

FLUORIDE REMOVAL BY INDUSTRIAL, AGRICULTURAL AND BIOMASS WASTES AS ADSORBENTS: REVIEW

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ABSTRACT

Fluoride and fluorosis issues are common in a few nations including India. Fluorosis is pandemic in more than 20 states of India. The fluoride comes into ground water by various ways, for example, weathering of rocks, industrial effluents and geochemical reactions. Alternate wellsprings of fluoride come to people in the form of air, foods, cosmetics, and so on. The traces of fluoride in ground water is beneficial for strengthening the dental enamel. Fluoride in overabundance amount higher than 1.5 mg/l causes dental and skeletal fluorosis other than infertility, kidney harm and affects nervous systems as well. The fluoride removal from drinking water and wastewater has been successful by different techniques, for example, coagulation and precipitation, adsorption, ion-exchange, membrane separation, dialysis, electro-dialysis, electrocoagulation and so on. Adsorption process for defluoridation has favoured for the most part in developing countries as it is techno-economical viable method, environmental friendly and straightforwardness in operation. The various adsorbents including activated carbon, activated alumina, metal oxides-hydroxides, bone chars and agricultural and industrial wastes were attempting to keep up the standard limit of fluoride concentration in drinking water by adsorption. Usage of plant materials and agricultural wastes as adsorbents are most adopted in developing country like India in light of the fact that they are low cost materials, available in abundance, biodegradable and natural existence. The industrial by-products are additionally needed to reuse them in advantageous ways for defluoridation as accessible in huge amount and economical. This paper reviews the fluoride uptake capacities of industrial by-products, agricultural wastes and biomass materials from plants, grass, etc. and their modified forms as adsorbents in batch and column performance against different experimental limits.

Keyword: - Defluoridation, Adsorption, Waste, Langmuir, Kinetic, Regeneration.

1. INTRODUCTION

The major source of fluoride to a human being is drinking water. The high level of fluoride (> 1.5 mg/l) in water is responsible for dental and skeletal fluorosis besides growth retardation. Many developing countries have been facing severe problems of fluorosis such as that of India. India and China have a severe fluoride problem as per World Health Organization (WHO) [1]. More than 66 million people in India is suffering from fluorosis. The problems are more serious in the states like Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujrat, Uttar Pradesh, Tamil Nadu, Karnataka and Maharashtra [2-3]. Defluoridation of water was done by several methods such as coagulation and precipitation, membrane separation, ion exchange and electrolytic deposition, but found expensive and non-suitable for developing countries [4-5]. Adsorption is a low cost technique used for effective removal of fluoride from drinking water through local adsorbent materials. The biomass from plants, agricultural wastes and industrial by-products can be used for efficient fluoride uptake as well as solving their disposal problem. These low cost materials are helpful in replacing the expensive commercial adsorbent like activated carbon that has again problem in regeneration. Agricultural waste (Biomaterials), plant materials and industrial waste are available in huge amount, biodegradable or non-biodegradable in nature are inexpensive and environmentally friendly disposable. The present study deals with the use of agricultural and industrial wastes besides plant materials as adsorbents for

defluoridation of water effectively under optimal conditions. The future adaptability and techno-economical viability were also checked by their field performance in fixed bed column.

2. INDUSTRIAL WASTE ADSORBENTS

The industrial wastes produced from various production lines and assets have been utilized as adsorbent and modified with some chemical and thermal treatments for defluoridation of drinking and wastewater.

2.1 Alum Sludge

Sujana *et al.* (1998) has explored defluoridation limit of alum sludge, which is a waste item created during the manufacturing procedure of alum from bauxite by the addition of sulphuric acid and for the most part comprises of oxides of aluminum furthermore, titanium with little measures of undecomposed silicates. The fluoride adsorption capacity of alum sludge was found to be 5.35 mg g^{-1} and the maximum fluoride adsorption occurs at pH 5.5 to 6.5 [6].

Nigussie *et al.* (2007) studied the fluoride removal by using a sludge produced during the manufacturing of aluminium sulphate (alum) from kaolin by sulphuric acid process. About 85% removal was achieved within 1 h at an optimal dose of 16 g/L for initial fluoride concentration of 10 mg/l. At pH 3 to 8, fluoride adsorption was constant but decreased above pH 10. The adsorption followed second-order kinetics and Dubinin - Radushkevich (D-R) is another model which has been fitted well to the adsorption capacity of 332.5 mg/g of the adsorbent. The adsorbent fluoride evacuation proficiency is influenced essentially with bicarbonate ion concentrations furthermore; practically had zero impact by different anions, for example, phosphates, chlorides, sulfates and nitrates [7].

2.2 Red Mud

Red mud is waste generated by the aluminium industry during the alkaline treatment of bauxite ore in the Bayer process. Red mud is highly alkaline in nature. Utilization of industrial waste like red mud for defluoridation will greatly reduce its volume on the land disposal problem, adulteration of soil and ground water and relief of land for alternative uses.

Cengeloglu *et al.* (2002) have studied defluoridation by using red mud as such and acid treated red mud by 5.5 M HCl for drinking purpose. The maximum fluoride removal was obtained at pH 5.5 and the time required to attain equilibrium was 2hr. The most extreme fluoride adsorption limits were observed to be 3.12 and 6.29 mg/g respectively [8].

Tor *et al.* (2009) has researched the fluoride evacuation limit of granular red mud in batch and column studies. The most extreme fluoride adsorption in batch study was 0.644 mg/g for initial fluoride concentration of 5 mg/L was obtained at pH 4.7 and equilibrium was attained in 6h while the column studied showed a more adsorption capacity of 2.05 mg F/l for a flow rate of 2 ml/min. The recovery of column adsorbent was accomplished by pumping 0.2M of NaOH solution through the adsorbent medium [9].

Wei *et al.* (2009) has used modified red mud with AlCl_3 (MRMA) and further modified by heat activated red mud (MRMAH) as adsorbent for removal of fluoride from water. The adsorption capacities of MRMA and MRMAH were 68.07 and 91.28 mg/g, separately which were much higher as compared to red mud (13.46 mg/g). The highest fluoride adsorption was achieved at pH 7-8. The Langmuir isotherm was best fitted for isotherm study [10].

Lv *et al.* (2013) have investigated zirconium hydroxide modified red mud porous material for removal of fluoride from aqueous solutions. The maximum adsorption was achieved at pH 3 and the equilibrium was reached within 1hr. The adsorption capacity of Zr-modified RMPM was 0.6 mg/g. The fluoride sorption procedure was all around fitted to the pseudo-second-order rate kinetics and pore diffusion models. The regeneration of adsorbent was achieved by using NaOH solution at pH 12 with over 90% of recovery ratio [11].

Soni *et al.* (2013) have studied red mud for defluoridation of water collected from Sitapura Industrial area, Jaipur (Rajasthan). The maximum fluoride adsorption was achieved at pH 5.5 and equilibrium was reached in 2 hrs. The removal of fluoride was mostly depended on chemical nature and specific interaction with metal oxide surfaces [12].

2.3 Spent Bleaching Earth

Mahramanlioglu *et al.* (2002) have studied the fluoride adsorption potential of acid treated Spent Bleach Earth (SBE) for drinking water. SBE is a solid waste generated from the edible oil processing unit, which mainly contains residual oil not removed by filter pressing and montmorillonite clay. The maximum fluoride adsorption was achieved at pH 3.5 and its fluoride adsorption capacity was found to be 7.75 mg/g. This low cost adsorbent is mostly used for water and wastewater treatment which ultimately minimizes the industrial waste disposal problem and can be used effectively and efficiently [13].

2.4 Fly ash

Chaturvedy *et al.* (1990) have conveyed that the fly ash (a waste from a thermal power plant) had a maximum Langmuir adsorption capacity of 20 mg/g at pH 6.5. The fluoride adsorption capacity of fly ash depends on pH, where the fluoride adsorption increased from 79 % to 94 % when pH of fluoride solution of 10 mg/l increased from 2.0 to 6.5. Further increased in pH up to 9.5 resulted in decreased fluoride adsorption capacity [14].

Nemade *et al.* (2002) have studied the batch adsorption capacity of fly ash and observed that fluoride adsorption decreased continuously between pH 2 to 12. The pH effect on fluoride removal in both studies may be due to the different composition of fly ash and an experimental conditions used [15].

Piekos and Paslawskar (1999) used 450 g of alkaline fly ash in packed column of size having length of 45 mm x 400mm for adequately expulsion fluoride from fluid arrangement having a concentration of 1, 5, 10, 20, 50 and 100 mg F/L at the flow rate of ≤ 2 ml/hr. The time required to bring down effluent fluoride concentration to 0 mg/l was 120 to 168 hours. The fluoride adsorption took place by chemical binding of fluoride on $\text{Ca}(\text{OH})_2$ and physical adsorption onto the residual carbon particles in the fly ash [16].

Singh *et al.* (2000) have studied the defluoridation of groundwater of Agra city with alum treated fly ash (ATF). The fly ash was soaked in 1% NaOH, then dried and treated with 2% $\text{Al}_2(\text{SO}_4)_3$ solution for half an hour and the white precipitate of $\text{Al}(\text{OH})_3$, thus obtained was dissolved in 1:1 HCl to adjust pH at 3.5. The fluoride solution having a concentration ranging from 0.5 to 4.5 mg/l was treated with 3.5 mg/100ml dosage of ATF resulted to remove 70 to 62.9 % of fluoride [17].

Xue *et al.* (2009) studied the fly ash filter materials A and S for removal of high fluoride from drinking water. The Freundlich adsorption capacity of A and S were 1.22 and 1.01 mg/g respectively. The quantity of A and S adsorbents to reduced concentration of fluoride from 4 mg/l to 1 mg/l for 1 m³ solution was 2.46 and 2.97 Kg respectively. From the column study it was observed that the high pH solution resulted into low turbidity of filtered water, efficiency of defluoridation rises with the upturn of fluoride concentration of influent and both the quantity of sifted water and effectiveness of the defluoridation increases with expansion of temperature [18].

Geethamani *et al.* (2014) utilized calcium hydroxide treated fly ash (CFA) for fluoride removal in batch study. More than 80% removal was achieved for fluoride solution of 10 mg/l at an equilibrium contact time of 120 minutes and 3 g/L of CFA dosage. The maximum fluoride removal took place at pH 7. The Langmuir monolayer adsorption capacity was 10.86 mg/g and pseudo-second-ordered kinetic was best fitted showing the chemisorption process. Similarly the process was endothermic in nature since removal efficiency increases with an increase in temperature [19].

2.5 Bottom ash

Ramesh *et al.* (2012) have investigated fluoride removal capacity of bottom ash in batch and column mode. The fluoride removal of 73.5% was achieved at 70 mg/100ml bottom ash dosage at the optimum contact time of 105 minutes. The maximum removal efficiency of 83.2% was observed at pH 6. The maximum monolayer adsorption capacity of 16.26 mg/g was obtained at 303 K. The column study was carried out by BDST model. The fluoride ion uptake increases with an increase in bed height was due to an increase in contact time. According to the Thomas model, the maximum adsorption capacity was found 0.3714 mg/g with rate constant of 0.0619 l/min.mg at 10 cm bed depth. From Yoon Nelson model it was observed that the 50 % of adsorbate time 2140 minutes run at the rate constant of 0.003 l/min [20].

2.6 Cenospheres

Xu *et al.* (2012) have studied fluoride removal in a fixed bed column by magnesia-loaded fly ash cenospheres (MLC) prepared by wet impregnation of fly ash cenospheres with magnesium chloride solution. From the Thomas model, the maximum fluoride adsorption capacity of 5.884 mg/g was achieved at a flow rate of 5 ml/min with 1.570 minutes of EBCT and found to be constant. Column adsorption was reversible and the regeneration operation was refined by pumping 0.2M of NaOH through the stacked MLC column [21].

2.7 Rice husk ash

Ganvir *et al.* (2011) have studied the removal of fluoride by using aluminium hydroxide coated rice husk ash. Rice husk ash is obtained by burning rice/paddy husk which is available in large quantity and is a low cost material. The fluoride adsorption capacity of adsorbent was 15.08 mg/g in batch and 9.5 mg/g in column study. The maximum fluoride removal was achieved at pH 5.0±0.5 and it showed that adsorption was not dependent on initial fluoride concentration. The adsorption capacity of materials used in filter was found to be 9 mg/g. A filter made of 750 g coated RHA was treated with 1250 L of 5 mg/l of fluoride spiked tap water and it was brought down to 1.5 mg/l. Freundlich isotherm with multilayer adsorption and pseudo second order kinetic were best fitted as per the study [22].

Mondal *et al.* (2012) have investigated the capacity of activated rice husk ash (ARHA) by washing and drying rice husk ash from the rice mill at 100°C for 8 hours in an electric oven, then crushed and ground it to obtain 250 µm sizes for fluoride removal through batch technique. The Langmuir adsorption capacity of ARHA was 0.402 mg/g and took place after the pseudo-second-order kinetics. The equilibrium was attained in 100 minutes and fluoride removal in percentage was found to be 88.30% [23].

2.8 Aluminum Treated Bagasse Fly ash

Gupta *et al.* (2014) has scrutinized aluminum treated bagasse fly ash (ABF) for defluoridation of drinking water having initial fluoride concentration of 1-10 mg/l at sorbent dose range 1-20g/l, pH 6.0, temperature 25°C, 150 rpm for 5hr and found that 59 % of removal was achieved for fluoride concentration of 10 mg/l for adsorbent dosage of 10g/L [24].

2.9 Maize ash

Jadhav *et al.* (2014) used maize husk fly ash as an adsorbent for eliminating fluoride from water in batch mode. The greatest fluoride evacuation was seen to be 86% at ideal condition having an agitation rate of 250 RPM, pH value of 2, and 2.0 g/50 ml of dosage and equilibrium time of 120 minutes. The Redlich-Peterson isotherm model ($R > 0.981$) was best fitted than Langmuir, Freundlich and Temkin model [25].

2.10 Tea ash

Mondal *et al.* (2012) studied defluoridation of water by using activated tea ash (AcTAP) generated by tea residue from tea stall of local market with repeatedly washing with boiling water, sun dried and blazed in mute heater at 500°C for 30 minutes. The Langmuir adsorption capacity of AcTAP was 8.55 mg/g and obeyed pseudo-second-order kinetics. The perfect pH for most extreme removal of fluoride is 6.0 and equilibrium time is 180 minutes [26].

Cai *et al.* (2015) used Al/Fe oxides loaded tea waste for removal of fluoride from drinking water. The bio-adsorbent with Tea-Al and Tea-Al-Fe were able to reduced the fluoride below 1.5 mg/l with an optimum pH range of 4.0 to 8.0 and contact time of 2 hours. The leaching of Al and Fe were within permissible limit when water was treated at a pH range of 5 to 10. The defluoridation capacity of original Tea, Tea-Fe, Tea-Al and Tea-Al-Fe were 3.83, 10.47, 13.79 and 18.52 mg/g respectively. The experimental data fitted well with a Langmuir isotherm model for metal loaded tea waste, whereas it followed Freundlich isotherm model for original tea waste. The adsorption process was followed by Lagergren pseudo-second-order kinetic model. The fluoride ions were adhered by positively charge surface sites (bi-metallic cations) in acidic phase and involved ligand exchange at pH>6 [27].

2.11 Waste carbon slurry

Gupta *et al.* (2007) have investigated waste carbon slurry for removal of fluoride. The waste carbon slurry was obtained from fuel oil based generators of a fertilizer industry. Maximum fluoride adsorption capacity of 4.861 mg/g was observed at 15 mg/L initial fluoride concentration using 1.0g/l adsorbent dose. The optimum contact time and pH for maximum fluoride uptake was 1hr and 7.58 respectively. Langmuir maximum adsorption capacity was found to be 4.3 -5.5 mg/g at different temperatures. The pseudo-second-order was best fitted as per kinetic analysis. The breakthrough capacity of the column was calculated as 4.155 mg/g at a flow rate of 1.5ml/min. Desorption was achieved under alkaline condition (pH 11.6) from exhausted carbon slurry [28].

2.12 Coal mining waste

Inhale *et al.* (2005) investigated the capacity of adsorbent produced from coal mining waste for removal of fluoride from aqueous solution. The Langmuir most extreme adsorption limit of the adsorbent was observed as 15.67 mg/g. The optimum pH for fluoride adsorption was found to be 3.5 [29].

Kumari *et al.* (2013) have used shale (coal mine waste) as adsorbent in the form of native shell (NS) and heat activated shale (HAS) at different temperature of 350°C, 450°C and 550°C for removal of fluoride from water. The maximum fluoride removal of 88% was obtained by HAS550 for 10 mg/l of initial fluoride concentration at pH 3 for contact time of 24 hours. The experimental results of adsorption were best fitted to Freundlich isotherm model and pseudo-second-order kinetic model. The Langmuir maximum adsorption capacity was found to be 0.358 mg/g [30].

2.13 Waste mud

Kemer *et al.* (2009) have assessed the fluoride adsorption uptake limit of waste mud acquired from the Cu-Zn mine industry in Cayeli, Rize/Turkey (Inmet Mine Corp. Canada). Three different forms of waste mud, original waste mud (o-WM), acid-activated (a-WM) and precipitated waste mud (p-WM) were checked for fluoride removal potential from water. The adsorbent, p-WM has maximum Langmuir fluoride adsorption capacity of 27.2 mg/g and followed the pseudo-second-ordered kinetics. The fluoride equilibrium was reached in 60 minutes at room temperature indicated that the reaction rate is very fast. The p-WM can be used for five cycles without regeneration [31].

2.14 Basic oxygen furnace slag

Islam *et al.* (2011) examined the capacity of blast furnace slag generated from local iron and steel industry for removal of fluoride from water. The basic oxygen furnace slag (BOFS) mainly contains 46.5% of CaO, 16.7% of iron oxide and 13.8% of SiO₂ by weight along with other constituents. Thermal activation of the BOFS by heating at 1000 °C for 24 hours increased the porosity and surface area leading to an increase in fluoride adsorption. The removal percentage of fluoride by thermally activated BOFS (TABOFS) (93%) was more than basic BOFS (70%) for initial fluoride concentration of 10 mg/l for 0.5g/100mL of dosage. The kinetic of reaction is very fast and equilibrium reached within 35 minutes. The maximum Langmuir adsorption capacity was 8.07 mg/g and followed the pseudo-first order kinetic model. The optimum pH for maximum fluoride removal was ranging from 6 to 10. A thermodynamic study showed that it is an endothermic process for fluoride adsorption. The fluoride removal by BOFS was governed by chemisorption, precipitation and surface chemical reaction with CaO present in the thermally activated BOF slag. Vicinity of different anions decreased F adsorption in the order, PO₄³⁻ > HCO₃⁻ > CO₃²⁻ > SO₄²⁻ > Cl⁻ > NO₃⁻ [32].

2.15 Spent catalyst

Lai and Liu (1996) used spent catalyst (a by-product of petrochemical industry) for fluoride removal from aqueous media. Spent catalyst mainly consists of porous silica and alumina which were responsible for the removal of fluoride. The fluoride adsorption decreased with an increased in pH. The maximum adsorption capacity was 28 mg/g at optimum pH of 4 and temperature of 50°C. The adsorption reaction of fluoride was endothermic in nature and reaction rate increase with temperature [33].

Tsai and Lui (1999) have investigated iron coated spent catalyst by coating with 0.1 and 0.5 M Fe (NO₃)₃ for removal of fluoride from aqueous solution. The maximum Langmuir adsorption capacity of 0.1 M Fe (NO₃)₃ coated spent catalyst and 0.5 M Fe (NO₃)₃ coated spent catalyst were 7.2 mg/g and 20.7 mg/g respectively. The optimum pH for fluoride removal ranged from 5.5-6.0 [34].

2.16 Bauxite

Das *et al.* (2005) used thermally activated titanium rich bauxite (TRB) for adsorption removal of excess fluoride from drinking water. Thermal activation at moderate temperatures (300–450°C) was responsible for increasing the adsorption capacity of TRB. The optimum pH range was 5.5-6.5 at which maximum uptake took place. The Langmuir maximum adsorption capacity of 3.8 mg/g was obtained at pH 5.5-6.5 with an adsorption dosage of 1 g/L and 10mg/l of fluoride solution. Adsorption reaction obeyed first order rate expression and both Langmuir and Freundlich isotherm fitted well. The presence of co-anions did not affect the defluoridation capacity. Nearly complete desorption of adsorbed fluoride from loading bauxite was achieved by treating with aqueous solutions of pH 11.1 (NaOH 0.015 Mol/dm³) [35].

Lavecchia *et al.* (2012) have studied high alumina (81.5%) content bauxite for the removal of fluoride from the contaminated water. The percentage fluoride removal of bauxite in preliminary test was 38.5%. A maximum fluoride uptake of 3.125 mg/g was obtained and Freundlich equation was best fitted with R² value of 0.986 [36].

Chaudhari and Sasane (2014) used bauxite for defluoridation of water. The optimum adsorbent dose was observed to be 1.8 g/50ml and equilibrium was reached in 90 minutes with the optimum pH of 6.0. The fluoride removal of 94% was obtained at optimum conditions and the experimental data fitted well with Langmuir isotherm model [37].

2.18 Hydrated cement, Brick powder and Marble wastes

Bibi *et al.* (2015) used hydrated cement, brick powder and marble powder for defluoridation and arsenic removal from water. The removal percentage by adsorbent were found in the order of Hydrated cement (HC) > Brick powder (BP) > Marble powder (MP). Hydrated cement showed highest percentage removal of 97% and 75% for arsenic and fluoride at neutral pH from an aqueous solution of 1000 mg/l of arsenic and 30 mg/l of fluoride at pH 7 and 8 with 60 min. of contact time and 30 g/l of dose. The adsorption followed the Langmuir isotherm model. The Langmuir maximum adsorption capacity of HC, BP and MP were 1.72, 0.84 and 0.18 mg/g at pH of 7, 8 and 7 respectively. The presence of co-anions had no significant effect on the removal efficiency of arsenic and fluoride. The field application of hydrated cement was carried out successfully [38].

2.19 Electrocoagulation sludge

Yilmaz *et al.* (2015) used calcined electrocoagulation sludge (CES) as adsorbent for defluoridation of water. The maximum adsorption capacity of CES was 44.248 mg/g at 293K. The CES was able to removed 99.99% of fluoride at optimum conditions (pH = 6, contact time = 2 h and dose = 4g/l) from fluoride solution of 2.5 mg/l. The adsorption process obeyed Freundlich isotherm and pseudo-second-order kinetic model. Defluoridation reaction was spontaneous and exothermic in nature. The leaching of boron solution was found within permissible limit at pH of 6.0 and low adsorbent dose [39].

2.20 Water treatment residual sludge

Zhang *et al.* (2015) used water treatment residual sludge (WTRS) and cerium modified water treatment residual sludge (Ce-WTRS) for removal of fluoride from aqueous solution. The optimum pH range was found to be between 3 to 9. The Langmuir maximum adsorption capacity of Ce-WTRS was 15.45 mg/g and 2 times greater than WTRS. The experimental data followed Langmuir and Temkin isotherm models as well as pseudo-second-order kinetic and intra-particle diffusion model. The adsorption response for Ce-WTRS was spontaneous and endothermic whereas reaction for WTRS was exothermic in nature [40].

3. AGRICULTURAL WASTE ADSORBENTS

Agricultural waste materials are found to be abundant in nature, at low-cost, economically viable and fruitful wastes with unique characteristics for treatment of water and wastewater.

Sivabalan *et al.* (2003) studied defluoridation of water by activated carbon cashewnut sheath (CSC) and commercial activated carbon (CAC) impregnated with 2% of aluminium sulphate solution in batch and column mode. The maximum fluoride removal percentage of CSC was 87.6% for an adsorbent dosage of 8 g/L at optimum pH of 6.9 with a contact time of 16 hr, whereas CAC could remove 56% of fluoride with adsorbent dosage of 14g/L at pH 6.9 and contact time of 6h. The Freundlich adsorption equation was best fitted for CSC and CAC [41].

Parmar *et al.* (2006) have studied the defluoridation capacity of untreated and aluminium chloride and calcium chloride treated powdered corn cob as an adsorbent for removal of fluoride from drinking water. Calcium treated corn cob powder was more efficient than aluminium treated corn cob powder. The optimum pH for maximum fluoride uptake varied in the range of 5.0-6.5. The breakthrough fluoride capacity was found to be 18.9 mg/g and 15.12 mg/g for Ca-ccp and Al-ccp respectively at pH 6.5 for initial fluoride concentration of 12.60 mg/l. The contact time for maximum fluoride uptake took place between 90 to 120 minutes. Freundlich isotherm was best fitted with exothermic adsorption process since adsorption decreased with an increase in temperature. The fluoride containing corn cob powder can be dumped as a solid waste material in the pits as the raw materials employed in preparation of the substrate are cheap and easily available. Leaching of alumina and calcium did not occur and exhausted adsorbent was dumped as solid waste in the pits [42].

Sathish *et al.* (2007) has investigated the potential of zirconium impregnated coconut (ZICSC) shell carbon for fluoride removal from water. ZICSC could remove more than 90 % of fluoride in the pH range of 2-9. The rate of adsorption was high and 91% of adsorption took place within 10 minutes of contact time for an initial fluoride concentration of 10 mg/l. The maximum fluoride adsorption was 7.51 mg/g at pH 6.0. The pseudo-second order chemical reaction kinetics was best fitted to experimental data of ZICSC [43].

Janardhana *et al.* (2007) have studied fluoride removal capacity zirconium impregnated groundnut shell, coconut shell and coconut fiber ,activated charcoal from water in continuous down flow column at the constant rate of 0.6-0.7 L/h. The zirconium ion impregnated coconut fiber, charcoal (ZICFC) showed maximum fluoride uptake after that the groundnut shell and coconut shell carbon showed it effect in decreasing order. ZICFC was treated in 21 litre of (8.0 mg F⁻ ion/L) test solution and 6 litre of (2.47 mg F⁻ ion/L) to bring down the fluoride concentration less than that of 1.5 mg/L. The optimum condition for the batch study of ZICFC was achieved by maintaining the pH of 4 on continuous stirring for 6 hours and 20 g/L adsorbent dosage. Regeneration of the ZICFC was accomplished by elution with 0.02 M of NaOH solution [44].

Daifullah *et al.* (2007) have investigated the potential of KMnO₄ modified activated carbon derived from steam pyrolysis of rice straw (RS₂/KMNO₄) as adsorbent for fluoride removal from water. The Langmuir-Freundlich adsorption capacity of fluoride in distilled water and phosphoric acid were 15.5 mg/g and 23.3 mg/g respectively. The optimal condition of the experiment was accomplished by maintaining the pH at 2 with contact time of 3 hours, 25°C temperature and 20 ppm of initial fluoride concentration. The kinetic study followed the pseudo-second-order model. The natural organic matter (NOM) decreased the fluoride adsorption from 15.5 mg/g to 5.7 mg/g. The adsorption capacity for fluoride decreased from 100% to 91% in case of sulfate and to 94 % in case of bromide but chloride had no significant effect on fluoride adsorption [45].

Satish *et al.* (2008) have investigated the applicability of zirconium impregnated coconut fiber carbon (ZICFC) as adsorbent for defluoridation of water. The maximum fluoride adsorption was obtained at pH of 4. The Langmuir maximum adsorption capacity of ZICFC was 40.016 mg/g at pH 4, with 6 hours agitating time and 20g/L of ZICFC adsorbent dosage as the optimum condition. The kinetic studied exposed that the pseudo-second order chemical reaction was best fitted with experimental data. Combinations of chemisorption and physisorption processes with intraparticle diffusion were responsible for the high defluoridation capacity of ZICFC [46].

Alagumuthu *et al.* (2010) has studied the potential of zirconium impregnated cashew nut shell carbon (ZICNSC) for defluoridation of water. The ZICNSC exhibited 80.33% of fluoride removal as compared to 72.67% removal of cashew nut shell carbon (CNSC) in contact time of 180 minutes at pH 7 and particle size of 53µm at room

temperature. The Langmuir adsorption capacity of 1.83 mg/g was obtained and experimental data was best fitted with pseudo-second-order equation. The maximum percentage removal of fluoride by the samples was observed at pH 3 with the pH_{zpc} for CNSC and ZICNSC been reported as 7.6 and 4.2. The presence of carbonate ions could reduce the fluoride removal from 80.33% to 60.23% ,while other co-ions showed no remarkable influenced on the removal. The exclusion of fluoride by ZICNSC was mainly due to physical forces and strong co-ordination between fluoride ions and zirconium ions adsorbed on CNSC. The used adsorbents could be regenerated by 96.2% of 2.5% Sodium hydroxide in 180 min [47].

Alagumuthu *et al.* (2010) have investigated fluoride removal capacity of zirconium impregnated groundnut shell carbon (ZIGNSC) from water. The fluoride evacuations of ZIGNSC and ground nut shell carbon (GNSC) were 84% and 63.67% respectively. The optimum contact time for maximum removal was 180 minutes for initial fluoride concentration of 3 mg/l at dosage of 2.0 mg. The adsorption capacity of ZIGNSC was 2.32 and 2.50 mg/g at temperature of 303K and 333K respectively. The kinetic study followed the pseudo-second-order equation. The bicarbonate ions was responsible for decrease of fluoride removal from 84% to 74.6% [48].

Kai *et al.* (2011) reported the capability of zirconium loaded garlic peel (Zr-GP) as adsorbent for removal of fluoride from water. The Langmuir maximum adsorption capacity of Zr-GP at equilibrium pH 2 and 6 were 1.10 and 0.89 ml (Fluoride)/kg respectively. The optimum pH for maximum fluoride adsorption was 2-4. The fluoride removal at pH 2 was 97.2% ,whereas at pH 7 it was reduced to 46.7%. The kinetic study revealed that experimental data was well fitted by pseudo-second-order rate equation and the corresponding adsorption rate constant was calculated to be 3.25×10^{-3} g/ (mg-min). The presence of phosphate could be able to decrease the adsorption of fluoride from 97.2% to 77.6% at pH 3 [49].

Joshi *et al.* (2012) have studied fluoride removal capability of zirconium impregnated lapsi seed stone activated carbon (ZILSSSAC). The optimal condition of fluoride removal was achieved at pH 3-4, contact time of 180 minutes and adsorbent dosage of 2.0 g/L for initial fluoride concentration of 10 mg/l. At pH 3, the maximum uptake of fluoride was observed to be 3.25 mg/g and at neutral condition the adsorption capacity was 1.6 mg/g [50].

Montoya *et al.* (2012) have observed that the carbon obtained from pecan nut shells modified with a calcium solution extracted from egg shells (CMPNS) were more effective for fluoride removal than nut shell precursor as such. Taguchi method was implemented to optimize the synthesis condition for best CMPNS composition. The optimum condition for fluoride removal was achieved by maintaining 150 rpm agitation, with pH 7, adsorbent dosage of 8.0g/L and fluoride concentration of 20 mg/l. The fluoride removal of CMPNS-4 was to be as 83-84% with a S/N ratio of 38.5 as per study. The Langmuir adsorption capacity of CMPNS varied in the range of 0.81-2.51 mg/l with correlation coefficient (R^2) varied from 0.90 to 0.96 for synthetic water. The calcium chemical species on the carbon surface played major role for fluoride removal than the carbon textural parameters. In addition to that hydrogencarbonate was observed to be the primary contender for the active sites of CMPNS during defluoridation. The CMPNS was also tested for ground water having fluoride concentration of 14.10 mg/l but the removal percentage was nearly 20% due to the complex nature of groundwater [51].

Rajan *et al.* (2013) have studied the fluoride removal capacity of zirconium impregnated walnut shell carbon (ZIWSC). The fluoride removal of ZIWSC and WSC were 94% and 81% at pH 3 respectively. The Langmuir maximum adsorption capacity of ZIWSC was 3.19 mg/g at 303K for optimum condition of 180 minutes of contact time size < 53 μ m and dosage of 1.5 gm/100 ml. The pseudo-second order was best fitted as per kinetic study. The thermodynamics study revealed that the process of adsorption was endothermic and bicarbonate ions reduced the removal efficiency by 85.67% to 54.94% [52].

Ardekani *et al.* (2013) has investigated the capability of bagasse, modified bagasse with 1 M of NaHCO₃ and chitosan for removal of fluoride from water. The modified bagasse could remove more than 90% of fluoride at optimum condition of pH 7, with a contact time of 60 minutes, adsorbent dosage of 2 g/L and initial fluoride concentration of 5 mg/L. Langmuir adsorption capacity of modified bagasse, bagasse and chitosan were 9.033, 2.034 and 1.463 mg/g respectively [53].

Yadav *et al.* (2013) have investigated the feasibility of activated bagasse carbon (ABC), sawdust raw (SDR) and wheat straw raw (WSR) for water defluoridation and compared them with commercial activated carbon (CAC). The

percentile fluoride uptake by CAC, ABC, SDR and WSR were 57.6, 56.4, 49.8 and 40.2% respectively from an aqueous solution of 5 mg/L fluoride at pH 6.0, with the contact period of 60 minutes and a dose of 4 g/L. The experimental data fitted well with Freundlich isotherm. The pseudo-second-order reaction was suitable as per kinetic study [54].

4. BIOMASS MATERIALS

4.1 Peels

Chakrapani *et al.* (2010) have used activated carbons prepared from the peels of *Citrus documana* (NCDC), *Citrus medica* (NCMC) and *Citrus aurantifolia* fruits (NCAC). The optimum contact time of NCDC, NCMC and NCAC were 30, 35 and 35 minutes for maximum removal of 5 mg/l of fluoride water sample at neutral pH, 120 rpm shaking speed, 1g/100ml adsorbents dose at $25\pm 2^\circ\text{C}$. NCDC exhibited a higher adsorption capacity followed by NCMC and NCAC. The regression coefficients of NCDC, NCMC and NCAC for pseudo-second-order kinetic model were 0.9946, 0.9971 and 0.997 respectively and found higher than pseudo-first-order model. The experimental data were fitted well with pore diffusion and Elovich equations indicating that pore diffusion plays a vital role in controlling the rate of the reaction [55].

Gandhi *et al.* (2012) have studied the adsorption capacity of certain low cost adsorbents like chalk powder, pineapple peel powder, orange peel powder, horse gram seed powder, red soil, ragi seed powder, multhani mati and concrete. The percentage removal of fluoride by low cost adsorbents having 12 mg/l initial fluoride concentration by 1g/100ml dose of adsorbents with 24 hours of contact time was found in the order of chalk powder and pineapple peel powder (86%) > orange peel powder (79%) > horse gram seed powder (75%) > red soil (71) > ragi seed powder (65%) > multhani mati (56%) > concrete (53%). The fluoride removal of 80% by the concrete adsorbent was achieved with 0.6 g dose of 10 mg/l of fluoride bearing sample with 60 minutes of contact time. The Freundlich isotherm model was best fitted to experimental data as compared to Langmuir isotherm model for concrete adsorbent. The coefficient of determination by pseudo first order kinetic model, Elovich model and pseudo second order kinetic model were found to be 0.886, 0.998 and 0.965 for 10mg/l of fluoride solution which indicated that the pseudo second order kinetic was favoured by experimental data [56].

Patil *et al.* (2013) have studied the 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). The fluoride uptake by adsorbents at equilibrium was found to be in the order of MPLP > CCP > TPLP > CLP > PPP > ATBP. The maximum removal of fluoride was obtained at pH 2.0. The ideal time for contact was 1 hour with an adsorbent dose of 10g/l for initial fluoride concentration of 5ppm. ATBP and PPP adsorbent followed the pseudo-first order kinetic model, whereas others followed the pseudo-second-order kinetics. All adsorbents followed Freundlich, Langmuir and Temkin isotherm models. The adsorption reactions by MPLP, CLP, TPLP and CCP were spontaneous and endothermic whereas ATBP and PPP showed that it was non-spontaneous and exothermic adsorption process. MPLP and CCP worked effectively for adsorption since 90% removal was achieved by 8 g/l MPLP and 10g/l CCP doses, but for other adsorbent, even 10g/L adsorbent dose was not enough for 90% removal of fluoride [57].

AashMohammad and Majumder (2014) have investigated the capacity of banana peel, groundnut shell and sweet lemon peel for defluoridation of synthetic wastewater (Industrial wastewater). The banana peel, groundnut shell and sweet lemon peel could remove 93.34, 89.90 and 59.55% of fluoride from aqueous solution of 20mg/L fluoride at pH of 6, 7 and 4 respectively. Contact time for banana peel, sweet lemon peel and groundnut shell were 60.0, 40 and 75.0 minutes respectively at doses 14, 16 and 12 mg/L. The experimental data was best fitted to the Langmuir isotherm model with pseudo-second-order kinetic model. The presence of other ions in the water had minor negative effects [58].

Dwivedi *et al.* (2014) have investigated the defluoridation capacity of *Citrus Limetta* (Mosambi) peel powder in a batch reactor. The experimental data fitted well for pseudo-second-order kinetic model and Freundlich isotherm model ($R^2=0.996$). The maximum Langmuir adsorption capacity of mosambi peel powder was 1.82 mg/g. The fluoride uptake increased from 0.089 mg/g to 1.35 mg/g with an increase in initial fluoride concentration from 1 mg/L to 20 mg/L. The fluoride removal of adsorbent was 82.5% when the initial fluoride concentration of the water

was 5 mg/L. Thus 0.9 mg doses of adsorbent was responsible to bring down the fluoride concentration of 5mg/L to less than 1.5 mg/l as per WHO standard for drinking water [59].

Christina and Viswanathan (2015) prepared immobilized saponified orange peel residue (SOPR) in alginate matrix and then matrix was loaded with 5% of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ where the composite adsorbent was referred as FSOPR and used for removing fluoride from water. The equilibrium adsorption information fitted well with the Langmuir isotherm model and pseudo-second-order kinetic model. The maximum adsorption capacity of FSOPR was 7 mg/g. Defluoridation process took place by electrostatic interaction and ion exchange mechanism. The fluoride uptake was mostly due to attraction of hydroxide and carbonyl groups with fluoride ions. The author used green waste of orange peel for effective removal of fluoride from aqueous solution [60].

Jha *et al.* (2015) used zirconium (IV) loaded carboxylated orange peel (ZCOP) for defluoridation from drinking water. The fluoride removal was achieved over a wide pH range of 3.0-8.0. The maximum removal of 97.2% was attained at pH 7 with 0.7 g/l doses of adsorbent, contact time of 50 min for initial fluoride concentration of 10mg/l. The adsorption data were well described by D-R isotherm model. The Langmuir maximum adsorption capacity was 5.605 mg/g at pH 6.0. The adsorption process followed the pseudo-second-order kinetic model. The adsorption reaction was spontaneous and endothermic in nature. The adsorption was governed by an ion exchange mechanism. The fluoride uptake was interrupted by the presence of phosphate and bicarbonate to some extent but nitrate, sulphate and chloride did not affect the fluoride removal efficiency. The reuse of adsorbent showed the fluoride removal of 83%, even in 8th cycle against 97% in 1st cycle. Desorption of 91% of adsorbent was done by 0.1M NaOH solution [61].

4.2 Seeds

Murugan and Subramanian (2006) have investigated the potential of 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 and defluoridation capacities decreased with an increase in temperature and particle size. The defluoridation followed first order kinetics and Langmuir adsorption isotherm with an adsorption capacity of 6.37 mg/g at 20°C. Desorption was carried out with 0.1N HCL and was 90%. Tamarind seed powder of 25 g encapsulated in single ceramic candle of domestic water filter was treated approximately with 40 liter of water containing fluoride concentration of 5 mg/l. Thus, for the treatment of 10 liter of drinking water per day for a three members of a family having a fluoride concentration of 5 mg/l required 2.75 g of Tamarind seed per day [62].

Subramanian and Ramalakshmi (2010) have studied defluoridation capacity of Pristine, purified and polyaniline coated tamarind seed (TS) from water. The adsorption capacity of 75 μ pristine TS, 150 μ pristine TS and 300 μ pristine TS were found to be 10.6, 1.4 and 4.24 mg/g for 10 mg/L of initial fluoride concentration. 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 75 μ Pristine TS were 10.7 mg/g and 7.48 mg/g, respectively for 10 mg/L of initial fluoride whereas 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 of initial fluoride concentration. Thus 50% Pani treated 75 μ Pristine TS had high potential to remove fluoride from water. The disobeying of the Langmuir isotherm by PriTS75, 50-Pani-PriTS and 90-Pani-PriTS showed that the fluoride uptake by TS adsorbent materials was not a simple monolayer process but could involve a complex mechanism [63].

Veeraputhiran and Alagumuthu (2011) have studied the potential of Phyllanthus emblica (Indian Gooseberry) activated carbon for removal of fluoride from water. The maximum fluoride removal capacity of 82.1% was obtained at neutral pH with 75 minutes of contact time at an adsorbent dosage of 0.75 g and 3 ppm initial fluoride concentration. 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 impacts of other co-anions. The order of interference for fluoride removal was observed in the order of $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$ [64]. Further, Veeraputhiran and Alagumuthu, 2012 have studied the kinetics and thermodynamics of Phyllanthus emblich (powdered seed) activated carbon. The experimental data followed the pseudo-second-order kinetic model with endothermic reaction as per thermodynamic results [65].

Vardhan *et al.* (2011) have studied the defluoridation of water by using physical-chemical process of adsorption and coagulation by using abundantly accessible and minimal effort materials like Rice Husk, seed extracts of Moringa

Oleifera (Drum stick), and chemical like Manganese Sulphate and Manganese Chloride. Rice husk removed 83% of fluoride from 5mg/l of initial fluoride solution at equilibrium time of 180 minutes at 6 g/L doses in the pH range of 2-10. The Langmuir adsorption isotherm fitted well for Rice husk. Moringa Oleifera seed extract, Manganese Sulphate and Manganese Chloride accomplished removal percentage of 92, 94 and 91 of fluoride from a 5mg/l aqueous solution at a dosage of 1000mg/l at an acidic pH of 6.0 [66].

Leal *et al.* (2012) have observed that Guava (*Psidium guaiava*) seeds powder (2 μ m) had adsorption capacity of 116.50 mg/g at 25°C with 5 mg/l of initial fluoride. The maximum removal was found at a pH range of 5-8. The experimental results fitted well with the pseudo-second-order model and Langmuir isotherm [67].

Jain and Gupta (2013) have investigated the fluoride removal capacity of acid treated Guava leaf powder (GL), Neem leaf powder (NL), Neem bark powder (NB), Black berry seed powder (BB), mixed adsorbent with a ratio of 1:1 for GL+BB and NL+NB and acid treated rice husk (RH) carbon from aqueous solution in batch method. The adsorptions kinetic of pseudo-first order model were best fitted to GL, NL, NB, BB and RH whereas a pseudo-second-order was best fitted to mixed adsorbents. All the adsorption obeyed Freundlich and Langmuir isotherm models [68].

Parlikar and Mokashi (2013) have studied the defluoridation efficiency of alkali and acid treated drumstick (*Moringa Oleifera*) seed powder from aqueous solution. The fluoride removal of alkali treated adsorbent was found better than acid treated adsorbent. The optimum dose of 400mg/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 at pH of 8 and contact time of 2 hours and 2.5 hours respectively [69].

Sanchez *et al.* (2013) have studied the removal of fluoride from aqueous solution by mechanically modified guava seeds (MGS) from water in batch mode. The experimental data fitted well for pseudo-second-order kinetic model and Langmuir-Freundlich isotherm model indicating that fluoride absorption onto MGS was characterized by chemisorption on heterogeneous surfaces. The adsorption capacity of MGS was 15.6 mg/g. The fluoride removal of 85% was achieved by 2 g dose of MGS for 100 mg/l of initial fluoride concentration, pH of 6, 120 rpm of speed, 300 minutes of contact time and 25 °C temperatures [70].

Mise and Gurani (2014) have used chemically activated (CaCl₂) carbon prepared from Phoenix *Dactylifera* (Date Palm) seeds at room temperature for removal of fluoride from water. The maximum fluoride removal was obtained at pH 7. The optimum contact time, adsorbent dose and pH for carbon with impregnation ratio 0.75 was 40 minutes, 140 mg and 7.0 respectively has given fluoride removal efficiency of 93%, 93.5% and 94.5% respectively [71].

Msagati *et al.* (2014) have investigated the defluoridation capacities of Lignite (L) and restructured surface of lignite (RSL) using a biomaterial called *Cuminum cyminum*. 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 \pm 0.03 respectively, with particle sizes of 150-90 μ m and 20g/L of dose. The experimental data fitted well for pseudo-second-ordered kinetic model along with the Langmuir isotherm model. The effect of co-anions on removal efficiency was found in the order of HCO₃⁻>SO₄²⁻>PO₄³⁻>NO₃⁻>Cl⁻. The regeneration was carried out by 0.01M NaOH and 57% and 60% fluoride removal were uptaken by lignite (L) and RSL even after the fifth cycle of regeneration. The disposal of L and RSL was not an issue since they have 22.01 MJ/kg and 26.90 MJ/kg heating value and can be used as fuel materials [72].

Rayappan *et al.* (2014) have studied defluoridation capacity of *Strychnos Potatorum* (SP) from aqueous solution in batch mode. The optimum condition for maximum removal of fluoride was at pH 7.0, with 60 minutes adsorption contact time and 120 rpm shaking speed. 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 (R²=0.9963) and Freundlich (R²=0.9895) isotherms. The presence of co-anions effects on removal of fluoride was found in an order of PO₄³⁻> SO₄²⁻> Cl⁻>CO₃²⁻> NO₃⁻ [73].

Ravikumar *et al.* (2014) used raw *Moringa oleifera* (MO) seed cake as natural coagulant and prepared composite coagulant by adding alum and starch with MO seed cake for removal of fluoride from aqueous solution. In both the cases, the fluoride was precipitated by coagulants and removed the fluoride below 1 mg/l but turbidity of water was very high for bear MO seed cake, whereas turbidity of treated water was less than 5 NTU (within standard limits of

drinking water) for composite coagulant. Hence, composite coagulant was used for defluoridation from drinking water of Alappuzha and Palakkad districts of Kerala [74].

Emmanuel *et al.* (2015) used low cost activated carbon from *Pitacelobium dulce* carbon (PLDC) for defluoridation of water and compared it with commercial activated carbon (CAC). The fluoride uptake was increased with an increase in dose of adsorbent, contact time and pH of the solution as well as a decrease in the initial concentration of fluoride. 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 and a dose of 3g/l for initial fluoride concentration of 3mg/l. The adsorption data were described by Langmuir and Freundlich isotherm model and best fitted by Langmuir. The adsorption process followed first order kinetic equation with regard to intra-particle diffusion rate [75].

4.3 Shells

Mise (2008) have used royal Gulmohar fruit shell activated carbon by $MgCl_2$ and H_3PO_4 by the impregnation ratio (I.R) of 0.25, 0.50 and 0.75. The I.R. of 0.75 gave the adsorbents with more surface areas and hence removed maximum fluoride at optimal pH of 7.0. The rate of adsorption obeyed first order reaction equation and Langmuir isotherm [76].

Sivasankar *et al.* (2010) investigated defluoridation capacities of activated and MnO_2 -coated tamarind fruit shell (TFS) in batch and column modes. The fluoride removal of ATFS and MTFS adsorbents was found to be 1990 mg/kg after the contact time of 30 minutes and at an optimum pH value of 6.5. The presence of HCO_3^- ions reduced the fluoride removal capacity. The pseudo-first order equation was best fitted for AFTS whereas Ritchie-second order was followed by MTFS. The kinetic data were found to fitted well Temkin isotherm for ATFS and Langmuir for MTFS. Thomas model was applied to the column experimental results [77].

Hanumantharao *et al.* (2011) have investigated the field removal capacities of activated carbon prepared from *Typha angustata* (TAC), *Lagenaria siceraria* shell carbon (LSSC) and *Acacia farnesiana* carbon (AFC) to remove fluoride 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 adsorbent dose of 6.0 g/L was needed for water sample having fluoride concentration between 2.0 and 3.0 mg/L whereas 4 g/L doses was required for fluoride sample between 1.5 to 2.0 mg/L of concentration to bring down fluoride concentration as per WHO permissible limit (≤ 1.5 mg/L). 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 [78].

Hanumantharao *et al.* (2011) have investigated the capability of *Acacia farnesiana* carbon (AFC) at room temperature for removal of fluoride from water. The maximum fluoride removal approximately more than 80% were found in the pH range of 6.5-7.0, with maximum adsorption at pH 6.9. The experimental data fitted well for Freundlich isotherm and pseudo-first-order equations. The equilibrium condition was achieved in about 40 minutes. The major effect of anions 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) [79].

Hanumantharao *et al.* (2012) have studied the capability of defluoridation by nitric acid activated carbon derived from *Typha angustata* plants. The observed data best fitted with Langmuir isotherm model and pseudo-second-order kinetic model. The range of optimal pH was 6.5-7.0 wherein more than 85% of fluoride were removed from water [80].

Hanumantharao *et al.* (2012) have investigated the potential of *Lagenaria siceraria* shell carbon (LSSC) for removal of fluoride from water. The experimental information were best fitted with pseudo-second-order kinetic model and Langmuir isotherm model. At the optimum pH range of 6.0 to 7.0, more than 85% defluoridation took place. The presence of co-anions reduced the fluoride removal capacity of LSSC in the order of $H_2PO_4^- > HCO_3^- > SO_4^{2-}$. LSSC was much cheaper than commercial activated carbon [81].

Sivasankar *et al.* (2012) have tried virgin (V) and ammonium carbonate (ACA) modified tamarind indica fruit shell (TIFS) carbons for fluoride removal. The fluoride removal capacity at pH 7.05 for V-TIFS and ACA-TIFS carbons were observed to be 91% and 83% respectively. ACA-TIFS carbon was used for treatment of ground water samples

to bring them within the permissible limit of WHO ($<1.5\text{mg/l}$). The fluoride desorption of 91.6% for 3m/l of initial fluoride concentration after 30 minutes using 0.05 M of NaOH solution was achieved [82].

Kumar *et al.* (2012) have used Tamarind fruit shell (TNFC) carbon in virgin and acid treated form for removal of fluoride from water. The Langmuir maximum monolayer adsorption capacities of virgin and treated TNFC were 4.14 mg/g and 6.11 mg/g respectively at 25°C. The optimum pH for maximum fluoride uptake was 6.0. The experimental data obtained was fitted well to both Langmuir and Freundlich isotherms. The presence of chloride ions reduced the removal of fluoride by 5 to 11%, whereas presence of sulfate ions reduced sorption capacity by 37% and 15% for virgin and treated TNFC respectively [83].

Bhagawati and Shivayogimath (2012) has used activated carbon prepared from almond shell with KOH activation for removal of fluoride from water in the down flow column. The optimal condition achieved by maintaining the 6 cm bed height, pH 4, flow rate of 15 ml/min, 25 OC temperature and 2 mg/l of fluoride water. The removal of fluoride by CGAC and AGAC was found to be 63% and 68% respectively [84].

Said and Machunda (2014) have used coconut shell activated carbon by 2M of H_2SO_4 ($\text{H}_2\text{SO}_4\text{CSAC}$) as adsorbent for removal of fluoride from synthetic and field water. The removal of fluoride by small size particles of 150 μ for field and synthetic water was 68.2% and 65.9% respectively. The maximum removal of fluoride occurred at pH of 2.0. The equilibrium contact time and dose of adsorbent was 120 g/L and 15 hours. The adsorption increased with an increase in a dose of adsorbent that treated the small concentration of fluoride influent water. The experimental data followed both Langmuir and Freundlich isotherm model having R^2 value of 0.9672 and 0.9826 respectively. The coconut shell activated carbon was locally available in Tanzania and also removed colour and mostly used in household filters [85].

Anusha and Murugadoss (2014) have investigated the activated carbon prepared from shell of Bale fruit (*Limoniaacidissima*) for fluoride removal from water 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 favourable condition of adsorption [86].

Montoya *et al.* (2014) prepared carbon obtained from the carbonization of peanut shells and plum kernels and carbon obtained by impregnation of calcium acetate solution prior to carbonization. The calcium impregnated carbon gave better fluoride adsorption capacity. The defluoridation capacity of peanut shell impregnated with calcium solution of 3151 mg/l and carbonized at 800°C (IC-PN-25) was found higher than others. The defluoridation capacity IC-PN-25, IC-PK-25, C-PN and C-PK was 2.5, 2.05, 2.0 and 0.69 mg/g respectively. The equilibrium isotherm of adsorption was well described by Slip model and followed the pseudo-second-order kinetic model. The adsorption process was spontaneous and endothermic in nature. The presence of co-anion affected fluoride uptake in the order of Carbonate > Hydro carbonates > Chloride > Sulphate. The Yan model described the breakthrough curve of column [87].

Mariappan *et al.* (2015) used chemically activated cotton nut shells carbon (CTNSCs) for defluoridation from drinking water. The CTNSCs effectively removed fluoride from water. The adsorption equilibrium data fitted well with Freundlich isotherm model and followed the pseudo-second-order kinetic model. The adsorption process was spontaneous and endothermic in nature and governed by chemisorption and physisorption [88].

Ajisha and Rajagopal (2015) used pyrolyzed *Delonix regia* pod carbon (PDPC) at 800°C for defluoridation of water. The maximum removal of 97% was obtained in optimum conditions (pH 2.0, a dose of 1.5g and contact time of 300 min). The adsorption equilibrium data fitted well with Freundlich isotherm model and followed the pseudo-second-order kinetic model. 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. The adsorption reaction was spontaneous, irreversible, steady and endothermic. The intra-particle diffusion model acted as a rate determining step. The presence of co-anions like chloride, nitrate, bicarbonates, sulphate and carbonates had insignificant effect on fluoride removal and found 90% removal except 300 mg/l of CaCO_3 that gave fluoride removal of 42% only. PDPC mostly removed high fluoride in acidic condition and hence used for defluoridation of polluted water and industrial water of lower pH [89].

4.4 Juices

Ghimire (2011) have studied the fluoride removal potential of aluminium (III), cerium (IV), tin (IV), iron (III) and lanthanum (III) loaded phosphorylated orange juice residue (POJR). Cerium loaded gels were having high fluoride removal capacity in acidic condition while lanthanum loaded gel performed well in acidic and neutral conditions. Their removal percentage is higher than commercial activated alumina. As per isotherm studies, the loading capacities were elevated 2.7 and 2.87 mol kg⁻¹ dry gel for cerium and lanthanum loaded POJR. The complete removal of fluoride by lanthanum loaded POJR in the batch study of 15mgdm⁻³ initial fluoride was achieved at solid to liquid ratio of 0.08 gdm⁻³ [90].

Paudyal *et al.* (2011) have tested the fluoride removal efficiency of metal loaded (i.e. Al³⁺, La³⁺, Ce³⁺, Sn⁴⁺ and V⁴⁺) saponified orange juice residue (SOJR) from water. Al-SOJR gel removed more than 80% of fluoride in the pH range of 5.5-6.05 whereas La-SOJR, Ti-SOJR and Sn-SOJR performed well in the pH range of 3-4. The Langmuir maximum adsorption capacity of Al-SOJR was found to be 1.01 mg/g at pH 6.0. It was observed that Al-SOJR dosages of 8g/dm³ were able to bring down the fluoride below 0.8 mg/dm³ as per Japanese standard, whereas 15g/dm³ dosages of Al-SOJR removed complete fluoride from water [91].

Paudyal *et al.* (2012) have investigated the potentiality of rare earth ions loaded saponified orange juice residue (SOJR) for removal of fluoride from water. The maximum adsorption capacity for Sc(III), Ho(III), La(III) and Sm(III) were found to be 0.60, 0.92, 1.06 and 1.22 mol/g respectively in the pH range of 4-5. The Japan standard limit of fluoride was 0.8 mg/l which was achieved by La (III)-SOJR at solid to liquid ratio of 6g/L whereas it was 15 g/L for Sm(III)-SOJR. Thus La(III)-SOJR was observed as a prominent adsorbent for the treatment of industrial effluents containing trace concentration of fluoride ions [92].

Paudyal *et al.* (2013) have used Zr(IV), Ce(IV) and Al(III) loaded dried orange juice residue (DOJR) in the amount of 0.90, 0.85 and 0.97 mol/g respectively as effective adsorbents for removal of fluoride from water. The maximum adsorption capacity of fluoride on the Zr(IV), Ce(IV) and Al(III) loaded DOJR were evaluated as 1.43, 1.22 and 0.67 mmol/g respectively. The maximum adsorption observed was achieved at a pH of 4 for Zr(IV)- and Ce(IV)-DOJR, whereas it was found to be 4.2-5.6 in the case of Al(III)-DOJR. The dosage of 1 g and 2.5 g of Zr(III)-DOJR and Al(III)-DOJR required per unit volume (1L) of low concentrated industrial effluent whereas 1.5g and 10 g of Zr(IV)-DOJR and Al(III)-DOJR respectively per unit volume of the solution of the high concentrated fluoride sample was needed. The dilute alkaline, 0.1M of NaOH solution was found to be most effective for regeneration of adsorbents [93].

4.5 Plants

Rao *et al.* (2009) have 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°C for 4hrs then washed and dried and afterward modified by 0.1M of HNO₃. 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 regeneration of exhausted adsorbent was carried out by 0.1N of NaOH solution. 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 [94].

Pandey *et al.* (2012) have utilized biomass of *Tinospora cordifolia* plant powder of 1.18 µm particle size after washing and drying in the sun and hot air oven at 60°C. The fluoride removal of 70% was achieved by 7g/50ml dose of adsorbent at pH of 7.0 with fluoride content of 5 mg/l and 120 minutes of standing time. The experimental data was best fitted to Langmuir and Freundlich isotherm models. The fluoride uptake capacity of 25 mg/g was observed by biosorbent. Pseudo-first-order kinetic model fitted well as compared to second-order kinetic model [95].

Singanan (2013) has used metal embedded biocarbon technology for defluoridation of water in the down-flow column. The aluminium metal embedded biocarbon (AMEBC) was prepared using analytical grade aluminium metal powder and activated biocarbon derived from *Tridax procumbens* (Asteraceae) in a weight proportion of 0.5:5 utilizing concentrated HCl for precipitation. The maximum removal of 98% with 2.0 g dosage of adsorbent at 27±2°C was achieved in 180 minutes at pH range of 3.5-4.0 for 20 mg/L of fluoridated water. The AMEBC adsorbent with 2.0 g/L dosage removed 80% of fluoride from field water having 3.6 to 0.7 mg/L of initial fluoride concentration. The fluoride removal mechanism involved ion-exchange process [96].

Shyam and Kalwania (2014) have used aloe (*Aloe barbadensis* Miller) and calcium chloride for fluoride precipitation and adsorption from aqueous solution. The optimum fluoride removal of 88% was achieved at pH 7.4 ± 0.1 with 40.0 g of aloe vera and 3.0 g calcium chloride in 1000ml sample with 40 minutes of contact time. The equilibrium adsorption data followed both Langmuir ($R^2=0.9834$) and Freundlich ($R^2=0.8903$) [97].

Rayappan *et al.* (2014) have investigated potential of *Cissus Quadrangularis* (CQ) powder for removal of fluoride from water in batch process. 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 and optimum initial fluoride concentration for CQ adsorbent is 1mg/50ml. The presence 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. The Langmuir ($R^2=0.99$) and Freundlich ($R^2=0.9679$) adsorption isotherms were fitted well as per the study[98].

4.6 Leaves

Jamode *et al.* (2004) have used leaf powder neem (*Azadirachta indica*), pipal (*Ficus religiosa*) and khair (*Acacia catechu* wild) trees with and without chemical treatment as adsorbents to remove fluoride from aqueous solution. The 10g/l of adsorbent dose for 50 ml sample volume with 15mg/l of fluoride ion concentration ,reduced to 0 mg/l within 180 minutes at $29 \pm 0.5^\circ\text{C}$. The experimental data fitted well with Langmuir adsorption isotherm with regression coefficient of 0.9309. The fluoride removal was more with the small particle size and hence 1.4 mm particle size removed 60 and 50 % for plain biosorbents and treated biosorbents while 600μ particle size adsorbent could remove 95 and 90% respectively for plain and treated biosorbents at dose of 10 g/L at pH 2.0. It was observed that near about 80% removal was achieved within 60 minutes of contact time at 10 g/l doses of treated adsorbent. The disposal of exhausted adsorbent showed no regeneration due to its availability in abundance and could be disposed of easily by burning or dumping in low laying areas as filler materials [99].

Kumar *et al.* (2008) have examined defluoridation capacity from a fluid arrangement by thermally initiated neem (*Azadirachta indica*) leaves carbon (ANC) and kikar (*Acacia arabica*) leaves carbon (AKC) in electric furnace at 400°C . The optimal pH and time were 6.0 and 60 minutes for both the adsorbent for 5ppm of fluoride solution. The removal of 0.3mm size of adsorbent was more than 1.0mm size of adsorbents. The optimum dose of ANC and AKC were 0.5g/100ml and 0.7g/100ml respectively. The experimental data was best fitted with Freundlich adsorption isotherm and Langmuir first order equation [100].

Choubey and Agrawal (2012) have studied defluoridation of drinking water sample from hand pumps of 15 villages of Rajgarh (Block), Madhya Pradesh (India) containing 2.5 to 4.0 ppm of fluoride by using drum stick leaves (DSL), drum stick bark (DSB), black clay soil (BCS) , alluvial soil (AS) , millet husk (MH) and wheat husk (WH). The fluoride removal with natural adsorbents were found in the order of $AS(71\%) > BCS(68.8\%) > DSL(48\%) > MH(30\%) > DSB(28\%) > WH(24\%)$ for an adsorbent dose of 1 g/100 ml at 5 ppm of initial fluoride concentration. The adsorption process followed Langmuir and Freundlich isotherm model. Peoples living in fluoride area were addicted to take drum stick vegetable in their diet and used pitcher cultivated from Black clay and alluvial soil for storing drinking water [101].

Kamble (2012) has investigated defluoridation capability of Basil (*Ocimum sanctum*, Lamiaceae) or Tulsi leaves, stem and extract of fresh leaves from aqueous solution in batch process. The maximum removal of 94%, 75%, 78% and 74% achieved from 5 ppm of fluoride solution by fresh basil leaves, fresh basil stem, dry leaves and dry stem at a dose of 75 mg/100 ml, 100 mg/100 ml, 250 mg/100 ml and 250 mg/100 ml at pH of 9.0, 6.0, 6.0 and 7.0 for a contact period of 20 minutes. This technique is cost effective and environmental friendly to treat the fluoride contaminated water at rural and urban regions as per Indian Standard for drinking (IS 10500: 1991) [102].

Bharali and Bhattacharyya (2014) have used Silikha (*Terminalia chebula*) leaf powder for defluoridation of aqueous solution. The fluoride removal of 74% was obtained at the natural pH of 6.8 and 303K temperature. The defluoridation measurements fitted well with the pseudo-second-order kinetic model. The equilibrium time of 120 minutes for defluoridation process indicated the high degree of affinity for fluoride sorption. Silikha leaf powder was used as a cost effective biosorbent for treating fluoride bearing water [103].

Bharali and Bhattacharyya (2014) have investigated the Devdaru (*Polyalthia longifolia*) leaf powder (DLP) as bisorbent for removal of fluoride from aqueous solution in batch process. The maximum fluoride removal of 77% was obtained at 303K with neutral pH. The optimum dose of adsorbent was 3.0 g/l for maximum rate of adsorption. Kinetic study showed that the DLP adsorption mechanism involved both chemisorption process and intra-particle diffusion. A Thermodynamic study uncovered that the adsorption procedure was exothermic in nature and performed well at lower temperature [104].

Dwivedi *et al.* (2014) have investigated the fluoride removal capacity from aqueous solution by *Ficus religiosa* (peepal) leaves powder of size less than 196 μm . The fluoride removal of 74% was obtained for 20 ppm of initial fluoride concentration at pH 7.0 with 10g/l of adsorbent dose, 40 minutes of the equilibrium time at 30°C. The Freundlich isotherm model fitted best ($R^2=0.995$) than Langmuir and Temkin isotherms. The Langmuir maximum adsorption capacity of adsorbent was 2.24 mg/g. The removal efficiency of peepal leaf powder was 85.7% when the initial fluoride concentration was 5ppm and finally the fluoride was brought down below the permissible limit [105].

Tomar *et al.* (2014) used powder of *Citrus limonum* (lemon) for fluoride removal from aqueous solution. The maximum fluoride removal of 70% was obtained at pH 2 for fluoride solution of 2 mg/l. The adsorption data fitted well with Freundlich isotherm than Langmuir isotherm model [106].

Sudarshan *et al.* (2014) studied efficacy of Tulsi (Holy Basil) leaves for removal of fluoride from groundwater. The fluoride removal of 95% from groundwater was achieved within 20 minutes as per previous literature review. The author stated that the fluoride solution of 5 to 7 mg/l was reduced to 1 or 2 mg/l by Tulsi leaf powder, but after 2 or 3 hrs the fluoride concentration increased again and reached to its original level. Thus, there was no appreciable reduction of fluoride by Tulsi leaves [107].

Yu *et al.* (2015) prepared lanthanum modified carbon (LMC) derived from *Sargassum sp.* for fluoride removal from water. The optimum pH range was 3-9. The adsorption reaction was high and 90% of adsorption occurred in first 1 h and reached to equilibrium within 4 h. The maximum adsorption capacity of LMC was 94.34 mg/g at neutral pH which was more than other commercial adsorbents. The fluoride uptake got affected by the presence of SiO_3^{2-} , SO_4^{2-} , HCO_3^- , PO_4^{3-} and AsO_3^- whereas efficiency remained unaffected by availability of humic acid. The adsorption mechanism was mainly controlled by outer-sphere complex, electrostatic attraction and ion-exchange. The LMC had awesome prospective in industrial application [108].

Kumari *et al.* (2015) used Sal (*Shorea Robusta*) leaf powder of particle sizes 0.3 and 1.0 mm for defluoridation of water. The fluoride removal by 0.3 mm was more than 1.0 mm size of adsorbent. The fluoride removal of 0.3 mm and 1.0 mm of Sal powder was 63.6% and 25.8% respectively at pH of 7.5 and dose of 1g per 50 ml solution. The fluoride removal of 98.6% was obtained for 0.3mm particle size of Sal powder at dose of 3g. The Langmuir maximum deluoridation capacity of Sal powder (0.3mm) was found to be 1.28 mg/g. The adsorption process obeyed Freundlich isotherm model [109].

4.7 Stems

Chakrabarty and Sharma (2012) have used heat activated neem stem charcoal for defluoridation of aqueous solution. The removal of 94 % was achieved from 10mg/l of fluoride bearing solution at pH of 5.0. Biosorption equilibrium was obtained within 180 minutes. The experimental data fitted well for both Langmuir and Freundlich isotherm model and the maximum Langmuir adsorption capacity was 1.27 mg/g [110].

Shyam and Kalwania (2013) have studied the fluoride removal capability of a Khimp plant (*Leptadenia pyrotechnica*) stem powder ,having sufficient positive (calcium) ions that adsorbed the negatively charged fluoride ions. The fluoride removal mechanism was mainly governed by precipitation and adsorption (CaF_2) onto khimp powder. The maximum fluoride removal of 97% was achieved at pH 6.7 ± 0.1 with an adsorbent dosage of 6.0g/L of biomass with a contact period of 60 minutes. Equilibrium adsorption data obeyed both Langmuir and Freundlich isotherms [111].

Yadav *et al.* (2014) have studied the potential of activated charcoal powder derived from dry stems or timber of Aralu (*Ailanthus exelsa*) tree by charring the biomaterials at 100-200°C for about 3-4 hours in muffle furnace. The removal of 94% and 80% was achieved for 10mg/l of initial fluoride concentration at pH 2 and 5 respectively at an

adsorbent dose of 0.5g/l. The adsorption process was rapid and removed 75% of fluoride within first 30 minutes and adsorption equilibrium was achieved within 180 minutes with 94% removal [112].

Suneetha *et al.* (2014) have used Nitric acid activated carbon prepared from the stem of an *Abutilon Indicum* plant (NAbIC) for defluoridation of water. The maximum removal of more than 80% was achieved at pH of 7, an adsorbent dosage of 5.0 g/L, equilibrium time of 60 minutes, particle size of 45 μ and temperature of $30\pm 1^\circ\text{C}$. The experimental data fitted well with a Langmuir isotherm model showing monolayer adsorption and pseudo-second-order kinetic model. The Temkin heat of sorption of 0.224 J/mol and Dubinin-Radushkevich mean free energy of 3.16kJ/mol indicated that the process was physic-sorption. The effect of co-ions was found in the order of $\text{PO}_4^{3-} > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$. The phosphate ions reduced the fluoride removal from 83% to 68.7% with 50 mg/L concentration [113].

Shivayogimath *et al.* (2014) prepared low cost materials like granular activated carbon from corn cob (CGAC) and *Acacia Nilotica* stalk (ACAG) by KOH activation as well as broken waste tiles (TBAG) and used them for batch study for defluoridation of water and results were compared with commercial activated alumina (CAAG). The BET surface area and pore volume of adsorbent at carbonization of 800°C for CGAC was 940 m^2/g and 81%, for AGAC was 1065 m^2/g and 83% and for TBAG was 365 m^2/g and 83%. The fluoride removal of adsorbents was found in increasing order of CAAG (92%) > AGAC (83%) > CGAC (81%) > TBAG (48%). The equilibrium data fitted well with Freundlich isotherm model ($R^2 = 0.966$ to 0.977) than the Langmuir isotherm model ($R^2 = 0.749$ to 0.827). The optimum pH range was found to be 4-6. The optimum condition was achieved by maintaining pH of 4.5, adsorbent dose of 1 gm/L, 90 minutes contact time and 120 rpm of shaking speed for 5 mg/l of initial fluoride concentration. The fouling of the alumina bed occurred due to high concentration of total dissolved salts (TDS). The regeneration was carried out after every 4-5 months [114].

4.8 Barks

Karthikeyan and Ilango (2007) have used *Moringa indica* bark activated carbon for defluoridation of aqueous solution. The minimum contact time for maximum fluoride removal was 25 minutes. The maximum removal of 80% was achieved for 3 mg/l initial fluoride concentration solution at 3g/l dose and pH of 2.0. The fluoride adsorption obeyed both Langmuir and Freundlich isotherms and followed a pseudo-second-order kinetic model and the adsorption reaction was endothermic in nature [115].

Mohan *et al.* (2011) have studied defluoridation of water by using low-cost pine wood and pine bark chars (derived as a byproduct from bio-oil production unit) that were obtained as a byproduct from fast pyrolysis in an auger reactor at 400°C and 450°C . The optimum pH was 2.0 and optimum equilibrium time was 48 hours with an adsorbent dose of 10 g/L. The fluoride adsorption decreased with an increase in temperature indicating an exothermic reaction. The Langmuir isotherm was best fitted to pine wood char whereas Freundlich isotherm was best fitted to pine bark char. The Langmuir monolayer adsorption capacity of pine wood and pine bark chars were 7.66 mg/g and 9.77 mg/g at 25°C . The rate of fluoride adsorption followed pseudo-second-order kinetic model. The pine biochars ($S_{\text{BET}} 2-3 \text{ m}^2/\text{g}$) removed more fluoride than activated carbon ($S_{\text{BET}} 1000 \text{ m}^2/\text{g}$) since these chars got swelled in water due to their high oxygen content (8-10%), opening into new inward pore volume which further promote fluoride adsorption. The defluoridation mechanism by biochars was mainly governed by ion-exchange and metal fluoride precipitation. The pine wood char was treated with 50 ml of a groundwater sample and 6.995 mg/l of initial fluoride from Mathura district of Uttar Pradesh (India) and reduce it to 0.973 mg/l with 15 g/l doses, 48 hours of equilibrium time, pH 2.0 and 25°C temperature. The pine biochar was mostly used for industrial wastewater then used for water treatment due to low pH of 2.0 [116].

Mamliwar *et al.* (2012) have used thermally treated Babul bark powder in a muffle furnace at 700°C for 2 hours for defluoridation of aqueous solution. The 5 g/l doses of adsorbent could remove 77.04% fluoride from aqueous solution bearing 5 mg/l fluoride concentration at pH of 8.0 with an equilibrium time of 8 hours and 303K. The experimental results in equilibrium were best fitted with Langmuir isotherm than Freundlich isotherm. Also, the pseudo-second-order kinetic model was best fitted as compared to the pseudo-first order [117].

Dutta *et al.* (2012) have investigated activated carbon prepared by carbonization of *Acacia Auriculiformis* scrap wood char at 750°C under nitrogen atmosphere followed by microwave heating for 5 minutes (AC750NMW5) for

removal of fluoride from water. The optimum pH for maximum fluoride removal was 4.0. The elimination of fluoride increases with an increase in dose and maximum removal of 97.2% was obtained with an adsorbent dose of 2g/l for 10mg/l of fluoride solution at 30°C at pH 4.0. A maximum removal of 84.8 % was achieved with particle size of 58 µm. The adsorption process was endothermic in nature and hence adsorption of fluoride increased from 84.8% to 97.33% when the temperature was increased from 30°C to 40°C. The Langmuir isotherm fitted well with an adsorption capacity of adsorbent where the value obtained was 19.92 mg/g and followed the pseudo-second-order kinetic model. The change of enthalpy and entropy were 6.094 kJ/mol and 19.022 J/mol-K respectively as per thermodynamic study [118].

4.9 Root

Harikumar *et al.* (2012) have investigated defluoridation capacity of Vetiver root powder as a adsorbent from water. The Vetiver had removed 80 to 90% of fluoride from water at pH of 6.0 to 7.0 for fluoride water of 2 mg/l. The equilibrium data obtained was fitted well with Langmuir and Freundlich isotherms [119].

4.10 Saw dust

Balouch *et al.* (2013) have investigated the defluoridation potential of brick powder, coal, saw dust and mixture of adsorbents from aqueous solution. The removal efficiency of natural adsorbent were found in the order of mixture of adsorbent > brick powder > saw dust > coal. The maximum removal of fluoride from 5 mg/l of fluoride bearing solution was achieved by maintaining the pH of 7, 100 rpm shaking speed, 30 minutes of equilibrium contact time and 2g/l of dose of adsorbents at 25°C. The removal of fluoride was 80 to 90% at pH range of 5-7. The adsorption obeyed both Freundlich ($R^2=0.976$) and Langmuir ($R^2=0.992$) isotherms model. The maximum Langmuir adsorption capacity was 0.6253mmol/g. The thermodynamic study uncovered that the adsorption response was unconstrained and exothermic. The coefficient of determination by Lagergren model, Morris-Weber model and Ho-Mackey model was found to be 0.9961, 0.876 and 0.998 respectively. The mixture of all was efficiently used for the removal of fluoride from groundwater sample [120].

Mann and Mandal (2014) have studied the adsorption capacity of sawdust from kail wood for defluoridation of aqueous solution in batch process. The maximum removal of fluoride more than 70% was achieved under optimum condition, including pH of 7.0, contact time of 120 minutes and the adsorbent dose of 2 g/L at room temperature. The experimental results were closely fitted well with Langmuir than Freundlich isotherm model indicating that the chemisorption was the key mechanism of adsorption. The defluoridation processes obeyed the pseudo-second-order kinetic model [121].

4.11 Coir

Chakrabarty and Sharma (2011) have investigated the defluoridation capability of thermal treated betel nut coir charcoal (BNC) powder at 200-300°C for 2-3 hours in a muffle furnace. The fluoride removal of 92% to 70% was achieved from aqueous solution of 2-10 mg/l fluoride concentration at 25°C. Adsorption equilibrium was achieved within 180 minutes. The ideal pH for most extreme fluoride evacuation was accomplished at pH6.0. The isotherm was fitted well for both Langmuir and Freundlich isotherms. The kinetic study revealed that result obeyed pseudo-second order for adsorption [122].

4.12 Grass

Alagumuthu *et al.* (2010) have investigated the cynodon dactylon (Burmuda grass) based thermally activated carbon for defluoridation of water. The maximum removal of 83.77% of fluoride was obtained by 1.25 g dosage of adsorbent for 3 mg/L of fluoride concentration for 105 minutes of contact time at neutral pH. The adsorption process followed Redlich-Peterson as well as Langmuir isotherms. The average monolayer adsorption capacity (q_m) obtained for cynodom dactylon was 4.702 mg/g. The adsorption process was unconstrained and endothermic in nature. The presence of bicarbonate ions reduced the fluoride removal from 83.7 % to 51.5% with an increase of bicarbonate concentration 0-300mg/L. The order of interference for fluoride removal detected was in the following order, $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- \geq \text{NO}_3^-$ for the adsorbent cynodon dactylon. The regeneration of exhausted adsorbent was done by 2% sodium hydroxide to regenerate 67.4% of adsorbent [123].

Manna *et al.* (2015) used alkali-steam treated water hyacinth and elephant grass for defluoridation of aqueous solution. The fluoride removal of 85% was obtained by 1.0 g and 1.5 g of water hyacinth and elephant grass respectively from initial fluoride solution of 5 mg/l. The defluoridation capacity of water hyacinth, elephant grass and activated alumina was observed to be 5 mg/g, 7 mg/g and 2 mg/g respectively. The optimum pH range and time of contact was 2-10 and 210 minutes respectively. The fluoride removal was increased with more contact time and decreased with an increase in initial fluoride concentration and pH of aqueous solution. The adsorption reaction was spontaneous ($-\Delta G$) as well as exothermic ($-\Delta H$) in nature and negative values of entropy ($-\Delta S$) indicated that the greater order of reaction was obtained during fluoride adsorption. The 80% recovery of untreated and basic steam treated biomass was acquired by 10mM of HCl solution [124].

Rout *et al.* (2015) prepared iron oxide based nanocomposite (IBNC), Titania based nanocomposite (TBNC) and micro carbon fiber by using Bermuda grass based nanocarbon carbon fiber upon warmth treatment at 800 °C in nitrogen atmosphere in the presence of metal oxides. The defluoridation capacity of IBNC, TBNC and micro carbon fiber was nearly to 97%, 92% and 88% at optimum condition (pH 4, a dose of 0.5 g/100ml, contact time of 60 min, temperature of 35 ± 5 °C and initial fluoride concentration of 10 mg/l). The experimental informations fitted well with Freundlich isotherm model and the adsorption process was found to be spontaneous in nature [125].

4. CONCLUSIONS

Most by far of the developing countries depends on the groundwater as drinking water such as that of India [126-133]. This paper describes the review on the utilization of industrial by-products, agricultural wastes and plant biomass as low cost materials and readily available materials for adsorption of fluoride from aqueous solution under different experimental conditions and their practical applicability on field by column study. The efficiency of fluoride removal increases with increase in dose and smaller particle size of adsorbent. The modification of adsorbent with suitable chemicals or composite adsorbents was also remarked for the enhancement of efficiency of fluoride removal from water. The equilibrium studies were fitted well either with Langmuir or Freundlich isotherm model. The adsorption kinetics were suitable to pseudo-first order or pseudo-second order with or without intra-particle diffusion model depending on types of adsorbent used for fluoride uptake. The nature of the reaction was in term of spontaneous or non-spontaneous as well as exothermic or endothermic depending on adsorbent tried for defluoridation. The column performance of some adsorbent was also explained for field trials. The future research should be focused on the economy and efficiency of industrial and agricultural wastes to replace commercial adsorbent for developing countries like India.

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