Defluoridation By Adsorption With Chitin - Chitosan-Alginate –

Polymers – Cellulose – Resins – Algae And Fungi - A Review

Sanghratna S. Waghmare[1], Tanvir Arfin[2]

[1] Senior Scientist, Environmental Materials Division, National Environmental Engineering Institute (CSIR-NEERI), Nagpur, Maharashtra, India.

[2] Scientist, Environmental Materials Division, National Environmental Engineering Institute (CSIR-NEERI), Nagpur, Maharashtra, India.

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Abstract - *The ground water are typically gets contaminated by a few wellbeing risk components like fluoride, arsenic, nitrate, phosphate, mercury, heavy metals, and so forth. Fluorosis is for the most part brought about by abundance concentration of fluoride in water. Fluorosis is a noteworthy wellbeing issue in a few countries. Fluorosis is epidemic in more than 20 countries in the world. In Indian alone, more than 19 states having high concentration of fluoride (more than 1.5 mg/l) in their ground water. The issues are more genuine in the states like Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujrat, Uttar Pradesh, Tamil Nadu, Karnataka and Maharashtra. The number of inhabitants in numerous creating countries depends on ground water as a main basis of drinking water. The major foundation of fluoride to an individual is drinking water. The trace amount of fluoride valuable for dental enamel advancement and gets to be dangerous when crossed the World Health Organization limit of 1.5 mg/l. Adsorption is great than other defluoridation systems like chemical precipitation, ion exchange, membrane techniques, electro-coagulation and electrodialysis methods and adsorption implemented to remove fluoride efficiently, economically, simplicity of operation and environmentally friendly. This review illuminated the fluoride uptake of different bio-polymers, polymers, celluloses, resins and their composites and defluoridation limits of algae and fungi in light of different overseeing components, for example, pH, contact time, agitation speed, the dose of adsorbent, initial fluoride concentration, particle sizes and temperature. The adsorption best fitted with isotherm, kinetic and thermodynamic modeling was likewise explained. The practicability of adsorption was described by reuse and recovery of adsorbents alongside investigation of the fixed bed column.*

Key Words: *Adsorption, Chitin, Chitosan, Cellulose, Resin, Defluoridation.*

1. INTRODUCTION

The main source of fluoride uptake by human is drinking water. The fluoride ions polluted ground water by different routes like soils, rocks, air and industrial effluents. The overabundance amount of fluoride (>1.5 mg/l) in charge for all kind of fluorosis, development retardation, fruitlessness and immunological imperfections. The trepidation of fluorosis prevails in a few countries in the world, including developing countries like India, Srilanka, Pakisthan, China and so on. [1-5].

Adsorption was for the most part adopted in developing countries than other costly fluoride removal technologies, for example, chemical precipitation, membrane separation, ion exchange and electro-deposition and so on [6]. The traditional adsorbents utilized for fluoride removal are commercial activated carbon and activated alumina yet they are costly and discovered hard to recover when deplete. To defeat these challenges, the natural biopolymers, cellulose and resins are utilized.

The chitosan globules as well as modified chitosan beads with metal oxides conquer the dissolution of chitosan into the water too clogging and friction issue in the fixed bed column. The chitosan has NHF groups to pull in fluoride ions effectively. Defluoridation by algae and fungi paved other method for adsorption and found suitable as commercial ones. The present study revealed the overview of different adsorption studies did successfully by utillizing chitin, chitosan, cellulose, resins, algae and fungi under different experimental conditions to meet the desirable level of fluoride as recommended by the World Health Organization (WHO) and their practical suitability in view of economy, reuse and regeneration besides column studies.

2. DEFLUORIDATION BY CHITIN, CHITOSAN AND THEIR MODIFIED ADSORBENTS

Ma *et al.* (2007) have utilized magnetic-chitosan particle prepared by co-precipitation method as adsorbent for defluoridation of water. The maximum fluoride adsorption capacity of magnetic-chitosan particle was observed to be 22.49 mg/g at pH 7.0±0.2. The recovey of exhausted adsorbent was done by 0.8-1.0 M NaOH solution and a reutilized adsorption removal of 98-99% was

accomplished. The experimental data were taken after the pseudo-second order kinetic equation [7].

Kamble *et al.* (2007) have utilized chitin, chitosan and 20%-lanthanum incorporated chitosan (20% La-chitosan) for fluoride uptake of water. The fluoride removal by Lanthanum chitosan adsorbent was amazing when contrasted with chitin and chitosan. The most extreme uptake of fluoride by Lanthanum chitosan adsorbent was seen at pH 6.7. The rate of adsorption was quick and most prominent uptake of fluoride was accomplished within 20 minutes. The most compelling fluoride adsorption limit of 3.1 mg/g was accomplished at acidic pH of 5.0 and adsorbent estimations of 1.5 g/l. The adsorption of fluoride in distilled water was more than field water because of the vicinity of competing ions in field water. The habitations of co-ions in the water extraordinarily influence the adsorption capacity. No noteworthy leaching of lanthanum was observed form adsorbent [8].

Sahli *et al.* (2007) have examined the defluoridation of salty water by adsorption on the natural chitosan and by electro-dialysis. The coupling of two techniques decreased the fluoride obviously. The adsorption by chitosan was extremely fast and come to a maximum at 5 minutes. The defluoridation was increased with increase in pH from 2 to 6 and after that diminshed up to pH 10. The chitosan cut down the 3.25 mg/l of fluoride in brackish water to 0.9 mg/l by a progressive batch reaction which was lower than the WHO standard of 1.5 mg/l [9].

Sundaram *et al.* (2008) has investigated the defluoridation capacity of Nano-hydroxyapatite/chitosan (n-HApC) composite adsorbent from drinking water. The defluoridation capacity of n-HApC was 1.56 mg/g, while defluoridation capacity of Nano-hydroxyapatite (n-HAp) was 1.3 mg/g. The adsorption procedure was controlled by pseudo-second-order and pore diffusion models. The experimental data fitted well with Freundlich and Langmuir isotherm models. The field study was likewise done by n-HAp to check its suitability for field application [10].

Viswanathan and Meenakshi (2008) have utilized La (III) incorporated carboxylated chitosan beads (La-CCB) for defluoridation of water. The maximum defluoridation capacity of La-CCB was 4.711 mg/g at neutral pH, while raw chitosan beads having only 0.052 mg/g adsorption capacity. The fluoride removal was marginally influenced by the vicinity of co-anions and the pH of the medium. The results fitted well with Langmuir and Freundlich isotherm models and also, the pseudo-second-arrange and intra-molecule dispersion energy models. The reaction was spontaneous and endothermic in nature. The field water was effectively diminshed within permissible limit by using La-CCB [11].

Viswanathan and Meenakshi (2008) have examined the fluoride removal capability of Fe (III) loaded carboxylated chitosan beads (Fe-CCB) from water. The defluoridation capacity of Fe-CCB was 4.230 mg/g more than defluoridation capacity of chitosan beads (CB) which was 0.052 mg/g at neutral pH. The adsorption procedure was independent of pH of the medium however marginally gets influenced by the vicinity of co-anions. The experimental data fitted well with Fruendlich isotherm model. The maximum Langmuir adsorption capacity of Fe-CCB was 15.385 mg/g at 303K. Kinetics of adsorption took after the pseudo-second-order besides intra-particle diffusion models. Defluoridation by adsorption procedure was spontaneous and endothermic in nature [12].

Sundaram *et al.* (2009) has prepared biocompatible nano-hydroxyapatite/chitin composite (n-HApCh) for defluoridation of drinking water. The fluoride uptake of n-HApCh and nano-hydroxyapatite (n-HAp) was 2.84 mg/g and 1.296 mg/g respectively. The adsorption data coordinated with both Langmuir and Freundlich isotherms however better fitted with Freundlich isotherm. The rate of reaction took after the pseudo-second-order and pore diffusion models. The adsorption procedure was spontaneous and endothermic [13].

Viswanathan *et al.* (2009) has utilized the protonated chitosan beads (PCB) for removal of fluoride from water. The maximum defluoridation capacity of PCB was 1.664 mg/g at neutral pH, though defluoridation capacity of raw chitosan beads was 0.052 mg/g. The experimental data fitted well with Langmuir and Freundlich isotherm models and in addition took after the pseudo-second-order and intraparticle diffusion kinetic models. The thermodynamics study revealed that the reaction was spontaneous and endothermic. Desorption of spending adsorbent was carried out by 0.1M HCl and 94.5 % desorption while H_2SO_4 and NaOH have 89% and 85% desorption efficiencies, respectively [14].

Viswanathan *et al.* (2009) has made multifunctional chitosan beads by chemical modification with NH^{3+} and $COOH^-$ functional groups by means of protonation and carboxylation remembering the finished objective to utilize both amine and hydroxyl groups for fluoride execution. The maximum adsorption capacity of protonated cum carboxylates chitosan beads (PCCB) at pH7 was observed to be 1.80 mg/g, though raw chitosan beads having an only adsorption capacity of 0.052 mg/g. The PCCB removes fluoride by hydrogen bonding. The experimental data fitted well with Langmuir and Freundlich isotherm models and in addition reaction took after the pseudo-second-order and intra-particle diffusion models. The reaction for adsorption was spontaneous and

endothermic in nature. The field trial of PCCB diminised the fluoride inside of as far as possible [15].

Jagtap *et al.* (2009) has utilized metal binds property of chitosan to incorporate titanium metal to upgrade the fluoride removal capacity. The maximum defluoridation capacity of 7.2 mg/g was obtained at pH of 7.0. The test information observed to be obeying both Langmuir and Freundlich isotherm models and besides the pseudo-first order kinetics and intra-particle diffusion models. The reaction was impulsive and endothermic because of the positive value of enthalpy (ΔHo). The vicinity of co-anions diminshed the evacuation limit of fluoride. Desorption of 85% was accomplished by treating the spent adsorbent with alum at pH of 12.0. The fluoride removal was diminished from 90% to 15% in fresh utilization and third reuses [16].

Bansiwal *et al.* (2009) have utilized lanthanum incorporated chitosan beads prepared utilizing precipitation for removal of fluoride from simulated water. The fluoride removal of 98% was obtained by 10% lanthanum loading on chitosan and show higher removal efficiency than bear chitosan. The maximum fluoride adsorption capacity of 4.7 mg/g was accomplished at pH of 5.0 without negligible lanthanum discharge. The experimental data fitted well with the Langmuir isotherm model and pseudo-first order kinetic model. The vicinity of carbonates and bicarbonate drastically lessened the fluoride uptake. The adsorption procedure was spontaneous and endothermic in nature. The 81.22% recovery of spent adsorbent was accomplished by 1M ammonium chloride solution. The adsorption capacity of LCB was same as simulated water for field water of Dhar district of Madhya Pradesh, India [17].

Sundaram *et al.* (2009) have utilized magnesia-chitosan composite (MgOC) prepared by mixing magnesium oxide and chitosan in the proportion of 3:2 for 24 hours in an aqueous solution took after by drying and calcination at 80°C and 400°C respectively. The most compelling fluoride uptake efficiency of MgOC and MgO was 4.44 mg/g and 2.175 mg/g respectively. As far as possible was not affected by pH of water, but instead treated water got the opportunity to be antacid in nature, having a pH somewhere around 10.1 and 10.4 in view of vital in nature of adsorbent. The vicinity of chloride, sulphate and nitrate ions were increased the defluoridation limit while bicarbonate decreases the fluoride removal efficiency. The experimental data fitted well with Freundlich isotherm and pseudo-second-order kinetic in addition to intra-particle diffusion models. The removal procedure by MgOC was spontaneous and endothermic in nature [18].

Yao *et al.* (2009) has utilized neodymium modified chitosan as adsorbent for removal of fluoride from water. The Langmuir maximum equilibrium adsorption was

observed to be 22.380 mg/g at 303K. The equilibrium data fitted well with Langmuir isotherm and pseudo-second-order kinetic model. The optimum pH for maximum adsorption by adjusting chitosan was 7.0. The recovery of spent adsorbent was carried out by 4 g/l of NaOH in 24 hours [19].

Vijaya and Krishnaiah (2009) have investigated fluoride removal potential of chitosan coated silica (CCS) from water. The FTIR result revealed that hydroxyl and amine groups were accountable for defluoridation of water. The monolayer adsorption capacity of Langmuir model was 44.4 mg/g at pH of 4.0. The experimental data fitted well with Langmuir and Freundlich isotherm models and in addition the pseudo-second-order kinetic model. Desorption of 91% was done by 60ml volume of NaOH solution in 60 minutes [20].

Viswanathan and Meenakshi (2009) have utilized Zr (IV) stacked carboxylated chitosan beads (Zr-CCB) for removal of fluoride from water. The adsorption furthest reaches of 4.850 mg/g was refined by Zr-CCB and higher than adsorption breaking point of carboxylated chitosan beads(CCB) and chitosan beads(CB) having defluoridation utmost of 1.385 mg/g and 0.052 mg/g independently. The exploratory data was best fitted to Freundlich isotherm model. The reaction was unconstrained and endothermic in nature. The pH did not have huge effects on defluoridation yet rather distinctive anions in water decreased fluoride takeoff unmitigated [21].

Viswanathan and Meenakshi (2009) utilized carboxylated cross-linked chitosan beads (CCB) for defluoridation of water. The defluoridation capacity of 1.385 mg/g was achieved by CCB while chitosan bead having 0.052 mg/g of capacity. The experimental information took after by both Freundlich and Langmuir isotherm models. The adsorption reaction was spontaneous and endothermic in nature. The sorption was mainly controlled by pseudo-second-order and intraparticle diffusion models. The recovery was completed by 0.1M HCl solution [22].

Swain *et al.* (2009) utilized aluminum impregnated chitosan (AIC) for defluoridation of water. The maximum fluoride removal of 84% by AIC was accomplished at pH of 6.5. The maximum Langmuir adsorption capacity of the AIC was 1.73 mg/g. The exploratory information fitted well with Freundlich isotherm model and adsorption took after the pseudo-first-order kinetic. Phosphate and bicarbonate ions were interfered with the adsorption procedure significantly. Desorption demonstrated 92% elution of adsorbed fluoride at a pH of 12.0 [23].

Viswanathan and Meenakshi (2010) utilized hydrotalcite-chitosan (HTCs) composite for delfuoridation of water. Defluoridation capacity of HTCs, HT and chitosan were

found to be 1.255 mg/g, 1.03 and 0.052 mg/g respectively. Maximum defluoridation capacity was observed at acidic pH than at an alkaline pH of the medium. The equilibrium data fitted well with the Langmuir isotherm model and also pseudo-second-order and pore diffusion models. The adsorption was spontaneous and endothermic in nature. The field trial of adsorbent demonstrated its suitability in practical application field water [24].

Meenakshi *et al.* (2010) have chitosan supported zirconium (IV) tungstophosphate composite (ZrWPCs) by dispersing the ZrWP into the chitosan bio polymeric matrix for defluoridation of water. The defluoridation capacity of 2.025 mg/g was accomplished at pH of 3.0 with a contact time of 30 minutes. The Langmuir adsorption capacity of ZrWPCs was observed to be 7.6 – 9.9 mg/g. The experimental data fitted well with Freundlich isotherm model. The rate of adsorption took after the pseudo-second-order and intra-particle diffusion models. The procedure of adsorption was spontaneous and endothermic in nature. The pH of the medium and the vicinity of co-anions in the water incredibly influence the defluoridation capacity [25].

Thakre *et al.* (2010) have set up the defluoridation limit of lanthanum futilized chitosan beads (LCB) arranged by the precipitation system for drinking water. The optimal condition for synthesis of LCB included 10 % lanthanum loading by weight, complexion time and precipitation time of 60 minutes each, drying at 75°C temperature for 72 hours. The maximum adsorption capacity of LCB was found to be 4.7 mg/g with the negligible release of lanthanum ions. The experimental data fitted well with Langmuir and Freundlich isotherm models. The adsorption capacity of LCB was four times greater than the adsorption capacity of activated alumina [26].

Thakre *et al.* (2010) have combined Ti^{4+} and Al^{3+} into chitosan to adjust the chitosan for defluoridation of water. The Ti-Al binary metal supported chitosan was calcined at 450°C and demonstrated a fabulous defluoridation capacity of 2.22 mg/g with the insignificant discharge of aluminum and titanium ions. The optimum dose of adsorbent was 4 g/l and adsorbent was dealing with an extensive range of pH between 3 and 9. The vicinity of bicarbonate, carbonate, other than phosphate particles in water were decreased the fluoride removal proficiency by 56%, 34% and 24% respectively. The experimental data fitted well with the Langmuir isotherm model and adsorption took after the pseudo-second-order and intra-particle diffusion model. The thermodynamic study revealed that the adsorption reaction was spontaneous and exothermic in nature. The recovery of 80% spent adsorbent was accomplished by alum [27].

Viswanathan and Meenakshi (2010) utilized alumina-chitosan composite (AlCs) for defluoridation of water. The defluoridation capacity of AlCs, alumina and Chitosan bead was 3.809 mg/g, 1.566 mg/g and 0.052 mg/g respectively. The defluoridation capacity of AlCs was not affected by pH of the solution, but rather diminished in the vicinity of bicarbonate. The experimental data fitted well with the Freundlich isotherm model. The Langmuir adsorption capacity of AlCs was 10.417 mg/g, 16.667 mg/g and 23.810 mg/g for temperature of 303K, 313K and 323K respectively. The nature of the reaction was spontaneous and endothermic. The adsorption reaction took after the pseudo-first-order and intra-particle diffusion models. The field trial of AlCs revealed its practical suitability [28].

Vijaya *et al.* (2010) utilized chitosan coated perlite (CCP) for defluoridation of aqueous solution. The experimental data fitted well with Freundlich and Dubinin-Radushkevich isotherm models. The Langmuir maximum adsorption capacity of adsorbent was observed to be 64.1 mg/g. The adsorption procedure was taken after the pseudo-second-order and intraparticle diffusion models. The optimum pH and contact time for maximum fluoride removal was observed to be 6 and 120 minutes respectively. The recovery of spent adsorbent was done by 0.1N NaOH solution. Breakthrough curves were obtained from column flow adsorption data [29].

Swain *et al.* (2010) utilized cerium impregnated chitosan (CIC) for defluoridation of water. The optimum pH for maximum fluoride removal was found in the range of 6.5-7.0. The optimum condition was accomplished by keeping up pH of 6.5, 8 g/l amount of adsorbent and 298K temperature with 10 mg/l of initial fluoride concentration. The experimental data fitted well with Freundlich isotherm model and adsorption took after the pseudo-second-order kinetic model. The maximum Langmuir linear adsorption capacity was 1.352 mg/g and 2.783 mg/g for the linear and the non-linear equation. The adsorption reaction observed to be spontaneous and endothermic in nature. The vicinity of co-anions did not have a huge effect on the elimination of fluoride. Desorption of 93% was refined at pH of 12.0 however utilization of recovered adsorbent reduced fluoride adsorption by 90% to 70%. The vicinity of phosphate and bicarbonate ions was lessened the adsorption capacity emphatically [30].

Jagtap *et al.* (2010) utilized chitosan based mesoporous alumina (MA450) with defluoridation capacity of 8.264 mg/g at an initial fluoride concentration of 5 mg/l which was vastly improved than activated alumina. The experimental data fitted well with Langmuir isotherm and took after the pseudo-second-order kinetic model. The adsorption reaction was spontaneous and exothermic in

nature. The field trial of MA450 was completed effectively [31].

Jagtap *et al.* (2011) have prepared lanthanum impregnated chitosan flakes (LCF) for removal of fluoride from water. The maximum adsorption capacity of 1.27 mg/g was obtained at optimum condition of synthesis of LCF by 20% lanthanum loading, 6 hours stirring time, 75°C drying temperature for 2 hours. The most compelling adsorption was procured at pH of 6.7, while in acidic and antacid pH, the fluoride evacuation was lessened. The experimental data fitted well with Freundlich isotherm and took after the pseudo-second-order kinetics and governed by intra-particle diffusion model. The fluoride removals were diminished by 2.5, 11.0 and 15.2%, respectively, after first, second and third utilization of adsorbent [32].

Karthikeyan *et al.* (2011) has studied the defluoridation capacity of polyaniline/chitosan (PANi/Ch) and polypyrrole/chitosan (PPy/Ch) from water. The fluoride removal was favorable at low pH and higher temperature. The defluoridation capacity of PANi/Ch and PPY/Ch was found to be 5.9 mg/g and 6.7 mg/g at 50°C for 10 mg/l of fluoride solution. The experimental data fitted well with Freundlich isotherm than Langmuir isotherm. The adsorption reaction in both the cases was endothermic in nature [33].

Miretzky and Cirelli (2011) has reviewed the fluoride removal from water by raw chitosan and chitosan derivatives and composite. The modified adsorbents with chitosan and other metal complexes demonstrated an enhanced defluoridation capacity when contrasted with raw chitosan beads. The review paper described the fluoride removal kinetic, thermodynamic, isotherm models, recovery, co-anions and field application study of various chitosan composites. A comparison with an adsorption capacity of other minimal effort adsorbents is additionally tabled [34].

Vijaya *et al.* (2011) utilized chitosan coated calcium alginate (CCCA) and calcium alginate (CA) beads for removal of fluoride from water. The maximum monolayer adsorption of CCCA and CA was 42 mg/g and 29.3 mg/g respectively. The optimum pH for CCCA and CA was 5 and 6 respectively. The experimental data fitted well with Langmuir and Freundlich isotherm models. The kinetic study exposed that the adsorption took after the pseudo-second-order and intraparticle diffusion model. The maximum desorption 90 and 93 % occurred at 30 ml of 0.1N NaOH solution and complete recovery 27 and 25% occurred at about 90 and 100 ml volume of 0.1N NaOH for both CA and CCCA respectively [35].

Lawrance *et al.* (2011) utilized chitosan nanoparticles for defluoridation from aqueous solution in batch and column

study. Defluoridation capacity of chitosan nanoparticles was lowest at pH 4 and 7. The maximum defluoridation occurred at alkaline and acidic pH. The experimental data fitted well with Freundlich isotherm (R^2=0.992) than Langmuir isotherm (R^2=0.9889) model. The Langmuir adsorption capacity of adsorbent was observed to be 0.360 mg/g which was more than the deluoridation capacity of raw chitosan which was 0.052 mg/g. The adsorption reaction took after the pseudo-second-order and intraparticle diffusion models. The adsorption was increased with increase in adsorption concentration and adsorption was higher with lower temperature. The column study of chitosan nanoparticles revealed that the maximum adsorption observed at maximum bed height of adsorbent (i.e. 4.5 cm) because of the availability of the more active sites. The adsorption capacity decreased with higher initial fluoride concentration of 450 ppm because of early occupation of all available sites. Further, the minimum adsorption was observed for low flow rate of 0.5 ml/min because of slow occupation of active sites. Adams-Bohart and Wolborska models indicated good approximation of the whole breakthrough profile [36].

Jayapriya *et al.* (2011) utilized chitin/cellulose composite adsorbent for defluoridation of water. The optimum reaction conditions were achieved by maintaining contact time (180 min.), pH (6.5) and adsorbent dose (3g). The experimental data fitted well by Langmuir isotherm (R^2=0.9990) than Freundlich isotherm (R^2=0.9969) model. The Langmuir maximum adsorption capacity was observed to be 83.75 mg/g. The kinetic study revealed that the pseudo-second-order equation described the adsorption reaction well when contrasted with the pseudo-first-order equation [37].

Dongre *et al.* (2012) investigated the defluoridation capacity of 20% zirconium doped chitosan beads from aqueous solution. The fluoride removal of about 90% was achieved at pH of 6.9. The optimum dose of 20% zirconium doped chitosan adsorbent was 3 g/l. The experimental data fitted well with Freundlich isotherm model having a coefficient of determination (R^2) of 0.939 and adsorption efficiency (K_f) of 3.27 mg/g. The adsorption reaction took after the pseudo-second-order model and intraparticle diffusion model. Desorption of 90% was obtained by 0.1N NaOH solution with 75% fluoride removal efficiency [38].

Rodriguez *et al.* (2012) utilized chitin based bio composite adsorbent for removal of fluoride from water in the fixed bed column. An empty bed contact time (EBCT) of 20 minutes sufficient to treat about 200 and 300 bed volumes of contaminated water with initial fluoride concentration of 5.1 mg/l before the saturation of packed column by bio composite or chitin respectively. Recovery of saturated bio composite was possible by using only 4 bed volume of

0.1 M NaOH solution and recovery of 85% and 84% were obtained for chitin and bio composite respectively. The vicinity of co-anions in the water affected fluoride removal efficiency in the order of sulphate > bicarbonate > fluoride > chloride > nitrate ions [39].

Peng *et al.* (2013) has investigated the fluoride removal capability of chitosan modified natural zeolite (Ch-Z) from aqueous solution. The maximum defluoridation capacity of Ch-Z was 4.16 mg/g from initial fluoride concentration of 40 mg/l which was three times more than unmodified zeolite. The maximum uptake of fluoride was occurred at pH range of 4.5-5.5. The experimental data fitted well with Freundlich and Redlich-Peterson isotherm models. The adsorption took after the pseudo-second-order and intraparticle dispersion models. The maximum adsorption capacity was found to be increased from 4.95 to 5.50 mg/g for an increase in the solution temperatures from 288 to 298 K, respectively which indicated that the adsorption was endothermic in nature [40].

Liang *et al.* (2013) prepared mixed rare earths modified chitosan (CR) and La (III)-modified chitosan (CL) for defluoridation of water. Mixed rare earths mainly contained lanthanum took after by cerium. The defluoridation capacity of CR and CL was found to be 3.72 mg/g and 3.16 mg/g at 2 hours respectively. The adsorption capacity was significantly influenced by the vicinity of bicarbonates and carbonates. The adsorption mechanism was governed by chemical reaction [41].

Kameshwar Rao *et al.* (2013) utilized chitosan biopolymer for defluoridation of water. The optimum pH was observed to be 5.0. The equilibrium data fitted well for both Langmuir and Freundlich isotherm models. The Langmuir maximum adsorption capacity was 0.275 mg/g. The vicinity of sodium carbonate and bicarbonate reduced the fluoride removal efficiency, while co-ions such as sodium chloride, sodium nitrate, sodium sulfate, copper sulfate and ferrous sulfate had positive effects. The removal of fluoride from distilled water was morewhen contrasted with field water [42].

Zhang *et al.* (2013) have prepared low cost bentonite-chitosan beads for defluoridation of aqueous solution. Bentonite was initiated and the beads were prepared using the inverse suspension polymerization method. The adsorption capacity of bentonite/chitosan beads was 0.895 mg/g with 3.0 g/l of dose, while chitosan beads had only 0.359 mg/g. The optimum pH value was observed to be 5.0 where the adsorption reached the maximum adsorption capacity of 1.164 mg/g. The adsorption was took after the Freundlich isotherm model and the pseudo-second-order kinetic model. The recovery of adsorbent was done by a sodium hydroxide arrangement however the adsorption limit was diminished from 0.92 mg/g to

0.69 mg/g with 25% less in five progressive adsorption tests [43].

Viswanathan *et al.* (2014) have scrutinized the lanthanum – III incorporated silica gel – chitosan (LaSGCS) composite for defluoridation of water in batch study. The defluoridation capacity of LaSGCG composite, SGCG composite, silica gel (SG) and chitosan (CS) was found to be 4.9 mg/g, 1.556 mg/g, 1.296 mg/g and 0.052 mg/g respectively. Maximum defluoridation capacity was observed at acidic pH of 3.0 while its capacity gets reduced in alkaline pH. The equilibrium data fitted well with the Langmuir isotherm model. The rate of adsorption took after the pseudo-second-order and intra-particle diffusion models. The adsorption reaction was spontaneous and endothermic in nature. The vicinity of bicarbonate ions only affected the defluoridation capacity of water. The field study of LaSGCG was carried out successfully [44].

Prabhu and Meenakshi (2014) have investigated the defluoridation capability of lanthanum (III)-zirconium (IV) mixed oxide (LZMO) and chitosan supported lanthanum (III)-zirconium (IV) mixed oxide beads (CLZMOB) from water. The optimum pH and optimum equilibrium contact time for both the adsorbent was 7.0 and 50 minutes respectively, with an adsorbent dose of 100 mg/l at room temperature. The experimental data for both the adsorbents were fitted well with the Langmuir isotherm model and the adsorption reactions were spontaneous and endothermic. The Langmuir adsorption capacity at temperature of 303K, 313K and 323K for LZMO were 11.841, 16.292 and 29.762 mg/g, respectively, while for CLZMOB were 6.406, 6.435 and 6.481 mg/g respectively. The recovery was accomplished by utilizing 0.1 M NaOH solution. The column experiment of CLZMOB at neutral pH was effectively utilized for removal of fluoride ions from synthetic water [45].

Prabhu and Meenakshi (2014) prepared silica gel/chitosan (SGCS) and cerium loaded silica gel/chitosan (Ce-SGCS) composites for defluoridation of water. The defluoridation capacity of Ce-SGCS and SGCS was 4.821 mg/g and 3.470 mg/g respectively at neutral pH. The maximum fluoride removal was achieved within 30 minutes. The exploratory information with Ce-SGCS was best fitted to the Langmuir isotherm model. The Langmuir adsorption capacity of Ce-SGCS at temperature of 303K, 313K and 323K was 8.724, 9.981 and 10.541 mg/g respectively. The adsorption reaction was spontaneous and endothermic in nature. The adsorption took after the pseudo-second-order and intraparticle diffusion models. The vicinity of bicarbonate ions influenced the fluoride removal capacity [46].

Prasad *et al.* (2014) prepared Zr nanoparticle using an aqueous extract of Aloe Vera and embedded into chitosan

biopolymer to formed nano-zirconium-chitosan (CNZr) composite adsorbent for removal of fluoride from contaminated water. Approximately 99% fluoride removal was obtained at pH 7.0. The harmony data fitted well with the Langmuir isotherm model and complained with the pseudo-second-order kinetic model. The most compelling adsorption utmost of CNZr was 96.58 mg/g at perfect exploratory conditions. The adsorption reaction was spontaneous and exothermic in nature. The adsorption procedure was because of chemisorption as per the value of mean free energy determined by D-R isotherm model. The recovery by desorption and reuse of CNZr for fluoride removal showed the great potential of the use of adsorbent on field level. Desorption was carried out by 0.1M NaOH solution [47].

Ma *et al.* (2014) utilized aluminum-doping chitosan-Fe (III) hydrogel (Al-CS-Fe) adsorbent for defluoridation of aqueous solution. The adsorption was well described by Langmuir isotherm and pseudo-second-order kinetic model. The adsorption was not affected by the pH of the solution and the vicinity of co-anions in water. Defluoridation capacity of 31.16 mg/g was achieved by Al-CS-Fe. The optimum pH for maximum fluoride removal was 5.0. The mechanism of adsorption was governed by the ligand and ion exchange happened on the metal centers and amino groups. After recovery by 0.1 M NaOH as desorption agent and by 0.1 M HCl as activating agent, Al-CS-Fe adsorbent performed well with higher removal efficiency before and removal rate of this hydrogel was up to 89.7% and 87.4%, 84.4% for the next two cycles [48].

Prabhu *et al.* (2014) utilized chitosan assisted ethylenediamine functionalized synthetic polymer blends viz. acrylonitrile/divinylbenzene/vinylbenzychloride (CS@AN/DVB/VBC-ED)and styrene/divinylbenzene/vinylbenzylchloride(CS@ST/DVB/VBC-ED) for defluoridation of water. The maximum defluoridation was achieved with a minimum contact time of 30 minutes. The maximum defluoridation capacity was observed to be 4.582 mg/g at pH 7 and minimum defluoridation capacity of 3.471 mg/g at pH 11 for CS@AN/DVB/VBC-ED while maximum defluoridation of 2.575 mg/g at pH 7 and minimum defluoridation capacity of 2.075 mg/g at pH 11 was obtained for CS@ST/DVB/VBC-ED. The mechanism of adsorption was governed by electrostatic attraction via hydrogen bonding. The adsorption took after Freundlich isotherm model. The Langmuir most extreme defluoridation limit was seen to be 6.530 mg/g and 4.660 mg/g at 323K temperature for CS@AN/DVB/VBC-ED and CS@ST/DVB/VBC-ED individually. The thermodynamic study uncovered that the adsorption response was unconstrained (-ΔG) and expanding irregularity in the adsorption procedure (+ ΔS) for both the adsorbent. The sorption responses were exothermic (-ΔH) and endothermic (+ΔH) for

CS@AN/DVB/VBC-ED and CS@ST/DVB/VBC-ED respectively. The suitability of CS@AN/DVB/VBC-ED was observed in field condition [49].

Liu *et al.* (2014) utilized titanium (IV) hydrated based on chitosan template (Ti-CHI) was prepared by using Ti $(SO_4)_2$ and chitosan for defluoridation from aqueous solution. The fluoride removal of 87.50% was achieved with Ti-CHI with initial fluoride concentration of 4.52 mg/l. The adsorption was favorable in the pH range of 4 to 9. The carbonate ions present in water reduced the fluoride removal capacity. The experimental data fitted well with Langmuir and Langmuir-Freundlich isotherm models. The maximum Langmuir adsorption capacity of Ti-CHI was 16.12 mg/g. The thermodynamic studies revealed that the adsorption procedure was impulsive [50].

Zhang *et al.* (2014) prepared La (III)-loaded bentonite/chitosan beads (La-BCB) for defluoridation from aqueous solution. The best defluoridation breaking point of La-BCB was 2.87 mg/g at pH 5 and 30°C of temperature. The exploratory information suitable with both Langmuir and Freundlich isotherm models. The adsorption kinetics conformed the pseudo-second-order kinetic besides particle and intraparticle diffusion models. The vicinity of carbonate and bicarbonate consolidated defluoridation limit of La-BCB while sulfate, nitrate and chloride demonstrated slight impact. The recovery of 83% was done by using sodium hydroxide. The defluoridation mechanism was mostly based on adsorption and ion exchange [51].

Wan *et al.* (2015) prepared gamma-AlOOH @CS magnetic nanoparticle (ACMN) for defluoridation from drinking water. The adsorption was very rapid and more than 80% removal was achieved in first 20 min and equilibrium was reached in 60 min. The adsorption procedure was a monolayer adsorption on a homogeneous surface. This procedure was spontaneous and endothermic in nature. The adsorption procedure was governed by electrostatic interaction and hydrogen bonding. The Langmuir maximum adsorption capacity of ACMN was 67.5 mg/g at optimum conditions (pH = 7.0 and temperatures = 20°C). The adsorption was occurred in wide pH range of 4-10. The vicinity of co-anions interrupt the defluoridation capacity in the order of phosphate > nitrate > chloride [52].

Teimouri *et al.* (2015) prepared chitosan/montmorillonite/zirconium (CTS/MMT/ZrO$_2$) nano-composite by varying the molar ratio of CTS to (MMT/ZrO$_2$) for defluoridation of water. The optimum condition for removal of fluoride were found to be a molar ratio of 1:1, pH of 4.0, temperature of 30°C, a dose of 0.1g/25 ml and initial fluoride concentration of 20mg/l.

The adsorption capacity of CTS/MMT/ZrO$_2$ was higher than CTS, MMT, ZrO$_2$, CTS/ZrO$_2$ and CTS/MMT. The adsorption was obeyed with Langmuir isotherm and the pseudo-second-order kinetic model [53].

Prabhu and Meenakshi (2015) has prepared the metals (Al^{3+}, Ce^{4+}, La^{3+} and Zr^{4+}) loaded dendrimer like polyamidoamine grafted chitosan beads (PAAGCB) for defluoridation of water. The equilibrium time of reaction was 40 minutes. The Zr-PAACGB has the maximum adsorption capacity of 17.47 mg/g at neutral pH and temperature of 323K. The adsorption procedure with Zr-PAACGB was took after Langmuir isotherm and pseudo-second-order as well as intra-particle diffusion kinetics models. The adsorption response was unconstrained and endothermic in nature [54].

Prabhu and Meenakshi (2015) prepared zirconium entrapped silica gel – chitosan (Zr-SGCS) composite adsorbent for defluoridation of water. The maximum defluoridation capacity was found to be 4.53 mg/g at 60 minutes and optimum pH was 7.0. The vicinity of bicarbonate ions greatly reduced the fluoride removal capacity of Zr-SGCS. The adsorption procedure obeyed Freundlich isotherm and pseudo-second-order and intraparticle diffusion model. The adsorption reaction was spontaneous and endothermic in nature [55].

Liu *et al.* (2015) inspected the defluoridation capacity of Zr (IV) loaded cross-linked chitosan (Zr-CCS) composite. The maximum adsorption capacity was found to be 48.26 mg/g at pH of 6.0 and temperature of 303K. The adsorption procedure obeyed Langmuir isotherm and pseudo-second-order-kinetic model. The adsorption reaction was spontaneous and endothermic in nature [56].

3. DEFLUORIDATION BY ALGINATES AND THEIR MODIFIED ADSORBENTS

Vijaya *et al.* (2011) utilized glutaraldehyde cross-linked calcium alginate (GCA) beads for defluoridation of water in batch and column modes. The optimum pH was observed to be 8.0. The experimental data fitted well with the Langmuir isotherm model and the maximum monolayer adsorption capacity by Langmuir isotherm was 73.5 mg/g. The adsorption procedure took after the pseudo-second-order kinetic model. The desired quality of water was obtained in a fixed bed column and desorption was effectively carried out by 0.05 M EDTA solution [57].

Swain *et al.* (2013) made Al-Ce loaded calcium alginate (Aluminum-Cerium-Calcium-Alginate (ACCA)) micro particle beads by mixing A/Ce mixed metal oxide nanoparticles in alginate polymeric material for defluoridation of water. The fluoride removal of 98% was achieved at pH of 7.0. The result was fitted well with Freundlich isotherm and adsorption procedure was revised the pseudo-second-order kinetic model. The

Langmuir adsorption capacity of hybrid adsorbent was found to be 1.438 mg/g. The energy of adsorption was 10 Kj/mol. Suggested that involvement of ion-exchange mechanism for adsorption. The adsorption reaction was endothermic (+ΔH) in nature as well as positive values of ΔG and ΔS indicated spontaneity and increasing randomness in the adsorption procedure. The vicinity of phosphate and bicarbonate ions in the water reduced the uptake of fluoride to 56 and 52% respectively. The reuse of ACCA from first to seventh cycle of batch operation, reduced the efficiency from 97.2 to 60%. Deception was negligible at acidic pH and nearly 88% fluoride could leach out at pH 12.0 [58].

Basu *et al.* (2013) prepared alumina impregnated alginate beads for fluoride removal from potable water. The best situation for synthesis of calcium alginate alumina (Cal-Alg-Alu) beads was 2% (wt/vol) had 22% alumina loading mixed with calcium alginate for 1 hour and then oven dried at 60°C for 8 hours. The fluoride uptake capacity of adsorbent was more than 90% up to pH 9.0 and composite beads could be utilized for fluoride removal without any pH adjustment in the pH range of 3.5 – 9.0. The equilibrium adsorption data best fitted with Langmuir isotherm (R2=0.99) than the Fruendlich isotherm model (R2=0.84). The Langmuir maximum adsorption capacity was found to be 17.0 mg/g. The adsorption kinetic was explained well by the pseudo-second-order model and the time needed for equilibrium was 300 minutes. The fluoride was not influenced by the vicinity of co-anions of sodium, potassium, calcium, chloride, magnesium, carbonate, sulphate and phosphate ions [59].

Gao *et al.* (2013) utilized millimeter sized Mg-Al-LDH nanoflake impregnated magnetic alginate beads (LDH-n-MABs) hybrid adsorbent for defluoridation of water in batch mode. The defluoridation capacity of adsorbent was observed to be 32.4 mg/g at pH of 5.0. The adsorption kinetic was took after pseudo-second-order model and the equilibrium adsorption data fitted well with Freundlich isotherm model. The maximum Langmuir adsorption capacities of hybrid adsorbent were 40.171, 46.318 and 61.843 mg/g at a temperature of 293, 313 and 333K respectively. The adsorption reaction was spontaneous (-ΔG) and exothermic (-ΔH) in nature as well as negative values of entropy (-ΔS) indicated that the greater order of reaction during fluoride adsorption. The removal efficiency percentage in the vicinity of anions decreased in the following order of H$_2$PO$_4^-$ > SO$_4^{2-}$> HCO$_3^-$ ≈ Cl$^-$> NO3$^-$. Humic acid slightly reduced the adsorption capacity. Fluoride adsorption by the LDH-n-MABs was by particle trade with nitrate to some degree [60].

Singh *et al.* (2013) utilized alginate nanoparticles prepared by nanoparticles of sodium alginate cross-linked ferric chloride for defluoridation of water. The efficiency

of fluoride removal was increased with increase in adsorbent dose, low initial fluoride concentration, at lower temperature. The ideal pH was observed to be 4.0 and after that defluoridation diminished steeply as pH increments from the acidic reach to alkaline range. The experimental data fitted well with Freundlich isotherm model. The Langmuir defluoridation capacity was observed to be 0.697 mg/g. The kinetic study revealed that the adsorption procedure was well defined by the pseudo-second-order equation and intra particle transport was not the rate limiting step [61].

Sujana *et al.* (2013) utilized hydrous ferric oxide doped alginate beads for fluoride removal from water. The beads of 0.8-0.9 mm size with 32-33% of Fe(III) having specific area and pH at point of zero charge (Ph$_{PZ}$ were 25.80 m2/g and 5.15 respectively. The composite beads demonstrated Langmuir adsorption capacity of 8.90 mg/g at pH 7.0. The adsorption reaction charted the pseudo-second-order kinetic model and intraparticle diffusion as the rate limiting step. Desorption of 80% of spening beads was carried out with 0.05M HCl. The vicinity of co-anions slightly decreased the fluoride removal efficiency [62].

Pandi and Viswanathan (2014) prepared alginate (Alg) bio encapsulating nano-hydroxyapatite (n-HAp) namely n-HapAlg for defluoridation of aqueous solution in batch mode to overcome the pressure drop problem with n-HAp powder. The defluoridation capacity of n-HapAlg, n-HAp and calcium alginate (CaAlg) were observed to be 3.87, 1.296 and 0.680 mg/g respectively. The adsorption of n-HapAlg took after the Langmuir isotherm model. The Langmuir adsorption capacity of n-HapAlg was observed to be 1.728, 1.811 and 1.532 at temperature of 303K, 313K and 323K respectively. The adsorption reaction was spontaneous and endothermic in nature. The adsorption took after the pseudo-second-order and intra-particle diffusion models. The vicinitys of co-anions slightly affect the removal efficiency. The field trial of adsorbent was carried out effectively [63].

Kaygusuz *et al.* (2015) utilized aluminum alginate beads for removal of fluoride from aqueous solution in batch mode. The adsorption equilibrium was achieved in 4 hours. The fluoride removal of 99.5% was achieved at pH 2 at 25oC. The exploratory information fitted well with Langmuir isotherm than the Fruendlich model, Dubinin-Radushkevich and Temkin isotherms. The Langmuir maximum adsorption capacity of adsorbent was found to be 75.2 mg/g at 298K. The mean sorption energy € was calculated as 2.75 Kj/mol from D-R isotherm indicating that the adsorption took after physisorption mechanism. The adsorption procedure took after the pseudo-second-order and Elovich kinetic models. The adsorption reaction was spontaneous (-ΔG) and exothermic (-ΔT) in nature. The vicinity of co-anions in water slightly affected the

fluoride removal efficiency and decreased in the order of nitrate > sulphate > carbonate > bicarbonate > chloride > phosphate ions [64].

Kaygusuz *et al.* (2015) utilized aluminum alginate – montmorillonite composite beads for defluoridation of water. Montmorillonite was dispersed in alginate solution and the mixture was cross-linked with aluminum chloride solution. The optimal condition for defluoridation was achieved at pH of 2.0 and the beads dose of 0.05g. The equilibrium of adsorption was reached in 120 minutes. The experimental data fitted well with the Langmuir isotherm model. The Langmuir maximum adsorption was observed to be 93.6 mg/g at 60oC while 31 mg/g at 25oC. The adsorption reaction was spontaneous and exothermic in nature. The adsorption procedure best fitted with Elovich kinetic model and adsorption was physical in nature. The vicinity of chloride, sulphate, nitrate, phosphate and carbonate did not affect defluoridation capacity [65].

Prabhu *et al.* (2015) utilized alginate-zirconium complex prepared with dicarboxylic acids media like oxalic acid (Ox), malonic acid (MA) and succinic acid (SA). The complexes like alginate-oxalic acid-zirconium (Alg-Ox-Zr), alginate-malonic acid-zirconia (Alg-MA-Zr) as well as alginate-succinic acid-zirconium (Alg-SA-Zr) were made and utilized for defluoridation of water. The maximum defluoridation capacity (DC) of Alg-Ox-Zr, Zr-Ox, Alg-Zr, Alg-MA-Zr and Alg-SA-Zr complexes were found to be 9.653, 5.376, 5.297, 4.851 and 4.059 mg/g respectively at acidic pH of 3.0. The maximum DC was obtained by Alg-Ox-Zr. The capacity was reached in 25 minutes. The bicarbonates ion present in water reduced the fluoride removal efficiency. The experimental data for Alg-Ox-Zr complex was fitted well with Fruendlich isotherm model. The adsorption reaction was impulsive and endothermic in nature. The adsorption was governed by a ligand exchange mechanism. Performance of Alg-Ox-Zr complex utilized for treatment of field water effectively [66].

Pandi and Viswanathan (2015) synthesized alginate beads filled with nano-hydroxyapatite and resulting solution was cross-linked with La (III) (n-HapAlgLa) for defluoridation of water. The maximum defluoridation capacity of n-HapAlgLa beads was 3.72 mg/g. The optimum condition was achieved at pH 7, contact time of 40 min, a dose of 0.1g and room temperature. The experimental data fitted well with Langmuir isotherm model and took after the pseudo-second-order kinetic model along with intra-particle diffusion model. The Langmuir maximum adsorption capacity of n-HapAlgLa bead was 4.536, 4.916 and 5.271 mg/g at 30oC, 40oC and 50oC temperature respectively. The adsorption procedure was spontaneous and endothermic in nature. The mechanism of adsorption was governed by adsorption, complexation and ion

exchange. The defluoridation by n-HapAlgLa beads were pH dependent and influenced by the vicinity of bicarbonates ions. The co-anions effect on defluoridation capacity was found in order of bicarbonate > nitrate > sulphate > chloride. The recovery of n-HapAlgLa was carried out by 0.1 M NaOH solution. The adsorbent could be utilized up to third cycles without some loss of defluoridation capacity after recovery and reuse (i.e. Fluoride removal of 90.84%, 81.56% and 74.18% was obtained in first, second and third cycle) [67].

4. DEFLUORIDATION BY MODIFIED POLYPYRROLE

Bhaumik *et al.* (2011) utilized polypyrrole/ Fe_3O_4 magnetic nanocomposite as novel adsorbent prepared by via in-situ polymerization of pyrrole monomer using $FeCl_3$ oxidant in an aqueous medium in which Fe_3O_4 nanoparticles were suspended. The defluoridation efficiency up to 97% was obtained at pH 12. The experimental data were well explained by Fruendlich and Langmuir-Freundlich isotherm models. The adsorption kinetic was described by the pseudo-second-order model. The adsorption reaction was spontaneous and endothermic by thermodynamic study. The fluoride removal mechanism was governed by ion-exchange [68].

5. DEFLUORIDATION BY MODIFIED POLYSTYRENE

Zhang *et al.* (2013) synthesized a novel hybrid material by encapsulating nano-zirconium phosphate onto macro porous polystyrene (ZrP-MPN) materials modified with quaternary ammonium groups for removal of fluoride from water. The adsorption procedure well described by the pseudo-first order kinetic model and defluoridation capacity of ZrP-MPN was observed to be 6.65 mg/g. The vicinity of sulphate, chloride and nitrate ions in the water affected the efficiency of fluoride removal. The exhausted ZrP-MPN could be regenerated by an alkaline solution. The column experiment was carried out in high speed hydrodynamic condition and superficial liquid velocity (SLV) and empty bed contact time (EBCT) were equal to 1m/h and 3 minutes respectively [69].

6. DEFLUORIDATION BY CELLULOSE AND THEIR MODIFIED ADSORBENTS

Zhao *et al.* (2008) utilized Fe(III)-loaded ligand exchange cotton cellulose adsorbent [Fe(III)LECCA] for removal of fluoride from drinking water. The saturation adsorption capacity was 18.6 mg/g at 25°C. The adsorption took after first-order reaction rate. The vicinity of co-anions did not significantly affect the adsorption capacity. The adsorption was found good in the pH range of 4 to 9. The column study revealed that the column gained 5.6 mg/g breakthrough adsorption capacity and 9.7 mg/g saturation adsorption capacity with 20 mg/l of initial fluoride

concentration at 26.0BV/h flow rate under 25°C. The 89% breakthrough adsorption capacity was observed for tap water in the column. The column was recovery with 1M NaOH aqueous solution and a deviation of saturation adsorption was less than 3.5% after 8 times adsorption-desorption-readsorption cycles [70].

Mandal and Mayadevi (2008) prepared cellulose supported layered double hydroxide (CSLDHs) for the defluoridation of aqueous solution. The defluoridation capacity of CSLDH was 2-4 times higher than that of unsupported LDH. The equilibrium adsorption capacity of cellulose (CS), Layered double hydroxide (LDH) and CSLDH-50 having an LDH loading of 27% in batch were 0.32, 4.10 and 13.42 mg/g respectively. The total uptake capacity of CSLDH-50 in the fixed bed column was found maximum (5.29 mg/g of CSLDH, 25.18 mg/g of LDH) and higher than activated alumina (1.45mg/g) and carbon nanotube (4.5mg/g) [71].

Anirudhan *et al.* (2010) utilized iron (III) – coordinated amine-modified poly (glycidylmethacrylate)-grated densified cellulose (AM-Fe-PGDC) with particle size of 0.096mm for defluoridation of industrial effluents. The adsorption of 99.9% was achieved at an optimum equilibrium Ph of 7.0 with 10 mg/l of fluoride concentration at an adsorbent dose of 5 g/l. The experimental data fitted well with the Langmuir isotherm model and adsorption took after the nonlinear form of the pseudo-second-order kinetic model. The adsorption reaction was spontaneous and exothermic in nature. Desorption of spening adsorbent was carried out by 0.1M HCl [72].

Tian *et al.* (2011) utilized modified native cellulose fiber by poly (N, N-dimethyl aminoethyl methacrylate) (PDMAEMA) adsorbent for removal of arsenic and fluoride from water with low concentration. The adsorption was very fast and reached at equilibrium within 1 min. The result was better fitted to the Langmuir isotherm model than Freundlich and Temkin models. The Langmuir adsorption capacity of F-, As(III) and As(IV) were 8.59, 8.96 and 27.93 mg/g, respectively with 1g/l of the adsorbent dose with 4 mg/l of initial fluoride concentration and 10 mg/l of arsenic concentration. The vicinity of chloride, bicarbonate sulphate ions in the water did not affected adsorption capacity of arsenic but significantly affected the fluoride removal that got decreased from 81.81% to 27.56% with vicinity of co-anions [73].

Barati *et al.* (2013) investigated defluoridation capacity of Al-Zr impregnated cellulose (Al-ZrIC) adsorbent from water. This adsorbent has defluoridation capacity of 5.76 mg/g and higher than defluoridation capacity of unmodified cellulose (i.e. 1.11mg/g). The Al-Zr cationic

complexes interacted effectively with fluoride in the pH range of 2.5-3.5. The removal of fluoride was significant in the range 0.3-0.5 g in 50 ml sample volume. The experimental data fitted well with Freundlich isotherm (r^2=0.96) than Langmuir isotherm (r^2=0.93). The adsorption procedure took after the pseudo-second-order kinetic model. The adsorption reaction was spontaneous and exothermic in nature [74].

Santra *et al.* (2014) studied Taguchi design and equilibrium modeling for fluoride adsorption on cerium loaded cellulose nanocomposite bead (CCNB). The pH of solution highly affected the defluoridation capacity with a maximum contribution of 80.78%. ANOVA was utilized for validation of adsorption. The experimental data fitted well with Temkin isotherm than Langmuir or Freundlich isotherm models. The recovery of 90% of spending adsorbent was carried out by 0.01N NaOH solution and showed that the CCNB can be utilized for three cycles without compromising the adsorption capacity [75].

Chatterjee *et al.* (2014) prepared flat sheet mixed matrix membrane by using cellulose acetate phthalate (CAP) and activated granular alumina with phase inversion technique. The removal of 91% was achieved by 35% weight of alumina and 20% weight of CAP. The maximum adsorption capacity for fluoride was 2.3 mg/g for the mixed matrix membrane at room temperature. The virgin membrane (24kDa) with 0.01 m² of surface area treated the water within safe limit with 11 hours in a continuous cross flow experiment. The recovery of the membrane and its reuse in five cycles was carried out [76].

Barathi *et al.* (2014) prepared zirconium impregnated cellulose (ZrIC) by using a novel ultrasonic method for effective removal of fluoride from water. The fluoride from aqueous solution interacts with the cellulose hydroxyl groups and the cationic zirconium hydroxide. The defluoridation capacity of ZrIC was observed to be 4.95 mg/g. The experimental data fitted well with the Langmuir isotherm model. The adsorption procedure took after the pseudo-second-order kinetic model. The thermodynamic study revealed that the adsorption reaction was spontaneous, exothermic and a decreased randomness at the adsorbent-solution interface [77].

Sarkar and Santra (2015) studied the defluoridation capacity of cerium loaded nanocomposite beads (CCNB). The maximum fluoride removal of 94% was observed for fluoride solution of 2.5 mg/l at optimum conditions of pH 3.0, dosage of 1g/L and temperature 313K. The adsorption procedure was took after Tempkin isotherm and pseudo-second-order-kinetic and film diffusion models. The recovery of adsorbent was carried out by NaOH (10^{-2} N) and can be utilized effectively for five successive cycles [78].

7. DEFLUORIDATION BY RESIN AND THEIR MODIFIED ADSORBENTS

Lopez *et al.* (1992) utilized Amberlite IRA-410 anion resin for removal of fluoride from aqueous solution and had made similar observations. The multicomponent anion exchange was found in the order of sulphate > chloride > bicarbonate > hydroxide > fluoride [79].

Ku *et al.* (2002) utilized aluminum formed synthetic resin, Amberlite IR-120 (MERCK, USA) for defluoridation of aqueous solution. The adsorption was highly dependent on pH of the solution and optimum pH was found to be in the range of 5 to 7. The adsorption of Amberlite IR-120 resin was increased in the vicinity of sulphate ions in solution. The experimental data fitted well with Langmuir isotherm (r^2=0.999) than Freundlich isotherm (r^2= 0.992). The Langmuir adsorption capacity of adsorbent was found to be 0.244 mmol/g. A second-order-kinetic model was well described the surface reaction. The BDST model was utilized for describing the removal behavior of fluoride in the column. Empty bed contact time (EBCT) responsible for improving the removal capacity and proper utilization of contact bed of adsorbent [80].

Luo and Inoue (2004) utilized metal(III) like lanthanum(III), cerium(III), yttrium(III), iron (III) and aluminum(III) loaded amberlite resins for defluoridation of water from hot springs in Japan. The fluoride removal capacity of metal(III) loaded 200CT resins at pH 4.5-8 were found in the order of La(III) $\geq$ Ce(III) > Ya(III) > Fe(III) $\approx$ Al(III). The fluoride removal of 90% and 60% was obtained at pH 4-8.5 by Ce(III)-loaded 200CT resin and Y(III)-loaded 200CT resin respectively. Small amounts of fluoride existing in hot spring water could be effectively removed with a column packed with La(III) and Ce(III) loaded 200CT resin at pH6.0. The maximum adsorption capacity of fluoride ions on La(III) loaded 200CT resin and Ce(III) loaded 200CT resin in the column were same and was found to be 1.34 mol/kg [81].

Meenakshi *et al.* (2007) utilized chelating resin like Indian FR 10 (IND) and Ceralite IRA 400 (CER), an ion exchange for removal of fluoride from water. The defluoridation performance of chelating resin was more than an ion-exchange resin. The experimental data fitted well with Freundlich isothermwhen contrasted with the Langmuir isotherm model. The Langmuir adsorption capacity of Indian FR 10 (IND) and IRA 400 (CER) were ranged between 1.305 to 1.356 mg/g and 1.504 to 1.658 mg/g at different temperatures (i.e. 303, 313 and 323K) respectively. The adsorption was took after by non-linear pseudo-second-order and particle diffusion kinetic models. The adsorption reaction was exothermic in nature and indicated that the fluoride removal was done by physic-sorption [82].

Boldaji *et al.* (2009) utilized a hybrid resin (Lewatit FO 36) for removal of fluoride from water. The fluoride removal

efficiency of 61% was obtained where the fluoride concentration was less than 4 mg/l. The optimum removal was observed at pH range of 3.0 to 5.5. Langmuir model was applicable to the present study and F- ions were exchanged with hydroxide ions in nano-scaled structures on the surface of sorbent [83].

Solangi *et al.* (2009) utilized modified Amberlite XAD-4 resin by introducing an amino group onto the aromatic ring for removal of fluoride from aqueous solution in batch and column modes. The optimum pH for maximum fluoride removal was found to be 9.0. The adsorption capacity of modified resin was 5.04×10^{-3} mol/g. The adsorption mechanism was governed by ion exchange as per D-R isotherm model. The experimental data fitted with Langmuir and Freundlich isotherm models. Desorption of fluoride achieved by using 10% HCl. The vicinity of co-anions slightly affected the adsorption capacity. This modified resin was utilized for defluoridation of drinking water of Thar Desert and regenerated several times with HCl [84].

Kumar *et al.* (2011) bi-metal (Fe and Al) doped micro- and nanoparticle based adsorbent for the removal of arsenic and fluoride from water. Al and Fe were effectively incorporated into polymeric beads during an intermediate step of the synthesis by suspension polymerization. The bi-metal doped, activated micron (~ 0.8mm) and nano (~ 100nm) size porous adsorbents were shown to possess significant loading of fluoride (~ 100 mg/g) with concentration of 0-90 ppm and arsenic (~40 mg/g) with concentration of 0-70 ppm [85].

Ku *et al.* (2011) utilized aluminum loaded Duolite C-467 resin for removal of fluoride from aqueous solution. The optimum pH was found to be in the range 5.0-7.0. The vicinity of sulphate ions highly affected the fluoride removal capacity. The Bed-Depth-Service-Time (BDST) model was adequately described the adsorption behavior of fluoride by aluminum loaded Duolite C-467 resin in a fixed bed column, also indicating that the adsorption rate of fluoride ion was mainly determined by the surface reaction step [86].

Choudhary *et al.* (2014) utilized quaternary aminated resins from sawdust for defluoridation of drinking water. The fluoride uptake by adsorbent was very fast; nearly 80% of uptake at equilibrium took place in less than 30 minutes. The uptake of fluoride was increased with decrease in pH of water. The uptake of fluoride increase with increase in cationic surfactant and decreased with increase in anionic surfactant. The removal efficiency of sawdust (SD) derivatives was founded in order of TMAHP-SD > DEAE-SD > TEAHP-SD. The K_d of saw dust derivatives was calculated at pH 8 and increases with the decrease in pH of water, which may be attributed to the neutralization of surface negative charge of SD derivatives [87].

Prabhu *et al.* (2014) utilized metal ions (Fe_3^+, Al_3^+, Na_3^+, Ce_3^+ and La_3^+)loaded Duolite (DLE) C 466 (Sodium form of iminodiacetic acid functionalized macro-porous cross-linked polystyrene) for defluoridation of water. The defluoridation capacity of the La, Ce, Al, Na and Fe loaded DLE resins were found to be 4.760, 4.519, 1.875, 1.759 and 0.784 mg/g respectively. Among all the resins, La-DLE was observed to be high defluoridation capacity. The optimum conditions for fluoride removal was achieved to maintain the pH of 7.0, 0.1 gm doses of adsorbent and shaking time of 60 minutes. The bicarbonate ions reduced the defluoridation capacity, while the vicinity of chloride, sulphate and nitrate ions had a slight effect on deluoridation capacity. The experimental data for La-DLE fitted well with Fruendlich isotherm model. The Langmuir maximum adsorption capacity of La-DLE was 9.967, 10.060 and 12.139 mg/g at a temperature of 303, 313 and 323K. The adsorption reaction took after the pseudo-second-order kinetic model. The adsorption procedure was spontaneous (-ΔG), endothermic (ΔH) and irreversible and stable (ΔS) [88].

Kumar *et al.* (2014) utilized dual function muslin based anion exchange for defluoridation of water. The muslin was modified by graft copolymerization with poly(4-vinyl pyridine) using c-ray initiation method. The adsorbent M-g-poly (4-VP) had maximum fluoride uptake at pH4, 20°C and 10 ppm of initial fluoride concentration. The maximum defluoridation capacity of 7.7 mg/g was observed when fluoride uptake was studied up to 10 cycles. The experimental data fitted well with Langmuir isotherm as well as adsorption reaction took after the pseudo-second-order kinetic model. The adsorbent also exhibits strong anti-microbial properties against both bacterium and fungus. The defluoridation reaction was exothermic. Desorption of adsorbent was carried out by NaCl solution and material could reuse in many treatments [89].

Barathi *et al.* (2015) prepared aluminum hydroxide impregnated macroreticular polymeric resin for defluoridation of water. The experimental data fitted well with the Langmuir isotherm model and took after the pseudo-second order kinetic model. The maximum Langmuir adsorption capacity of Al(OH)3 impregnated polymeric resin adsorbent was 92.36 and 36.61 mg/g at pH 3.0 and 7.0 respectively. The fluoride uptake in tap water was 32.927 mg/g at pH 7.0. The adsorption procedure was spontaneous and exothermic in nature. The adsorption was mainly governed by ion-exchange and hydrogen bonding mechanism. The column study revealed that with this adsorbent dose of 0.75 g, fluoride solution of 5.43 ppm was reduced to 1.5 ppm with specific safe water yield of 550 ml. The desorption of spent adsorbent was carried out effectively with 10 ml of 0.05 mol/l of NaOH solution [90].

Prabhu and Meenakshi (2015) utilized oxalic acid mediated polyacrylamide-zirconium complex (Ox-PAAm-Zr) prepared by one-pot synthesis method for defluoridation of aqueous solution and tested for field samples. The maximum adsorption capacity of Ox-PAAm-Zr complex was 9.60 mg/g.

The optimum contact time was 20 minutes and adsorption mechanism was governed by a ligand exchange mechanism. The adsorption procedure was obeyed Fruendlich isotherm and pseudo-second-order-kinetic model. The adsorption reaction was spontaneous and endothermic in nature. The recovery of adsorbent was carried out by using 0.1 M NaOH for about 60 minutes and could be utilized for fourth successive cycles [91].

Nasr *et al.* (2015) utilized Purolite A520E resin for defluoridation of simulated and field water. The fluoride removal capacity of 2 mg/g was achieved at 30°C for fluoride solution of 5 mg/l with per unit mass of Purolite A520E resin while the Langmuir maximum adsorption capacity of the resin was observed to be 5.26 mg/g at 30°C. The adsorption procedure obeyed Langmuir isotherm and the reaction was spontaneous and endothermic in nature. The field sample of Louza 2 was reduced from 3.39 mg/l to 1.20 mg/l by using resin dosage of 2 g/l and shaking time of 30 minutes. The recovery of 98% was achieved by 6% NaCl solution [92].

8. DEFLUORIDATION BY ALGAES AND FUNGIES

Bhatnagar *et al.* (2002) utilized micro-algal biomass (Anabaena fertilissima and Chlorococcum humicola) for defluoridation of water. Algal biomass pretreated with Ca2+ was also utilized for removal of fluoride. Maximum biosorption of Ca2+ was at 50mg Ca2+/l with both Anabaena fertilissima (2.8 mg Ca2+/g dry wt.) and Chlorococcum humicola (4.4 mg/l). Data for both Ca^{2+} and F^{-} biosorption fitted well the Langmuir adsorption isotherm indicating monolayer adsorption at a constant energy [93].

Sinha *et al.* (2003) utilized Eichhornia crassipes biomass, commonly known as water hyacinth in non-carbonized and carbonized form at two different temperatures (carbon activated at 300 and 600°C) for removal of fluoride from aqueous solution. The defluoridation capacity of carbonized E. crassipes was more than un-carbonized plant. H-type carbon activated at 600°C (72-98%) exhibited better removal than L-type carbon activated at 300°C (51-93%). The experimental data were fitted well with Freundlich isotherm and adsorption took after Lagergren first-order equation. The adsorption reaction was endothermic in nature since adsorption increases with increase in temperature. The column capacity was 4.4 mg/g to 15 mg/l of initial fluoride concentration and the effluent volume at breakthrough was found to be 100 bed volumes [94].

Mohan *et al.* (2007) studied the removal of fluoride onto algal biosorbent Spirogyra sp.-IO2 from aqueous media. The experimental data fitted well with the Langmuir isotherm model and adsorption was took after pseudo-first order kinetic equation. The fluoride removal of 54% was achieved at neutral pH. The Langmuir adsorption

capacity of 1.272 mg/g was obtained by algal biosorbent. The maximum removal of fluoride was observed at lower pH and at 30°C operating temperature. Desorption was carried out by inorganic solution and distilled water. The defluoridation mechanism was mainly because of ion-exchange and physical adsorption [95].

Mohan *et al.* (2007) utilized algal Spirogyra IO1 for removal of fluoride from aqueous media in batch mode. The adsorption result was best fitted with Langmuir isotherm and adsorption procedure was took after pseudo-second-order kinetic model. The Langmuir maximum defluoridation capacity was 1.272 mg/g. The maximum defluoridation was occurred at lower pH because of availability of more positive sides [96].

Miretzky *et al.* (2008) utilized aquatic macrophyte biomass (Eleocharis acicularis) pretreated with Ca^{2+} for the removal of fluoride from aqueous solution. The maximum defluoridation capacity was 0.110 mmol/g with an efficiency of 64.5% occurred at pH of 6 with 5.0 g/l doses of adsorbent [97].

Rao *et al.* (2009) utilized algal biosorbent prepared by Ulva fasciata for removal of fluoride from water. The amount of fluoride adsorption increased with increase in adsorbent dose of Ulva fasciata, decrease in particle size of adsorbent and with a decrease in initial fluoride concentration. The adsorption equilibrium was achieved within 45 minutes. Maximum fluoride adsorption was observed at 30°C operating temperature. The experimental data fitted well with the Langmuir isotherm model [98].

Prajapat *et al.* (2010) utilized saw dust, Aspergillus penicilloides and Mucor racemosus as potential biomaterials for calcium and fluoride removal. Maximum Ca^{2+} sorption was carried out by sawdust while Aspergillus penicilloides and Mucor racemosus showed better performance for the removal of fluoride after Ca^{2+} treatment since positive cations on biomass surface attracted a negative charge anion thus improved adsorption performance [99].

Merugu *et al.* (2012) utilized fungal biomass prepared from Fusarium moniliforme after treating with calcium and alkaline for removal of fluoride from water. The adsorption of fluoride decreased with increase in pH of media. Fluoride removal capacity was found to be 24% at pH of 5.0 and 11% at pH of 8.0. The vicinity of bicarbonate in water highly affected the removal performance. The adsorption was rapid for a period of 1 hours and subsequently get slower afterward [100].

Merugu *et al.* (2012) investigated the defluoridation capacity of fungal biomass prepared from Aspergillus

Niger after calcium and alkaline treatment. The adsorption was mainly governed by vicinity of Ca^{2+} on the surface of fungal biomass after treatment with calcium. The adsorption was decreased with increase in pH. The adsorption capacity was 30% at pH 5.0 and 21% at pH8.0. Fluoride removal decreased with increased bicarbonate concentration but was independent of the vicinity of chloride and sulphate. The kinetic of adsorption was very fast within 1 hour and then became slower during the subsequent period [101].

Merugu *et al.* (2013) utilized Aspergillus nidulans fungal bioadsorbent for removal of fluoride after treatment with calcium and alkali. The adsorption was pH dependent and adsorption was decreased with increase in pH. The fluoride removal was 29% at pH 4.0 and 14% at pH 8.0. The fluoride removal was decreased with an increase in the bicarbonate concentration, while vicinity of chloride and sulfate did not affect he fluoride removal performance. The rapid phase of binding was observed for a period of 1.5 hours and a slower phase of binding occurred during the subsequent period [102].

Hiremath *et al.* (2013) utilized non-living biomass of Spirilina platenisis for defluoridation of water. The optimum condition for maximum removal of fluoride in batch mode was achieved at pH of 2.0, initial fluoride concentration of 500 ppm, adsorbent dose of 4g/l and contact time of 20 minutes. The maximum fluoride removal of 90.2 mg/g was obtained at optimum condition. The experimental data fitted well with the Langmuir and Freundlich isotherm model. The adsorption procedure was took after the pseudo-second-order kinetic model [103].

9. CONCLUSIONS

The huge greater part of the developing nations relies on the groundwater as a source of drinking water like India [104 - 109]. This paper elaborated an outline of different bio-polymers, synthetic polymers, celluloses, resins, algae and fungi in lieu of costly commercial adsorbents for fluoride uptake of water. The fluoride removal efficiency depends on dose of adsorbent, initial fluoride concentration, pH, temperature, contact time, speed of agitation, etc. The removal capacity enhanced with high doses of the adsorbent and smaller size of the adsorbent. The equilibrium data fitted well to the adsorption isotherms such as Langmuir and Freundlich. A review of different adsorbents introduced here great affinity towards fluoride removal from water. The utilization of commercially available adsorbents can be exchanged by the inexpensive and effective bio-polymers and synthetic polymers. The future exploration ought be focutilized on evaluating the usefulness of adsorbents regarding expense and feasibility for the removal of fluoride.

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BIOGRAPHIES

Sanghratna S. Waghmare is working as a senior scientist at Environmental Materials Division, National Environmental Engineering Research Institute (CSIR-NEERI), Nagpur. He has experience in condition assessment of RCC buildings and bridges using NDT and PDT techniques also engaged in development of building materials from wastes, design and development of instant houses and polymer composites from sisal fibers. Currently, he has been involved in defluoridation and carbon dioxide sequestration.

Tanvir Arfin is currently working as the Scientist at Environmental Materials Division, CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), India. Dr. Arfin has been actively engaged in research related to various fields of electrochemistry, platinum group materials, polymer science, membrane, hybrid materials, graphite oxides and biomass energy. He has published more than 30 scientific peers reviewed journal papers and 10 book chapters.