehsana district of North Gujarat state of India were found to develop the mild to severe range of fluorosis problems in India (Susheela, 2001; Chinoy et al., 1992). At the contrast at higher fluoride concentrations (>1.5-2.0 mg/L) in daily drinking water adversely leads to dental fluorosis. Besides, the skeletal fluorosis gets inflicted upon intake of higher quantity of fluoride (>> 1.5 mg/L) for a prolonged period which causes defect in the bones and ligaments. Similarly, intakes of 20 to 40 mg F/day over long period results are more dangerous as it creates crippling skeletal fluorosis. Nevertheless, such excess fluoride concentration also affects the metabolism of Ca,

P in human body that leads to bone diseases called fluorosis, mottling of teeth and lesions of organs viz; endocrine glands, renal, thyroid and liver (Singh et al., 2007; Steinberg et al., 1955; Whitford et al., 1976). Fluorosis has hardly any cure; the only way to control it is to reduce fluoride in drinking water, if change of water source is not economically feasible. World Health Organization puts 1.5 mg/L as the tolerance limit of fluoride concentration in drinking water (WHO: 1997, 2006; BIS, 1991). The biological effects of excess fluoride contaminations via drinking water, food and air are mentioned in Table 1 (Dean et al., 1935).

Baseline status of fluoride pollution in Indian scenario

Globally, India is one among the twenty nations that has

a distress of fluorosis due to consumption of excessive fluoride through drinking water (Susheela and Majumdar, 1992; Susheela, 2003; Choubisa et al., 2001). The fluorosis research and rural development foundation, New Delhi, India had reported the fluoride contamination in ground water which was found to be in the range of 1.5 to 39 mg/L. The fluorosis affected regions are about 30% districts in Punjab, Haryana, Madhya Pradesh, Maharashtra and Bihar whereas 50% districts in Uttar Pradesh, Rajasthan, Gujarat, Andhra Pradesh and Tamil Nadu. As per Rajiv Gandhi national drinking water mission survey, some districts are comparatively less affected in Delhi and Kerala than other states. Until, 1992, 16 out of the 32 states of India were classified as fluorosis-endemic areas (Teotia and Teotia, 1984). Fluorosis and rural development foundation working for UNICEF, New Delhi, India had reported almost 12 million of the 85 million tons of fluoride deposits on the earth's crust are found in India; as a result fluorosis is endemic in almost sixteen Indian states (UNICEF, 1999; Carton, 2006). Besides, most seriously effected areas are Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh (Kumaran et al., 1971; Teotia et al., 1984). Rajiv Gandhi national drinking water mission survey projected about 25 million natives in 8700 villages that have drinking water with excess fluoride. Some studies reported that fluoride level in groundwater of many areas exceeds the permissible 1.5 ppm (Gupta et al., 1995; Manik and Biswapati, 2009; WHO, 2006). Moreover, some researchers had reported fluoride concentrations in ground waters of the worst affected countries like India are in the range of 0.5 to 48 ppm (Susheela, 2003).

Hence, it is imperative and significant to mitigate excessive fluorides from drinking water. Defluoridation of drinking water is the only practicable option to overcome problems associated with fluoride contamination in water, where alternate source is not available. Numerous procedures with diverse operation modes were reported for defluoridation including Nalagonda (Bulusu, et al., 1979; Nawlakhe and Paramasivam, 1993) and other methods like precipitation (Ku and Chiou, 2002), alumina adsorption (Haron et al., 1995), Ion-exchangers (Turner et al., 2005), reverse osmosis (Joshi et al., 1992), nano-filtration (Simons, 1993), membrane separation-dionandialysis (Ruiz et al., 2003) and electro-dialysis (Amor et al., 1998). Amid these processes, adsorption is the most extensive applied for water defluoridation. Now days, considerable attention has been devoted on utility of different types of low-cost materials like; china/kaolinitic clay, agricultural by-products, red mud, fly ash, carbon slurry, biogas residual slurry, zeolite, bone char, flax sieve and many more (Cengeloglu et al., 2002; Mahramanlioglu et al., 2002; Fan et al., 2003). But, most of these techniques owes limitations viz; maintenance, low capacities, cumbersome chemical and

mechanical procedures, non-availability of adsorbents, tedious regeneration etc makes them unsuitable universally. At rest, adsorption is an extensively used cost-effective technique for defluoridation of water especially in India where impact of fluorosis issue is highly intense and touching (Nawlakhe et al., 1975; Nawlakhe and Bulusu, 1989). Most of the available adsorbents exploited in adsorption techniques are either expensive or technically non-feasible at field scale (Bulusu et al., 1983; Bulusu et al., 1990; Bansiwali et al., 2010). Adsorption success too, mainly hinges on the development of environmentally benign, economically viable and technically feasible adsorbents. Hence, criteria for selection of an adsorbent mostly include its potential adsorption capacity for fluoride removal, benign features and its cost. In this direction, a number of adsorbents with very high potential had been developed, with limiting utility and high cost. Hence, we utilized local biomaterials like chitosan to grow bio-composite that can be safely and easily used at both household and community levels for water defluoridation without affecting its quality. Chitin is a (1 \pm 4)- β -linked natural homo-polymer of N-acetyl-D-glucosamine, produced enormously in biosphere, shrimp, crab shell, waste product of canning industries (Peter, 2002). Chitosan is a deacetylated form of chitin and both are low-cost, environmental friendly biodegradable and biocompatible (Goody et al., 1999). Both owe outstanding metal binding capacities (Chassary et al., 2004) with high selectivity and efficiency in dilute as well as in concentrated solutions due to excellent solute diffusion properties. Accordingly, chitosan derivatives were considered for removal of anions like arsenate (Katrina et al., 2009), molybdates (Niu and Volesky, 2003), chromates (Rojas et al., 2005; Boddu et al., 2003) and fluoride (Menkouchi et al., 2007) etc. Consequently, we modified parental chitosan skeleton by doping with 20% zirconium (IV) to make sorbent with control morphologies as discussed on the basis of SEM and Fourier transform infra red (FTIR) studies. 20% zirconium doped chitosan is potential sorbent in relatively small amount at optimum p^H besides its fluoride uptake characteristics at par competitive to commercial activated alumina. Further, kinetic studies for 20% zirconium (IV) doped chitosan governs a rapid adsorption, indicated its practicable operation as in packed columns. Besides findings encourage blends of sorbent with synthetic polymers to offer a viable option for defluoridation of water.

EXPERIMENT

Synthesis of adsorbent/composite materials

Raw chitin was purchased from M/s BR Corporation, Mumbai, in coarse grains. Deacetylation (80%) of chitin was done by 10 N NaOH solution. The biosorbent were synthesized by doping 20% Zirconium oxychloride hexahydrate with deacetylated chitosan.



Figure 2. Particle size development of chitosan- doped metal bio-composite bid.

Characterization analysis of 20% zirconium (IV) doped chitosan

Scanning electron microscope (SEM with EDAX) and FTIR study of 20% zirconium (IV) doped chitosan were done. The bulk density of sorbent was found to be 2.33 g/cm^3 . The pH of zero point charge (pHzpc) was 10.32. The BET surface area of biosorbent before and after defluoridation treatment was also calculated. The particle size development of 20% Zirconium doped chitosan bids are shown in Figure 2.

Fluoride adsorption procedure

About 100 ml of 10 ppm fluoride synthetic/prepared fluoride containing distilled water sample was taken in a PVC bottle and 10 g/L of bio-adsorbents was introduced to the sample bottles. The sample bottle was then kept on a rotary shaker for 24 h to attain equilibrium. Subsequently, the solutions were filtered through Whitman filter paper number 42 and corresponding filtrates were analyzed for residual fluoride concentration by ion selective electrode method. Similarly the well water sample collected from Pusad, Yavtmal district were used under same adsorption conditions. All adsorption studies were performed at NTP, 30°C .

Adsorbate, reagents and stock solutions

All chemicals and reagents used in this research study were of standard or analytical grade. Sodium fluoride (NaF, Merck) was used for preparation of the standard fluoride that is, stock solution in double distilled water. Further, all the synthetic fluoride solutions used for adsorption and analysis were prepared by appropriate dilution of this stock solution in de-ionized (DI) water. Only plastic wares (PVC) and viols were used for handling fluoride solution and for analysis. No glass containers are used. All plastic ware were washed in dilute HNO_3 acid and rinsed thoroughly with deionized water prior to its use. The natural fluoride rich drinking water was collected from Pusad village of Yaotmal district in Maharashtra state of India. The characteristics of ground water are illustrated in following Table 2.

Fluoride analyses of sample

The fluoride concentration in water samples was determined electrochemically, using the USEPA ion selective electrode method

which is applicable to the measurement of fluoride in drinking water up to range of 0.1 to 1,000 mg/L. The electrode used was an Orion 96 to 09 fluoride electrode, coupled to an Orion 420-A electrometer. Standards fluoride solutions (0.1 to 10 mg/L) were prepared from a stock solution (100 mg/L) of sodium fluoride. All the experiments were carried out in duplicates and were shown reproducible results with $\pm 3\%$ error.

RESULTS AND DISCUSSION

Analytical interpretation of biosorbent

Surface area property of 20% zirconium (IV) doped chitosan

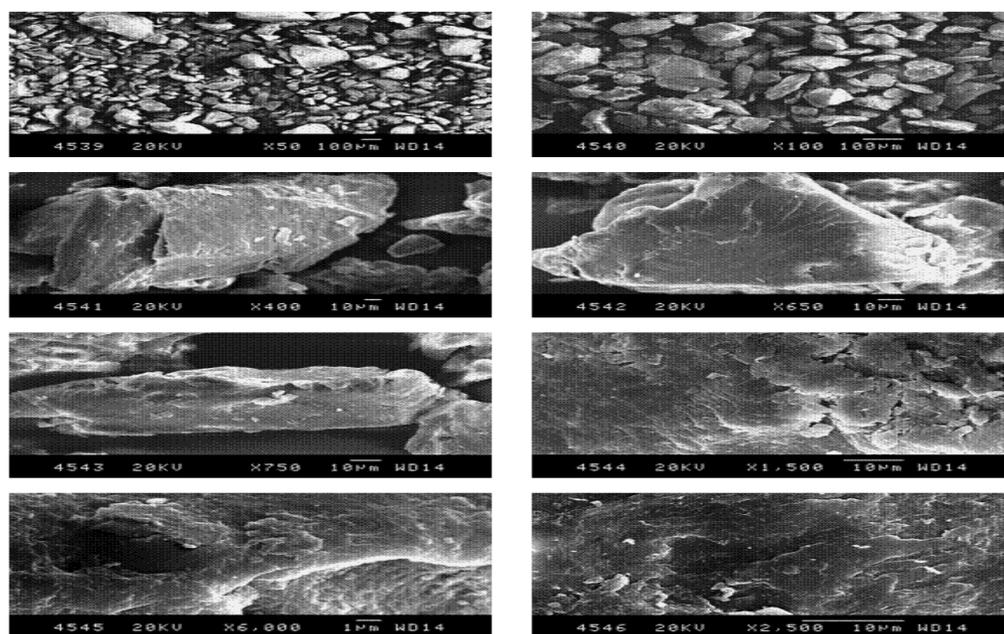
Physico-chemical characteristics in terms of density, particle size, moisture contents, soluble analysis of 20% zirconium (IV) doped chitosan showed good density 1.8 g/cm^3 and particle size nearly 150 mesh. The moisture content is less than 2% indicated opening and blocking of pores with inherent moisture that hardly affects defluoridation/adsorption. Surface area of 20% Zr (IV) doped chitosan were investigated and estimated by BET method which was found to be $93.394 \text{ m}^2/\text{g}$ (before adsorption) indicated marginal porosity/mesoporosity and formation of voids. Whereas, after defluoridation, this initial high surface area is reduced to maximum extent of $19.623 \text{ m}^2/\text{g}$ indicated blockages of mesopores/voids may be due to fluoride and other co-impurities interactions present in the water.

Scanning electron microscopy of 20% zirconium (IV) doped chitosan

Mesoporosity of 20% zirconium (IV) doped chitosan was elucidated by scanning electron microscopy (SEM) scanned on varied magnification (10 to $100 \mu\text{m}$) indicated different crystallinity with variable porosity and surface morphology as shown in Figures 3 and 4. SEM showed

Table 2. Physicochemical characteristics of well water sample from Pusad village.

S/ N	Parameter	Before defluoridation treatment	After defluoridation treatment by adsorption on 20% zirconium (IV) chitosan
1	Fluoride	5.65 ppm	1.01 ppm
2	pH	8.1±0.4	7.2±0.2
3	Turbidity	2.6 NTU	2.1NTU
4	Dissolved oxygen	3.1	2.9
5	BOD	1.8	1.1
6	Acidity	Nil	Nil
7	Alkalinity	388	290
8	Chloride	210 mg/L	210 mg/L
9	Total hardness (calcium carbonate)	356 mg/L	195 mg/L
10	Total organic carbon	59.08	18 mg/L
11	Total dissolved solids (TDS)	750 mg/L	250 mg/L
12	Total suspended solids (TSS)	312 mg/L	96 mg/L
13	Total phosphorous	0.032 mg/L	0.032 mg/L
14	Silica (SiO ₂)	39.22 mg/L	39.22 mg/L
15	Ammonia nitrogen	0.328 mg/L	0.3 mg/L
16	Boron	0.33 mg/L	0.33 mg/L
17	Sodium	14.0 mg/L	11.1 mg/L
18	Potassium	6.0 mg/L	2.0 mg/L
19	calcium	120 mg/L	41 mg/L
20	magnesium	45 mg/L	14 mg/L
21	carbonates	85 mg/L	40 mg/L
22	bicarbonates	35 mg/L	18 mg/L
23	nitrate	10 mg/L	8 mg/L
24	sulphate	91 mg/L	75 mg/L
25	phosphate	2.4 mg/L	2 mg/L
26	Electrical conductivity in dS/m	2.1 (medium)	0.9

**Figure 3.** SEM morphology of 20% zirconium (IV) doped chitosan before defluoridation.

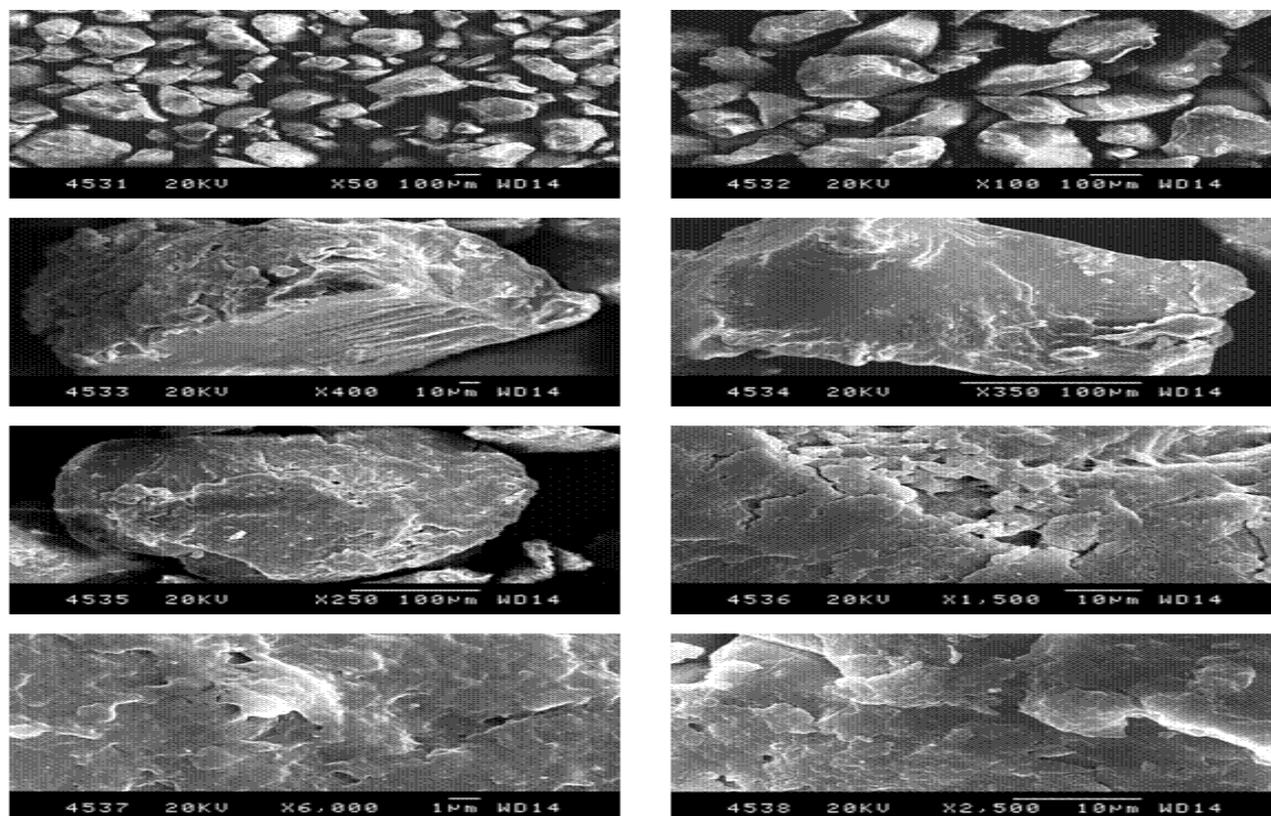


Figure 4. SEM morphology of 20% zirconium (IV) doped chitosan after defluoridation.

less porous crystalline structure with fewer voids/pores as manifested by surface area of sorbent before adsorption treatment. The initial high surface area of 20% zirconium (IV) doped chitosan is reduced up to $19.623 \text{ m}^2/\text{g}$ is attributed to blockages of mesopores/voids by means of fluoride as well as other cationic and anionic co-impurities present in the water. SEM topography after doping with zirconium showed cavities/pores as marked with a dark black color among a sharp boundary against white color as the particle reinforcement. SEM indicated reinforcement of particle size in the doped biosorbent matrix may be attributed to 20% zirconium loadings which is much smaller than dimensions of $43 \mu\text{m}$ (greater than 325 mesh size). SEM micrograph also provides information of structural changes after 20% zirconium doping in parent chitosan skeletons. The high surface area ($93.394 \text{ m}^2/\text{g}$) of mesoporous 20% Zr (IV) doped chitosan composite accounts for matrix framework development due to metal doping in chitosan. This also results in too much cavities/voids in mesoporous bicomposite and leads to crack formation in chitosan skeleton that probably due to these developed pores (visible in magnified SEM internal cavities). Measurement from SEM showed average pore diameter about few micrometers (μm).

Fourier transform infra red (FTIR) spectroscopy analysis of 20% zirconium (IV) doped chitosan

Twenty percent zirconium (IV) doped chitosan sorbent was scanned for Fourier transform infra red (FTIR) to observe facade functional groups attached on its surface which plays vital role in chemical interaction during fluoride adsorption besides its high surface area would be discussed. Based on FTIR band characterization, functional groups were identified with linkages and bond stretching within sorbent skeleton (Zawadzki, 1989; Nakamoto, 1986).

The chitosan, is a cationic polymer and shows characteristic of FTIR peaks in the range of 1500 to 1690 cm^{-1} are due to primary amine group ($-\text{N}-\text{H}$) of pure chitosan (crude/without doped). The FTIR peak in the range of 100 to 1320 cm^{-1} is due to C-O bond bending and peak at 3634.50 cm^{-1} is due to stretching of free hydroxyl groups in chitosan. The broad band at 2889.21 cm^{-1} is due to aldehyde ($\text{H}-\text{C}=\text{O}$) stretching in pure chitosan which is shifted to 2362.41 cm^{-1} in chitosan bicomposite due to zirconium (IV) doping in polymeric skeleton. The band at 1569.21 cm^{-1} in pure chitosan is due to C-H bending frequency and new bands at 1177.51 cm^{-1} , 1260.95 and 1205.87 cm^{-1} in doped chitosan is due

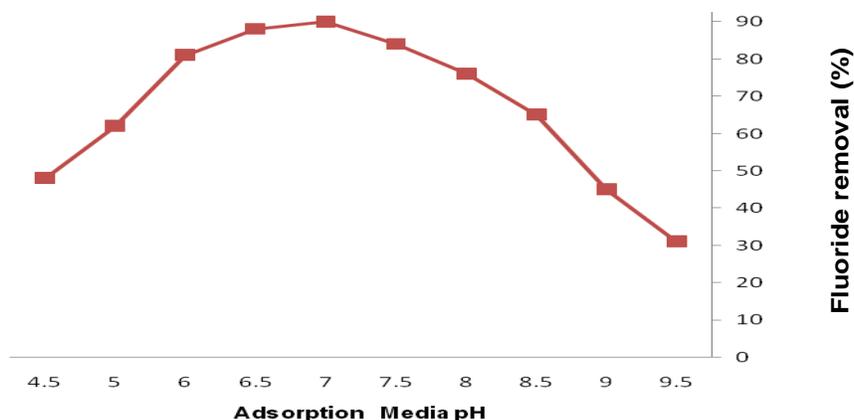


Figure 5. Effect of pH on fluoride adsorption using 20% Zr (IV) doped chitosan.

to linkage of zirconium with anionic sites of chitosan. Absorption at 1076.90 cm^{-1} is due to C-N stretching mode of chitosan and absorption peak at 856.27 to 959.85 cm^{-1} is due to C-H bending vibrations.

The FTIR bands at 1675.92 cm^{-1} and 2876.13 (after defluoridation treatment) is expected due to fluoride and other co-impurities like nitrate, carbonate and sulphate etc entrapped in 20% zirconium doped chitosan bio-composite. The FTIR band at 1645 cm^{-1} in doped chitosan after defluoridation treatment is due to vibration mode C=O group of amide linkage gets shifted by 45 cm^{-1} due to fluoride adsorption. Broad band range of 917 to 1250 cm^{-1} is due to Zr-O-Zr bonding via oxygen atom. The band at 795 to 950 cm^{-1} is due to bending of Zr-O-C bonds. IR band at 490.76 and 602.64 cm^{-1} is also due to Zr-O-C stretching mode. This FTIR data supported complete bonding of Zirconium metal with chitosan and ultimately accountable for chemical interaction/physicochemical adsorption of fluoride onto cationic sites of sorbent.

Performance of fluoride adsorption by 20% of zirconium (IV) doped chitosan

The key factor governing fluoride adsorption by 20% of zirconium (IV) doped chitosan includes pH, Zirconium (IV) metal loading and adsorbent dose and initial fluoride concentration.

Effect of pH

pH has a very significant effect in determining fluoride biosorption on 20% zirconium (IV) doped chitosan from water. Fluoride adsorption on 20% zirconium (IV) doped chitosan as a function of pH is shown in Figure 5. The maximum adsorption capacity was found at p^H 6.5 to 7 (slightly neutral conditions). However, at alkaline pH (>8)

defluoridation capacity of 20% zirconium doped chitosan was found to be decreased by almost 40 to 50%. The decrease of fluoride uptake at alkaline/basic pH conditions may be due to electrostatic repulsion of fluoride to negatively charged surface of 20% zirconium doped chitosan, besides competition for active cationic site bindings by excessive presence of hydroxyl anions. The pH affects surface charges of pretreated chitosan at specific functional sites like, hydroxyl and amino groups (Vilar et al., 2005). The maximum fluoride removal was reached at pH 5.0 with the removal efficiency of $Q_m = 0.98\text{ mg/g}$ of sorbent as calculated according to following equation:

$$Q_m = (C_i - C_{eq}) V/m, \text{-----} Eq^n \quad (1)$$

where V is volume of sample solution (ml), m is the mass of 20% zirconium (IV) doped chitosan sorbent (g), C_i and C_{eq} are the initial and equilibrium/final concentration of fluoride in solution (mg/L) respectively.

However, at acidic conditions 20% zirconium doped chitosan was found to be unstable and not working significantly for defluoridation purpose and, under extreme acidic conditions $pH \ll 4$, chitosan is not much stable due to leaching effect of metal from bio-adsorbent skeleton (Guibal, 2004). So, the pH range 5 to 9 was chosen for preliminary study and pH of 6.9 kept fixed for further experimental defluoridation of water.

Effect of zirconium (IV) metal loading on chitosan

The optimum breakthrough ratio of zirconium (IV) metal loaded on chitosan was found to be 20% (w/v). Amongst zirconium (IV) metal loading in chitosan sorbents used for fluoride removal from water, 20% metal doped in chitosan exhibited excellent water defluoridation capacity with optimized sorbent's dose of 10 g/L as shown in Figure 6.

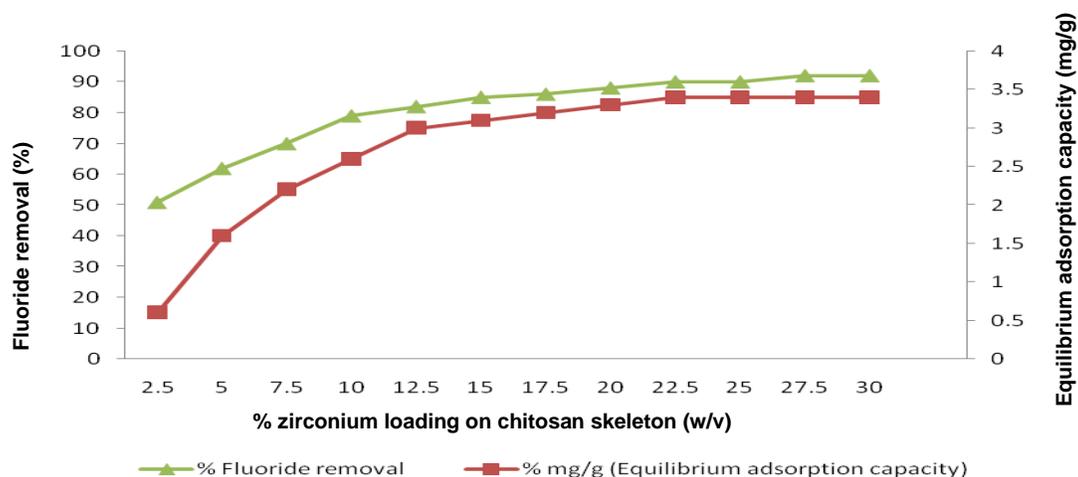


Figure 6. Effect of % Zirconium (IV) loading on chitosan skeleton for fluoride removal, sample concentration 5.6 ppm, pH-6.9 and time 24 h.

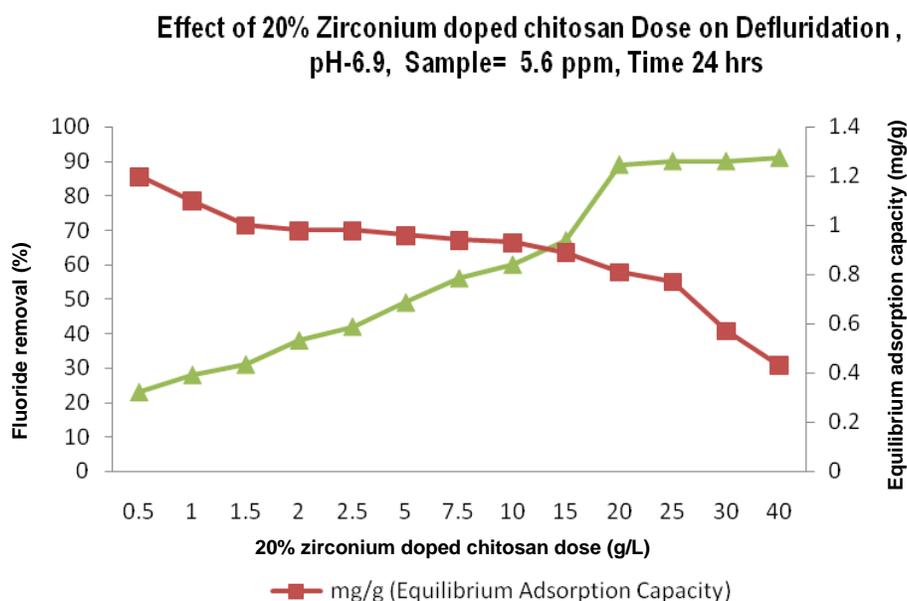


Figure 7. Effect of Zirconium (IV) doped chitosan dose on fluoride removal.

Effect of 20% zirconium (IV) doped chitosan dose on fluoride removal

The optimization of adsorbent dose of 20% zirconium (IV) doped chitosan was found optimum at pH range of 6.5 to 6.9. At above 20% zirconium (IV) metal capacity doped on chitosan exhibited leaching during fluoride adsorption; further the stringent fluoride concentration of 1-1.5 mg/L was achieved with 20% zirconium (IV) doped chitosan. Preliminary defluoridation studies for well water samples from Pusad, Yaotmal, were done under same experimental conditions with optimum dose of 10 g/L as

shown in Figure 7. The fluoride removal markedly increased up to adsorbent dose of 10 g/L due to increase in bio-adsorbent/fluoride ratio as shown in Figure 7. But, further increase in adsorbent dose doesn't shown appreciable improvement in defluoridation capacity is due to saturation of bio-adsorbents surfaces that exhibited low fluoride uptake.

Effect of initial fluoride concentration

The amount of fluoride distribution amongst sorbent and

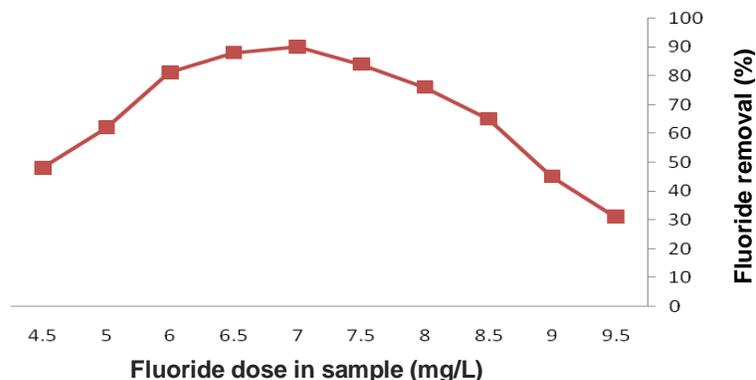


Figure 8. Effect of Initial Fluoride Concentration on fluoride removal, pH-6.9, time 24 h.

solution at equilibrium is vital in determining maximum fluoride adsorption capacity of adsorbent. So, the effect of initial fluoride concentration on sorption capacity of 20% zirconium (IV) doped chitosan was investigated at optimized pH 6.7 ± 0.2 . Defluoridation rate substantially increased by increasing initial fluoride sample concentration from 4.5 to 8.0 mg/L (range of 90 to 75% but maximum of 90% defluoridation at 6 ppm fluoride sample concentration). This is because, higher initial fluoride concentration provides driving force to overcome all mass transfer resistances between solution and 20% zirconium (IV) doped chitosan surface, consequently fluoride adsorption capacity increases. Besides, the number of collisions between fluoride and 20% zirconium (IV) doped chitosan increase as parallel with initial fluoride concentration (Guibal, 2004). Moreover, fluoride adsorption rate decreases with increasing initial fluoride concentration from 8 mg/L onwards may be due to the saturation of active sorption sites available for fluoride anions on the surface of 20% zirconium (IV) doped chitosan. Thus, optimum initial fluoride sample concentration was found in the range of 5 to 8 ppm (mg/L) as shown in Figure 8.

Adsorption study

Adsorption capacity (mg F^- per gram of adsorbent) is assessed through equilibrium sorption data generated by continuously batch studies, using 'best-fitted' isotherm models to dictate optimum model parameters. Adsorption studies for equilibrium sorption data were conducted by changing concentrations of fluoride and also by adsorbent's dose. However, most of the reported isotherm studies are on concentration variations in synthetic that is, deionized/distilled water (which lacks fluoride impurity) which lose the 'real-life' flavors and characteristics of natural samples. Normally, apart from adsorbate concentrations, pH of adsorption medium as

well as presence of other competing/impurity ions drastically alters sorbent's defluoridation capacity in aqueous solutions (József and Klára, 2005; Dongre et al., 2010). Rationally, defluoridation of synthetic water cannot be properly demonstrated for its adsorption potential in field scale; hence, defluoridation too was, conducted with well water collected from Pusad village of Yotmal district in Maharashtra state of India, which showed enthusiastic results.

Adsorption isotherms and sorption kinetics

In simulating equilibrium data, Langmuir, and Freundlich isotherm adsorption models were studied. The satisfactory description of equilibrium data matched/fitted to linearly transformed Freundlich isotherms equation: $\log(x/m) = \log K_f + 1/n \log C_e$, is like adsorption on heterogeneous surfaces. The value of K_f and n were calculated and found to be 41.50 and 0.136 for pure chitosan and 3.27 and 0.67 for 20% Zr (IV) doped in chitosan skeleton respectively. Freundlich isotherm correlation coefficient was found to be $R^2=0.939$ as shown in Figure 9. All defluoridations were studied at room temperature.

Mechanism of defluoridation on 20% of zirconium (IV) doped chitosan

Literature reveals chitosan-derivative sorbents were used for removal of cations, due to free electron lone pairs in O and N-atoms of chitosan linkage. Thus, metals like zirconium (IV) get catches at primary $-\text{NH}_2$ and OH groups of chitosan due to electrostatic attraction. This metal doped chitosan cationic site is vital in fluoride anion sorption mechanism (Abe et al., 2004). Besides, fluoride adsorption capacity was found 55% at pH = 8 and further decreases fluoride removal above pH > 8. This

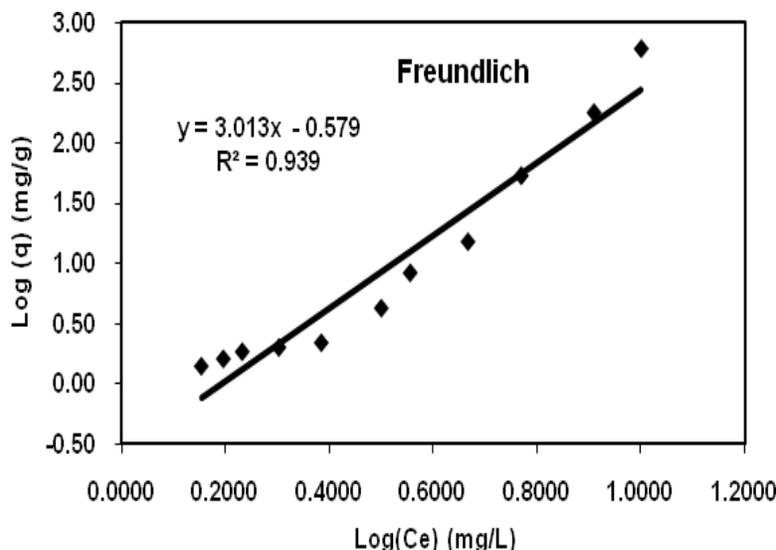


Figure 9. Freundlich adsorption isotherm for 20% Zr-chitosan composite.

decreased defluoridation rate is interpreted as hydroxide anions competent to fluoride on coordinated sites of 20% zirconium (IV) chitosan composite via ligand-exchange mechanism. Equilibrium solution pH had a remarkable effect on fluoride adsorption capacity, suggested electrostatic columbic forces (attractive/repulsive) playing major role in binding of monovalent fluoride on cationic sites of modified/doped chitosan skeleton (Ravi, 2000).

Biosorbent displayed a surface controlled adsorption, indicating a monolayer sorption by interactions between F^- anion and 20% zirconium doped chitosan through heterogeneous distribution of sorption energies. It is expected that fluoride anion gets diffused into the skeleton of 20% metal doped chitosan due to its suitable atomic size as entrapped via chemi-adsorption and intra-particle diffusion phenomenon. Besides, presence of calcium, magnesium also assisted this binding of fluoride in to biocomposite as supported by their depleted concentrations after defluoridation treatment on well water sample. This is because cations like calcium, sodium, magnesium and anions like nitrate, sulphate, bicarbonates in well water sample were found little depleted as some of which may share important philicity for concern adsorption sites of bio-composite along with fluoride. Experimental defluoridation capacity of 20% Zr (IV) doped chitosan is found more than commercially reported adsorbents (Viswanathan et al., 2009; Meenakshi and Viswanathan, 2009). This 20% zirconium (IV) doped chitosan owes an ability to mitigate fluoride level to stringent concentration even in case of natural well water sample from Pusad district with equal potential and regeneration, therefore can be applied to manifold defluoridation of drinking water.

Adsorption–desorption cycle/regeneration of adsorbent

Water defluoridation is economical if adsorbent is regenerated, besides, aids in reducing environmental impacts of solid waste disposal. Fluoride desorption from 20% zirconium (IV) doped chitosan and its regeneration was done at pH 10 using 0.1 N NaOH solution. About 90% of adsorbed fluoride was desorbed; indicated defluoridation as a reversible phenomenon. However, residual fraction of adsorbed fluoride which would not have been desorbed exhibits its tight bonding at cationic sites of doped biosorbent. The regenerated 20% zirconium (IV) doped chitosan were reused in another defluoridation, with adsorption capacity 75% (of original capacity) for a solution containing 10 mg F^- /liter. This reduced defluoridation capacity may be due to residual/undesorbed fluoride previously available onto sorbent's surface. Nevertheless, further optimization of adsorption–desorption cycle was proposed for future column dynamic studies, to improve its regeneration.

Conclusions

Adsorption studies indicated 20% zirconium doped chitosan acted as potential sorbent for defluoridation of water in benign way for batch adsorption study. The following conclusions are drawn from defluoridation research:

- 1) 20% zirconium (IV) doped chitosan proved to be a better adsorbent for defluoridation of water with

adsorption capacity about 90% (practically well at ambient pH range 6 to 6.9) in synthetic/prepared fluoride water sample, moreover fluoride removal capacity depleted to almost half at pH=8 and further decreased pH>8.

2) Optimum dose of 20% zirconium (IV) doped chitosan adsorbents was 3 g/L, moreover sorbent were regenerated conveniently at pH=10 and reused for another cycle of water defluoridation with reduced adsorbing capacity.

3) Linearized form of isotherm drawn indicated direct proportionality of adsorbate/fluoride with 20% zirconium (IV) doped chitosan. The sorption dynamic followed pseudo-second-order equation, so adsorption process was complex, both boundary of liquid film (surface adsorption) and intra-particle diffusion contributed to rate-determining step of defluoridation.

4) Experimental defluoridation data fits Freundlich model with efficiency $K_f=3.27$ mg/g and adsorption coefficient of $n=0.939$.

5) Rapid adsorption kinetic signifies the developed treatment as a viable option for water defluoridation even up to 1-1.5 ppm stringent limit both in case of prepared fluoride sample and well-water, nevertheless after defluoridation the concentrations of metal cations like calcium, sodium, magnesium and anions like nitrate, sulphate, bicarbonates in well water sample were found little depleted as some of which may share viable adsorption sites towards bio-composite along with fluoride. An attempt was done to develop low cost, benignly effective and simple defluoridation technique by utilizing 20% zirconium (IV) doped chitosan sorbent.

ACKNOWLEDGEMENTS

Authors are thankful to the Head, Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur and Director, NEERI, Nagpur, India for providing necessary laboratory facilities to carry out this project work. The project's principal investigator RSD is also thankful to University Grant Commission (UGC F.No37-568/2009(SR), New Delhi, India for sponsoring this minor research project entitled "*Development of Benign Bio-polymeric Adsorbents for Fluoride Removal from Drinking Water*".

REFERENCES

- Abe I, Iwasaki S, Tomiko T, Kawasaki N, Nakamura T, Tanaka S (2004). Adsorption of Fluoride Ions onto Carbonaceous Materials. *J. Colloid Interface Sci.*, 275: 35-39.
- Amor Z, Malki S, Taky M, Bariou B, Mameri N, Elmidaoui A (1998). Optimization of fluoride removal from brackish water by electro dialysis. *Desalination*, 120: 263-271.
- Arjunan TV, Aybar HS, Nedunchezian N (2009). Status of solar desalination in India: Review Article. *Renewable and Sustainable Energy Rev.*, 13(9): 2408-2418.
- Bansiwal A, Pillewan P, Biniwale, RB, Rayalu SS (2010). Copper oxide incorporated mesoporous alumina for defluoridation of drinking water. *Microporous Mesoporous Mater.*, 129(1-2): 54-61.
- Biswas K, Saha SK, Ghosh UC (2007). Fluoride removal efficiency from aqueous solution by synthetic iron (III) – aluminum (III) mixed oxide. *Ind. Eng. Chem. Res.*, 46: 5346.
- Boddu VM, Abburi K, Talbott JL, Smith ED (2003). Removal of Hexavalentchromium from wastewater using a new composite chitosan biosorbent. *Environ. Sci. Technol.*, 37: 4449-4456.
- Bulusu KR, Sundaresan BB, Pathak BN, Nawlakhe WG, Kulkarni DN, Thergoankar VP (1979). Fluorides in water, defluoridation methods and their limitation. *J. Inst. Eng. Environ. Eng. Div.*, 60: 1-25.
- Bulusu KR, Nawlakhe WG (1983). Activated Alumina as Defluoridation medium. *I E (I) J. EN*, 64: 19.
- Bulusu KR, Nawlakhe WG (1990). Defluoridation of water and activate alumina: Absorption in continuous contacting systems. *Ind. J. Environ. Health*, 32: 197.
- Bureau of Indian Standard (BIS) (1991). Indian standard specification for drinking water, IS, 10500: 2-4.
- Carton RJ (2006). Review of the United States National Research Council Report: Fluoride in Drinking water. *Fluoride*, 39: 163-172.
- Cengeloglu Y, Kir E, Ersoz M (2002). Removal of fluoride from aqueous solution by using red mud. *Sep. Purif. Technol.*, 28: 81-86.
- Chassary P, Vincent T, Guibal E (2004). Metal anion sorption on chitosan and derivative materials: A strategy for polymer modification and optimum use. *Reactive and Functional Polymers*, 60: 137-149.
- Chinoy N, Narayana MV, Sequeria E, Joshi SM, Barot JM, Purohit RM (1992). Studies on effects of fluoride in 36 villages of Mehasana district, North Gujarat. *Fluoride*. 25: 101-110.
- Choubisa S (2001). Endemic Fluorosis in southern Rajasthan of India. *Fluoride*, 34: 64-70.
- Dean HT, Dixon RM, Cohen C (1935). Mottled enamel in Texas. *Public Health Reports*, 50(13): 424-442. http://www.who.int/water_sanitation_health/publications/fluoride_drinking_water_full.pdf. 2009-01-24.
- Dongre RS (2010). Development of Eco-friendly Defluoridation Technique for Drinking Water, PhD. Thesis awarded by R.T.M. Nagpur University, Nagpur-33, India, Nov.
- Fan X, Parker DJ, Smith MD (2003). Adsorption kinetics of fluoride on low cost materials. *Water Res.*, 37: 4929-4937.
- Fawell J, Bailey K, Chilton J, Dahi E, Fewtrell L and Magara Y (2006). Environmental occurrence, geochemistry and exposure: Fluoride in Drinking water. IWA Publishing, Alliance House, London SW1H 0QS, UK, ISBN 92-4-156319-2. www.iwapublishing.com.
- Giridharadas A (2005). Water-scarce India, too, weighs a Return to Ancient Practices. *International Herald Tribune News Paper*, 20 Aug 05.
- Gooday GW (1999). Physiology of microbial degradation of chitin and chitosan. *Biodegradation*, 1: 177-190.
- Guibal E (2004). Interactions of metal ions with chitosan-based sorbents: A review. *Separation Purif. Technol.*, 38: 43-74.
- Gupta SK, Sharma P (1995). An approach to tackling fluoride problem in drinking water. *Current Sci.*, 64: 774.
- Haron MJ, Wan Yunus WSN, Wasay SA (1995). Sorption of fluoride ions from aqueous solutions by an yttrium loaded poly (hydroxamic acid) resin. *Int. J. Environ. Stud.*, 48: 245-255.
- Joshi SV, Mehta SH, Rao AV (1992). Estimation of sodium fluoride using HPLC in reverse osmosis experiments. *Water Treat.*, 7(19): 207-211.
- József H, Klára P (2005). Determination of surface properties of iron hydroxide-coated alumina adsorbent prepared for removal of arsenic from drinking water. *J. Colloid Interface Sci.*, 284(1): 71-77.
- Katrina CM, Kwok V, Lee KC, Gerente C, Gordon M (2009). Novel model development for sorption of arsenate on chitosan. *Chemical Eng. J.*, 151: 122-133.
- Kumaran P, Bhargava GN, Bhakuni TS (1971). Fluorides in ground water and endemic fluorosis in Rajasthan. *Indian J. Environ. Health*, 13: 316-324.
- Ku Y, Chiou HM (2002). The adsorption of fluoride ion from aqueous solution by activated alumina. *Water Air Soil Pollut.*, 133(1-4): 349-

- 360.
- Mahramanlioglu M, Kizilcikli I, Bicer IO (2002). Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth. *J. Fluorine Chem.*, 115: 41–47.
- Manik CK, Biswapati M (2009). Assessment of potential hazardous of fluoride contaminated drinking groundwater of an intensively contaminated district in West Bengal in India. *Environ. Monitor. Assess.*, 152(1-4): 97-103.
- Meenakshi S, Viswanathan N (2009). Defluoridation of water using magnesia/chitosan composite. *J. Hazard Mater.*, 162: 920-930.
- Menkouchi S, Annouar MA, Tahaik S, Mountadar M, Soufiane M, Elmidaoui A (2007). Fluoride removal for underground brackish water by adsorption on the natural chitosan and by electro dialysis. *Desalination*, 212(1-3): 37-45.
- Nakamoto K (1986). *Infrared and Raman spectra of Inorganic and Coordination Compounds*. 4th ed., Wiley, New York.
- Nawlakhe WG, Paramasivam R (1993). Defluoridation of potable water by Nalgonda technique. *Current, Sci.*, 65: 10.
- Nawlakhe WG, Kulkarni DN, Pathak DN, Bulusu, KR (1975). Defluoridation of Water by Nalgonda Technique. *Ind. J. Environ. Health*, 17: 226.
- Nawlakhe WG, Bulusu KR (1989). Nalgonda Technique; A Process for removal of excess fluoride from water. *Water. Qual. Bull.*, 14: 218-220.
- Niu H, Volesky B (2003). Characteristics of anionic metal species biosorption with waste crab shells. *Hydrometallurgy*, 71: 209-215.
- Peter MG (2002). Chapter 15: Chitin & Chitosan from Animal Sources. *Biopolymers*, 6: 133.
- Ravi KMN (2000). A review of chitin & chitosan applications. *React. Funct. Polym.*, 46: 1–27.
- Rojas G, Silva J, Flores JA, Rodriguez A, Ly M, Maldonado H (2005). Adsorption of chromium onto cross-linked chitosan. *Separation and Purification Technol.*, 44: 31-36.
- Ruiz T, Persin F, Hichour F, Sandeaux J (2003). Modification of fluoride removal in Donnan dialysis. *J. Membr. Sci.*, 212: 113–121.
- Simons R (1993). Trace element removal from ash dam waters by nanofiltration and diffusion dialysis. *Desalination*, 89: 325–341.
- Singh B, Gaur S, Garg VK (2007). Fluoride in drinking water and human urine in southern Haryana of India. *J. Hazardous Mater.*, 144(1–2): 147–151.
- Singh R, Maheshwari RC (2001). Defluoridation of drinking water—A review. *Ind. J. Environ. Prot.*, 21(11): 983–991.
- Steinberg CL, Gardner DE, Smith FA, Hofge HC (1955). Comparison of rheumatoid (ankylosing) spondylitis and crippling fluorosis. *Annals of Rheum Disease*, 14: 378–384.
- Susheela AK, Majumdar K (1992). Fluorosis control programme in India. 18th WEDC Conference; Sept 13-15; Kathmandu, Nepal, 229-231.
- Susheela AK (2001). Sound planning and implementation of fluoride and fluorosis mitigation programme in an endemic village. *Proceedings: International workshop on fluoride in drinking water: Strategies, management and mitigation, Bhopal, India*, pp. 1-12.
- Susheela AK (2003). *A Treatise on Fluorosis*, Revised 2nd ed., Fluorosis Research and Rural Development Foundation, New Delhi, India, p. 23.
- Teotia SP, Teotia S, Singh M, Rathour DP, Singh RS, Tomar, NPS (1984). Endemic fluorosis: Changes to deeper bore wells as a practical community acceptable approach to its eradication. *Fluoride*, 17: 48–52.
- Teotia SPS, Teotia M (1984). Endemic fluorosis in India: a challenging national health problem, *J. Association of Physicians of India.*, 32:347-352. http://www.nih.ernet.in/nih_rbis/india_information/AnnualWaterRequirements.htm.
- Turner BD, Binning P, Stipp SLS (2005). Fluoride removal by calcite: evidence for fluorite precipitation and surface adsorption. *Environ. Sci. Tech.*, 39: 9561–9568.
- UNICEF (1999). *States of the Art Report on the Extent of Fluoride in Drinking Water and the Resulting Endemicity in India*. Report by Fluorosis and Rural Development Foundation for UNICEF, New Delhi. UNICEF Study 2002: Vol. 31.
- Vilar VJP, Botelho CMS, Boaventura RAR (2005). Comparative Study of Various Bio-sorbents for removal of Chromium ions from Industrial Wastewaters. *Process Biochem.*, 40: 3267–3275.
- Viswanathan N, Meenakshi S (2009). Selective sorption of fluoride using Fe (III) loaded carboxylated chitosan beads. *J. Fluorine Chem.*, 129: 503-509.
- Whitford GM, Pashley DH, Stringer GI (1976). Fluoride renal clearance A-334 pH-dependent event. *American J. Physiol.*, 230: 527–532.
- WHO (1997). *Guideline for Drinking Water Quality Health Criteria and Other Supporting Information*, 2nd ed. Geneva, 2: 122.
- WHO (2006). *Guidelines for Drinking-Water Quality: Incorporating First Addendum. Recommendation*, World Health Organization, 20 Avenue Appia, 1211 Geneva 27, Switzerland, 1(3): 375–376.
- Wood JM (1974). Biological cycles for toxic elements in the environment. *Sci.*, 183: 1049–1052.
- Zawadzki J (1989). *Infrared Spectroscopy in Surface Chemistry of Carbons*. In: *Chemistry and Physics of Carbon*; P. A. Thrower, Ed.; 21; Marcel Dekker; New York, pp. 147-386.