Available online at www.jobpcr.com

ISSN-2394:3076
CODEN(USA) : JBPCBK

Journal of Biological Pharmaceutical And Chemical Research , 2017,4(3): 1-13

(http://www.jobpcr.com/arhcive.php)

FLUORIDE REMOVAL BY BIOSORBENTS-A REVIEW

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ABSTRACT

Fluoride ion is one of the most harmful environmental pollutants. Enlarged mechanized expansion has led to the introduction of large quantities of fluoride ions into the environment, which causes potential hazards to animals and human health through food chain. Elevated concentration can cause dental, skeletal fluorosis and also non-skeletal problems. Research was done on defluoridation by using different methods, widely used is the adsorption process. Dissimilar low cost adsorbents were developed using a variety of raw materials. Utilization of suitable adsorbent is the key for adsorption process. Different biosorbents were developed for the removal of fluoride. This paper reviews the biosorbents used for fluoride removal.

Key words: Adsorption, Biosorbents, Removal of fluoride.

INTRODUCTION

REVIEW ARTICLE

Fluorspar, cryolite, fluorapatite and hydroxyl apatite are the key sources of fluoride. Concentration of fluoride in water is due to various factors such as velocity of flowing water, pH, temperature, solubility of fluoride minerals etc. Fluoride ions are engrossed by calcium in teeth and bones due to positive charged ions. Because of this tendency and high concentration of fluoride in water caused major health problems such as mottled enamel, damage to teeth, Osteofluorosis and damage to bones in all ages of people [1-7].

The highest permitted limit of fluoride in drinking water was decided by WHO (1996)) which is 1.5 mg/1.Study on excess fluoride removal was done by different methods such as adsorption, chemical treatment, use of resins, electrolytic defluoridation, separation by membrane, electro dialysis etc.

Biosorption shows potential for the removal of fluoride from the solution. Biosorption is nothing but a process in which biomass dead or alive is used to eliminate substance from the solution. Substances may be organic, inorganic, and in soluble or insoluble form. A variety of biosorbents were developed according to the local environment. This paper reviews synthesis and application of these biosorbents for fluoride removal.

2. Fluoride removal by Chitosan and its derivatives

Yao and et al. used neodymium-modified chitosan as adsorbent. The effect of various parameters like weight of adsorbent, particle size, temperature and occurrence of co-anions was studied. Maximum adsorption was found at pH 7 and by using 0.1mm particle size. Regeneration of adsorbent was achieved in 24 h [8]. Defluoridation was studied by lanthanum incorporated chitosan beads. For synthesis of chitosan beads optimization of different parameters was done. Characterization of the beads was done to identify the internal structure, functional groups and surface area. Change in enthalpy was positive so adsorption was endothermic in nature. Fluoride removal efficiency was obtained 97% at pH 5 [9]. NH3+ and COOH groups were introduced by protonation and carboxylation in chitosan beads. Fluoride removal was observed maximum (1664 mg) in protonated beads as compared to raw chitosan beads (52mg).Effect of presence of another ion on adsorption process was observed [10]. Use of chitin, chitosan and 20% lanthanum included chitosan as adsorbent was studied for the removal of surplus fluoride. Exceptional result was obtained for Lanthanum-chitosan adsorbents as compared to chitosan and chitin. Author studied parameters like pH, concentration and type of co-anions for the removal of fluoride. At pH 6.7 nearly all of the fluoride removal was observed [11]. Synthesis of LCB (lanthanum loading 10%) was done by use of optimized parameters like precipitation time, lanthanum loading and ammonia strength. Its application in the removal of fluoride was studied. Fluoride removal capacity of LCB was 4.7 mg/g. Comparison of defluoridation capacity was checked with commercial activated alumina which was four times superior to commercial activated alumina [12]. Complex of hydrous ferric oxide (HFO) and alginate was synthesized and used for removal of fluoride. Defluoridation capacity was checked for different parameters such as pH, temperature, adsorbent weight. The fluoride removal capacity was 8.9 mg/g at pH 7.Presence of anions and pH was the two important factors which influenced the fluoride removal. Kinetics of the process was well explained by Langmuir adsorption isotherm [13].Titanium was incorporated in the chitosan by the precipitation method and used as an adsorbent .Adsorbent was characterized by SEM, XRD, and FTIR. For removal of fluoride various parameters were studied like temperature, pH, concentration adsorbent dose and initial concentration. Fluoride removal was highest at neutral pH. Fluoride removal was less in acidic and alkaline pH. Existence of co anions showed negative effect on removal of fluoride [14].Chitin and chitin based biocomposite was studied as adsorbent in fixed bed column. At saturation adsorption capacity was 1.7 mg/g for biocomposite and for Chitin it was 3.4mg/g. Desorption of fluoride was checked using NaOH solution. The regeneration efficiencies for chitin and biocomposite were found to be 85% and 84% respectively [15]. Adsorption capacity of fluoride and effect of various parameters like contact time, adsorbent dose, initial fluoride concentration and co ions on fluoride removal was studied. Author used La-Ce modified chitosan and La (III) modified Chitosan as adsorbent. Authors reported adsorption capacity of La-Ce modified chitosan and La(III) modified chitosan. For two hours the fluoride adsorption capacity was 3.72 mg/g and 3.16 mg/g respectively. Bicarbonate and carbonate ions affected the adsorption capacity to a great extent [16]. Lanthanum incorporated chitosan beads were prepared using impregnation method which showed enhancement in defluoridation capacity. Authors optimized the conditions for amalgamation of LCF. Various parameters for synthesis of LCF were lanthanum loading, time for stirring which affected the fluoride removal. Maximum adsorption capacity was observed 1.27 mg/g [17].Multifunctional groups such as amine and hydroxyl were impregnated to the Chitosan beads and tested for defluoridation. The capacity for fluoride removal was increased from 52 mg to 1800mg of fluoride per kg. Freundlich and Langmuir isotherm was fitted for experimental data. Fluoride removal was somewhat decreased due to other ions [18].

3 Fluoride removal by Biomass and Biowaste

A recently developed amalgam material of Fe/Zr mixed oxide immobilized in biopolymer alginate was synthesized. The average size of the particle was 70.89 nm and 477.7 nm. In XRD pattern presence of Fe/Zr was found. For fluoride adsorption the reaction followed second order kinetics. At pH 12 desorption showed 89% removal of fluoride [19]. Biomass of *Tinospora cordifolia* was used as biosorbent for defluoridation. Biosorption was fast. Equilibrium was achieved in 120 min. 25mg/l of fluoride removal capacity was observed during experimentation at pH 7. Langmuir and Frendlich models were very well fitted to the experimental results [20]. The extent of Defluoridation was found by using fungal biosorbent prepared from *Fusarium moniliforme.* For increased pH less fluoride was removed. As pH was increased the fluoride removal capacity found to be decreased [21]. Orange waste was utilized for making innovative adsorbent which was prepared by alkaline hydrolysis reaction with solution of calcium hydroxide. Impregnation of rare earth metal ions such as Sm (III), Ho (III), La(III) and Lu (III) on the adsorbent was done. These adsorbents were tried for removal of fluoride. Re-loaded orange waste removed the trace concentration of fluoride ion successfully. Alkali solution used to desorb the loaded fluoride. Maximum removal of fluoride was obtained by La(III) and Sm(III) loaded adsorbent [22].

Comparison of defluoridation capacity of brushite-calcite and two biosorbents (Neem and Pipal leaves) was done. By using brushite calcite fluoride removal efficiency was 76% in 90 minutes and in 18 hrs it was 80%.For biosorbents removal efficiency was found to be 20% in 90 minutes and it was 35.6% in 18 hrs. It was concluded from the result that brushite calcite was superior to the local biosorbents [23]. Waste fungal biomass (Pleuratus astreatus 1804) resulting from the laccase fermentation process was used for fluoride removal. Ability of fluoride adsorption was found by batch adsorption studies. Process followed pseudo first order kinetics [24].Rice husk surface was modified by covering of aluminum hydroxide .Fluoride removal was checked and found in between 9 to 10 mg/g [25]. Author used orange peel residue and Fe_3O_4 nanoparticles for removal of fluoride. In first case Fe_3O_4 nanoparticles were immobilized in sodium alginate matrix and in the second case with orange peel residue nanaoparticles were immobilized in the same matrix. Highest adsorption capacity obtained was 58.24 mg/g and 80.33 mg/g for both adsorbents respectively [26].

Vetiveria zizanioides, a herbal plant was used for the removal of fluoride. Dose of adsorbent played very important role. Vetiver root treated with Phosphoric acid showed good adsorption capacity than the fresh powdered Vetiver root. For increase in dose of adsorbent there was increase in fluoride removal. Optimization of different parameters was done [27].Nano composite of cellulose and hydroxyapatite was synthesized by hybridization. The composite having high surface area and affinity towards fluoride showed good defluoridation capacity which can meet to the drinking water quality. The experimental data were fitted to the Langmuir and Freundlich isotherm [28]. Low cost adsorbents were selected for defluoridation as chalk powder, pineapple peel powder, horse gram seed powder, red soil, orange peel powder, ragi seed powder, multhani mati and concrete. For chalk powder pineapple peel powder and concrete the fluoride removal was 86%, 79% and 80% respectively. Other adsorbents showed less fluoride removal [29]. Defluoridation of wastewater in batch process by using natural adsorbents like Mangrove plant leaf powder (MPLP), Toor plant leaf powder (TPLP), Pineapple peel powder (PPP), Chiku leaf powder (CLP), Almond tree bark powder (ATBP) and Coconut coir pith (CCP) was investigated . The fluoride uptake by adsorbents at equilibrium was found to be in the order of MPLP > CCP > TPLP > CLP > PPP > ATBP. At pH 2.0 maximum fluorides was removed for 5 ppm using 10 gm of adsorbent in 60 minutes. Regeneration of adsorbent was possible at higher pH [30].Adsorption capacity of banana peel, groundnut shell and sweet lemon peel for defluoridation of wastewater (Industrial wastewater) was studied.

Percentage removal of fluoride by banana peel, groundnut shell and sweat lemon peel was 93.34, 89.90 and 59.55% respectively. Langmuir isotherm was fitted to the experimental data. Kinetics was explained by pseudo second order [31]. The defluoridation capacity of Citrus Limetta (Mosambi) peel powder was studied. The maximum Langmuir adsorption capacity of mosambi peel powder was 1.82 mg/g. The fluoride removal was 82.5% for 5 mg/l fluoride concentration [32]. Author used immobilized saponified orange peel residue (SOPR) with alginate matrix. The mixture was loaded with 5% of $FeCl_3.6H_2O$ where the composite adsorbent was referred as FSOPR. The maximum adsorption capacity of FSOPR was 7 mg/g. Mechanism of defluoridation was electrostatic interaction and ion exchange. Mostly due to attraction of hydroxide and carbonyl groups with fluoride ions fluoride was removed [33].Zirconium (IV) loaded carboxylated orange peel (ZCOP) was used for defluoridation. Over a wide pH range of 3.0-8.0 fluoride removal was achieved. The maximum removal of 97.2% was attained at pH 7 with 0.7 g/l doses of adsorbent in 50 minutes. The Langmuir maximum adsorption capacity was 5.605 mg/g at pH 6.0 [34]. Experiments were carried out for tamarind seed, a household waste that was left after removing the tamarind pulp for food preparation that mainly contains polysaccharide. The maximum defluoridation was achieved at pH 7. As temperature and particle size was increased capacity of fluoride removal was decreased. Contribution of energetic forces such as columbic interaction in sorption was the reason for above results of defluoridation [35]. Defluoridation capacity of Pristine, purified and polyaniline coated tamarind seed (TS) from water was studied. For 10 mg/l initial fluoride concentration the adsorption capacity of 75µ pristine TS, 150µ pristine TS and 300 µ pristine TS were found to be 10.6, 1.4 and 4.24 mg/g. The adsorption capacity of 300 µ purified TS for 2 mg/l of initial fluoride was merely 1.38 mg/g. The adsorption capacity of 50% and 90% Pani treated 75µ Pristine TS were 10.7 mg/g and 7.48 mg/g, respectively .Adsorption capacity of 50 % and 90% Pani treated 300 µ purified TS were 2.32 mg/g and 0.26 mg/g for 2 mg/l. 50% Pani treated 75µ Pristine TS removed maximum fluoride [36]. Activated carbon synthesized from Phyllanthus emblica (Indian Gooseberry) used as adsorbent for defluoridation. Fluoride removal efficiency was found 82.1% at neutral pH in75 minutes for adsorbent dose of 0.75g. The vicinity of bicarbonate was definitely found to decrease the fluoride removal capacity from 82.1% to 47.22% with an increase in concentration of 0 to 500mg/l while there was no significant impact of other co-anions. The order of obstruction for fluoride removal was observed in the order of $HCO_3^->SO_4^{-2}->Cl^->NO_3^-$ [37].Researcher had studied the defluoridation of water by using physical-chemical process of adsorption and coagulation by using Materials like seed extracts of Moringa Oleifera(drum sticks),rice husk and chemicals like Manganese Sulphate and Manganese Chloride. Rice husk removed 83% of fluoride for initial concentration of 5ppm in 180 minutes. The Langmuir adsorption isotherm fitted well for Rice husk. For Moringa Oleifera seed extract, Manganese Sulphate and Manganese Chloride, fluoride removal percentage was 92, 94 and 91 respectively [38].

Guava (Psidium guaiava) seeds powder (2µm) was used as biosorbent and had adsorption capacity of 116.50 mg/g at 25^0C for 5 mg/l of initial concentration of fluoride. Removal of fluoride was maximum at pH range of 5-8. Adsorbent showed good affinity towards fluoride as compared to conventional adsorbent [39]. Defluoridation efficiency of alkali and acid treated drumstick (Moringa Oleifera) seed powder from aqueous solution was studied. The fluoride removal of alkali treated adsorbent was found better than acid treated adsorbent. The optimum dose of 400 mg/l alkali treated adsorbents removed 76% and 68% of 10 mg/l of initial fluoride concentration by 212 µ and 600 µ particle size adsorbents in 2 and 2.5 hours respectively [40]. Mechanically modified guava seeds (MGS) was used for removal of fluoride from aqueous solution. Langmuir-Freundlich isotherm model indicated that fluoride absorption onto MGS was characterized by chemisorption on

heterogeneous surfaces. The adsorption capacity of MGS was found to be 15.6 mg/g [41]. Chemically activated ($CaCl_2$) carbon synthesized from Phoenix Dactylifera (Date Palm) seed at room temperature was used as adsorbent. At pH 7 maximum removal of fluoride was obtained. The parameters were optimized like impregnation ratio, contact time, pH and adsorbent dose. [42]. Defluoridation capacity of *Strychnos Potatorum* (SP) from aqueous solution was studied by batch experiments. The optimum dosage and initial fluoride concentration of SP adsorbent was 50mg/50ml and 1mg/50ml respectively. The removal of fluoride was expressed with Langmuir and Freundlich isotherms. Removal of fluoride was affected by existence of co-anions was found in an order of $PO_4^{3-} > SO_4^{2-} > Cl^- > CO_3^- > NO_3$ [43].Raw Moringa oleifera (MO) seed cake as natural coagulant and its composite coagulant prepared by adding alum and starch with MO seed cake was used for fluoride removal. In both cases, fluoride was precipitated by coagulants and removed the fluoride below 1 mg/l but turbidity of water was very high to tolerate MO seed cake, whereas turbidity of treated water was less than 5 NTU (within standard limits of drinking water) for composite coagulant [44]. Activated Tamarind Fruit Shell and tamarid fruit shell coated with MnO_2 was used for adsorption experiments. For batch experiments various parameters were studied like adsorbent dose, pH, concentration .From kinetics it was confirmed that Temkin isotherm was fitted for activated tamarid fruit shell whereas for MnO_2 coating Langmuir was fitted. Column experiments were carried for variables like bed height and flow rate. As bed depth was increased, the breakthrough capacity was also increased for activated tamarid fruit shell [45].

Ficus religiosa leaves were used for the removal of fluoride from water. Experiments were conducted for different parameters like time, dose of adsorbent, pH and rpm. Both batch and continuous experiments were conducted. 70% removal of fluoride was observed for 2.5 g of adsorbent dose in 2 hours. [46].

Fluoride removal by Activated carbon prepared from biowaste

From Cynodon dactylon activated carbon was prepared and used for fluoride removal. For the adsorbent dose of 1.25g at neutral pH fluoride removal efficiency was 83.77% for 3 mg/l initial concentration of fluoride. Presence of bicarbonate decreased the fluoride removal. Author also studied the kinetics of the process which was pseudo-second order kinetics and was endothermic [47]. Bone char was used as biosorbent for removal of fluoride. Batch experiments were conducted. It was concluded from batch experiments that fluoride removal was increased as fluoride concentration was increased. Continuous experiments were conducted by varying parameters like bed height and flow rate. A mass transfer model was developed. Consistency was observed with the experimental results and data predicted by model [48]. A byproduct of fast pyrolysis (pine wood and pine bark) was used as adsorbent for removal of fluoride. Batch experiments were conducted for different parameters. Maximum defluoridation was occurred at pH 2.Inctrease in temperature reduced the fluoride removal capacity. The char performance was evaluated by using different adsorption models [49].For removal of fluoride, *Ichhornia crassipes* and its activated carbon were selected as adsorbent. Batch and continuous studies were carried out which showed that activated carbon from this plant showed maximum removal as compare to the *Ichhornia crassipes*. The process was temperature dependant. At 600^0C carbon synthesized showed improved performance than at 300^0C. Column experiments were conducted for different parameters such as bed depth, flow rate. The column capacity was designed as 4.4 mg/g [50]. Three low cost biosorbents were used for defluoridation. Activated bagasse carbon showed maximum amount of fluoride removal as compared to other two biosorbents for 5 ppm solution of fluoride. The optimized conditions were pH 6, time required one hour and 4 gm adsorbent was used. All three adsorbents results were compared with commercial activated carbon. Commercial activated carbon showed only 1%

increase in defluoridation[51].Naturally available fruit shell of *Tamarindus indica* and, fruit shell was loaded with ammonium carbonate and carbonized. The carbonized material was used for the excess fluoride removal from water. Characterization of the adsorbent showed the presence of calcium compounds. For both the adsorbents batch experiments were conducted for defluoridation by operating at different variables. Various types of kinetic models were tested for experimental data. Defluoridation capacity for natural adsorbent was 91% while for carbon it was 83% [52]. Peels of Citrus Documana (NCDC), Citrus medica (NCMC) and Citrus aurantifolia fruits (NCAC) were carbonized and activated and was used for adsorption of fluoride. After optimizing parameters, maximum fluoride removal was found for Citrus documana. Pseudo second-order equation was obeyed. Adsorption process was described by pore diffusion [53]. From Pitacelobium dulce carbon (PLDC) low cost activated carbon was prepared and used for defluoridation of water and compared it with commercial activated carbon (CAC). The fluoride uptake by PLDC and CAC was 81.60% and 40.20% at pH 9 respectively. The adsorption capacity of PLDC and CAC was 0.81 mg/g and 0.2267 mg/g at pH 7 for initial fluoride concentration of 3mg/l [54]. Royal Gulmohar fruit shell activated carbon was prepared. Activated carbon treated by $MgCl_2$ and H_3PO_4 by the impregnation ratio (I.R) of 0.25, 0.50 and 0.75., and without treatment also it was checked for defluoridation capacity. Increased surface area of the adsorbent with I.R. of 0.75 was observed. [55]. Author synthesized activated carbon prepared from Typha angustata (TAC), Lagenaria siceraria shell carbon (LSSC) and Acacia farnesiana carbon (AFC) .These were tested for the field samples of hand pumps (F- concentration: 1.07 to 2.62 mg/l) and bore wells (F- concentration: 1.25 to 2.8 mg/L) of 24 gram panchayats (Villages) of the Kanduku sub division of Prakasam district in Andhra Pradesh. The contact time was fixed between 45-60 minutes with 200 rpm of stirring speed. The adsorption capacities of the adsorbent were of the order: TAC>LSSC>AFC [56]. Activated carbon synthesized from banana (Musa paradisiacal) peel and coffee (Coffee Arabica) husk was tried for fluoride removal by conducting batch experiments. Operating parameters were pH, time, concentration and dose of adsorbent. After optimizing the variables the fluoride removal efficiency was obtained between 80 to 84% for these biosorbents [57]. The potential of Lagenaria Siceraria shell carbon (LSSC) for fluoride removal was studied. At the optimum pH range of 6.0 to 7.0, more than 85% defluoridation was observed. Fluoride removal capacity was reduced due to co-anions of LSSC in the order of $H_2PO_4^-$> HCO_3^->SO_4^{2-}. LSSC was much cheaper than commercial activated carbon [58]. Capability of fluoride removal of Acacia farnesiana carbon (AFC) at room temperature was studied. The maximum fluoride removal was found at pH 6.9. The equilibrium condition was achieved in 40 minutes. The major effect of other ions on the fluoride adsorption followed the order: H_2PO^{4-}>HCO_3^->SO_4^{2-}.The AFC was found more economical as compared to commercial activated carbon (CAC[59]. Researcher studied the capability of defluoridation activated carbon treated with nitric acid derived from Typha angustata plants. The range of optimal pH was 6.5-7.0 wherein more than 85% of fluoride was removed from water [60].Kumar *et al.* have used Tamarind fruit shell (TNFC) carbon in virgin and acid treated form as adsorbent. The Langmuir maximum monolayer adsorption capacities of virgin and treated TNFC were 4.14 mg/g and 6.11mg/g respectively at 25^0C. At pH 6 maximum fluoride uptake was observed. Chloride ions reduced the removal of fluoride form 5 to 11% whereas presence of sulfate ions reduced sorption capacity by 37% and 15% for virgin and treated TNFC respectively [61]. From Almond shell carbon was prepared and activated with KOH. This was used for removal of fluoride from water in the down flow column .The optimal condition was achieved by maintaining the 6cm bed height, pH 4, flow rate of 15 ml/min, 25^0C temperature and 2 mg/l of fluoride water. The removal of fluoride by CGAC and AGAC was found to be 63% and 68% respectively [62].

Coconut shell carbon activated by 2M of H_2SO_4 was used as adsorbent to remove fluoride from

synthetic and field sample. The removal of fluoride by small size particles of 150μ for field and synthetic water was 68.2% and 65.9% respectively. The maximum fluoride was removed at pH of 2.0. The coconut shell activated carbon was locally available in Tanzania and also removed color and mostly used in household filters [63]. Capability of the activated carbon prepared from shell of Bale fruit (Limoniaacidissima) for fluoride removal was studied in batch process. The maximum removal was found to be more than 63%. The optimum pH, contact time and dosage were 5.0, 20 minutes and 1.5 g respectively. The regression coefficient of Langmuir isotherm was 0.9587 which showed the favorable condition of adsorption [64].Carbonization of peanut shells and plum kernels was done. Impregnation of calcium acetate solution was done prior to carbonization. The calcium impregnated carbon gave better fluoride adsorption capacity. The defluoridation capacity of pea nut shell impregnated with calcium solution was 3151 mg/l and carbonized at 800^0C (IC-PN-25) was found higher than other adsorbents. The defluoridation capacity of IC-PN-25, IC-PK-25, C-PN and C-PK was 2.5, 2.05, 2.0 and 0.69 mg/g respectively [65].For defluoridation from drinking water chemically activated cotton nut shells carbon (CTNSCs) was used as adsorbent. The CTNSCs effectively removed fluoride from water [66]. For defluoridation of water pyrolized Delonix regia (PDPC) and was used as adsorbent. The maximum removal of 97% was obtained in optimum conditions. Freundlich isotherm indicated multilayer adsorption which had maximum adsorption capacities of 33.4 mg/g and 107.15 mg/g at 303K and 333K respectively. PDPC mostly removed high fluoride in acidic condition and hence used for defluoridation of polluted water and industrial water of lower pH [67]. Author used activated Dolichos Lablab carbon (NDLC) for defluoridation of drinking water obtained by pyrolysis of aerial parts of dolichos lablab (Fabaceae) in electric furnace at 600^0C .The NDLC removed 83.6% of fluoride from 5 ppm initial fluoride water in the first cycle and could be used in five cycles to bring down the drinking water as per WHO standards with an adsorbent dose of 3g/l for 30 minutes of contact time. The NDLC was used to purify field water of 15 Panchayats from Krishna district of Andhra Pradesh (India) having fluoride concentration from 1.4 to 4 ppm and reduced them below 1.5 mg/l for drinking purpose [68]. Metal embedded bicarbon technology for defluoridation of water in the down-flow column was used. The aluminum metal embedded biocarbon (AMEBC) was synthesized using analytical grade aluminum metal powder and activated biocarbon derived from Tridax procumbens (Asteraceae).The maximum removal of 98% with 2.0 g dosage of adsorbent at 27 ± 2^0C was achieved in 180 minutes at pH range of 3.5-4.0 for 20 mg/l of fluoridated water. The fluoride removal mechanism involved ion-exchange process [69].New starch based adsorbent for defluoridation was synthesized with impregnation of cerium. Adsorbent Surface area was 685 cm^2/g. Various parameters were checked for removal of fluoride. The highest defluoridation capacity of CeDC was 52 mg/g at a pH of 8.07.Adsorption kinetics was studied by applying various isotherms. The Langmuir adsorption capacity (q_m) was found to be 209 mg/g with a high R_L value of 0.699 [70].

Fluoride removal by Miscellaneous

Batch and column experiments were conducted using granular red mud as adsorbent. Highest defluoridation capacity was observed at pH 4.7 for batch studies. Continuous experiments were performed for different bed height and flow rate. As flow rate is increased breakthrough capacity decreased. Experimental results were used for Thomas model. Column was regenerated using NaOH [71].

Eggshell powder was used as adsorbent for defluoridation. Batch experiments were carried out for different parameters. At pH 6, removal efficiency was maximum and the process was pH dependant. Langmuir isotherm was found just right for the process. Process obeys pseudo-second-order model. Process showed nature of reaction was chemisorption. Applicability of adsorbent was tested for

water collected from pretentious areas [72].

Lignite (L) and restructured surface of lignite (RSL) using a biomaterial called Cuminum cyminum was used as biosorbents for the removal of fluoride. The RSL has BET surface area 3.12 times greater than lignite and the carbon content was increased by 13%. The fluoride removal capacity of RLA and L adsorbents was 15.8 mg/g and 13.8 mg/g at pH 7.93 ± 0.03 respectively. The effect of co-anions on removal efficiency was found in the order of HCO_3 $=>SO_4^{2-}>PO_4^{3-}>NO_3^->Cl^-$ .The regeneration was carried out by 0.01M NaOH and 57% and 60% fluoride was removed by lignite (L) and RSL even after the fifth cycle of regeneration [73]. Aloe (Aloe barbadensis Miller) along with calcium chloride precipitation was done and used for adsorption. The optimum fluoride removal of 88% was achieved at pH 7.4 with 40 g of aloe vera and g of calcium chloride [74].Potential of Cissus Quadrangularis (CQ) powder for fluoride removal was tested. The fluoride removal of 90% was obtained at 10 mg/50ml dosage of CQ adsorbent for 60 minutes of contact time and 120 rpm shaking speed. The optimal pH for maximum fluoride removal was 7.0 .The presences of phosphate ions showed a highly negative effect for the adsorbent that reduced the defluoridation from 89% to 7%, while the carbonate, sulphate, chloride and nitrate showed little negative effect on adsorption [75].

CONCLUSION

This paper reviews defluoridation by using different biosorbents only. There are various technologies available for removal of fluoride but because of ease of operation and low cost adsorption is considered better. Fluoride removal depends on various factors like pH, temperature, total dissolved solids, and hardness. From the review of biosorbents we can conclude that the fluoride removal process is pH dependent .Commercial adsorbents are costly, so an alternative solution is biosorbents which are cheap and ecological can be used for removal of fluoride depending on the local situations. The local materials showed greater potential to remove fluoride but its having its own advantages and disadvantages also. Few biosorbents have been summarized in table 1.

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