



A Review on Assessment of Defluoridation of Water Using Bio-Absorbents

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Abstract : Fluoride is one of the anionic contaminants which is found in excess in surface or groundwater. 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. This paper reviews the fluoride uptake capacities of industrial by-products, agricultural wastes and biomass materials.

Key words : Defluoridation, Low cost adsorbents, fluoride removal materials, water, Techniques.

Introduction:

Water is important for functioning of the human being and one cannot survive without it. Quality water is necessary for all the people, the water quality can be affected by different pollutants. The water is polluted due to the presence of large amounts of pollutants.¹ Also the long discharge of industrial effluents, domestic sewage, use of fertilizers & pesticides, waste dump causes the groundwater pollute and health problems created.² In India, water bodies need to be treated by various means before using it in domestic applications. Various ions, salts are present in ground water, so if such type of water used as potable water, then it leads to various water-borne diseases.³ Rapid development in industrialization and urbanization leads to deterioration in the quality of groundwater.⁴ The most important and natural resource present in earth is water. Fluorine is 13th most abundant element present on earth's crust and available fluoride ion present in various compounds in earth's crust such as fluor spar, sodium fluoride, sodium fluorosilicate etc. Fluoride is highly electronegative among all other elements.⁵ It is well known that the excess intake of fluoride may cause fluorosis (dental and skeletal), and also damage neurological system.⁶ Removal of fluoride from water is important because it shows harmful effects. Exposure of fluoride in drinking water reflects number of adverse effects on human health. Including crippling skeletal fluorosis that is a significant cause of morbidity in a number of regions of the world. Fluoride is more toxic than lead, or just like lead, even a minute dose of it accumulates to damage the brain and development of children. Also produces abnormal behaviour in animals and reduces human IQ too.⁷

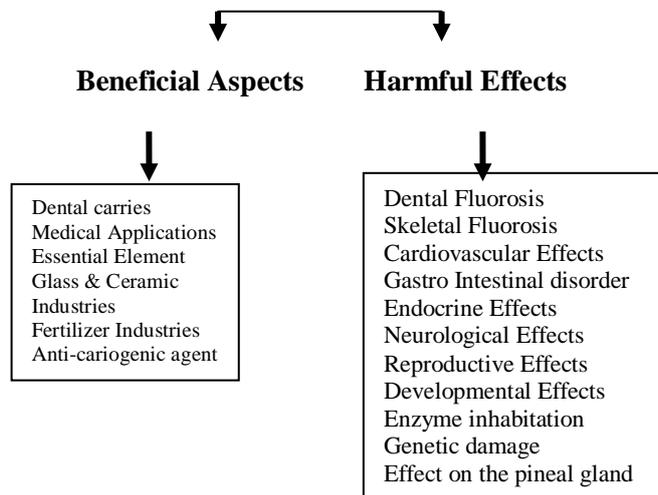
Various studies have revealed that major of the kidney diseases have a great inclination of toxicity of fluoride and a high dose and short term exposure of fluoride can exterminate the kidney function. Several research groups reported that fluoride can interfere with the function of pineal gland as well as brain. Pineal gland is one of the major fluoride accrued site in body with high concentration of teeth and bones. The high concentration of fluoride diagnosed bladder cancer.⁸ Drinking water standards for fluoride prescribed by various authorities are listed in Table 1.⁹ Throughout the world, large number of fluoride contaminated areas are

founded where ground water contain exceed levels of fluoride. In worldwide, India is most severely fluoride affected country. The 85 million tons of fluoride deposits on the Earth’s crust, in which 12 million found in India.¹⁰

Table 1: Drinking water standards for fluoride prescribed by various authorities

Sr. No.	Authorities	Permissible limit of fluoride concentration (mg/L)
1.	World Health Organization (International Standard for drinking water)	0.5
2.	US Public Health Standard	0.7-1.2
3.	Bureau of Indian Standards (BIS)	1.0-1.5
4.	Indian Council of Medical Research (ICMR)	1.0-2.0
5.	Central Public Health and Environmental Engineering Organisation (CPHEEO)	1.0-1.5

Fluoride



1. Various Methods used for De-fluoridation: On the basis of mode of action de-fluoridation methods are divided into two types.

- Nalgonda technique (chemical reaction with fluoride)
- Adsorption process

1.1 Nalgonda technique chemical reaction with fluoride

The Nalgonda technique is functions on flocculation principal. It is a combination of several unit operations such as it involves rapid mixing, chemical interaction, flocculation, sedimentation, filtration, disinfection and sludge concentration to recover water and aluminium salts. Commonly, hydrated aluminium salts used as coagulant for water treatment to flocculate the fluoride ions in the water sample. This process is carried out under alkaline condition by addition of lime and bleaching powder which added for the disinfection. The chemical elements coagulant in to flocks are settle down in the bottom after through stirring. Improvement understanding of fluoride-adsorbent interactions was the background for experimental studies. Theoretically, the adsorption of fluoride on the solid particles normally takes three essential steps. The adsorbent was prepared by co-precipitated aluminium and iron (III) hydroxides from chloride mixture in equal-molar quantities using ammonia. After aging and drying, the resulting mixed hydroxide adsorbent was better adsorbent for fluoride than aluminum hydroxide or iron (III) hydroxide.¹¹ Several researcher groups studied the adsorption of fluoride on

soils, also the effect of varying levels of exchangeable sodium on the adsorption of fluoride on to sonic-soils.¹² For de-fluoridation fill and draw type plants are very useful. These plants consist of a hopper-bottom cylindrical tank (depth 2m) whereas their diameter is depends upon how much water should be treat. In same vessel of mixing, flocculation and sedimentation are performed with stirring mechanism, which can be either hand operated or power driven. Raw water pumped to the unit and required quantities of alum, lime and bleaching powder was added. Than contents stirred for 10 min and allowed to settle for 1-2 hrs. The settled sludge discarded, de-fluoridated supernatant is filtered and supplied through stand posts.¹³

2. Adsorption process (Bio-absorbents)

Tea ash:

Tea ash used Al/Fe oxides loaded tea waste for removal of fluoride from drinking water has been reported.¹⁴ The bio-adsorbent with tea-Al and tea-Al-Fe were able to reduce the fluoride below 1.5 mg/L with an optimum pH range of 4.0 to 8.0 and contact time was 2 hrs. At pH range of 5 to 10 water was bleached with Al and Fe within permissible limit. The de-fluoridation 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. It was observed that the adsorption process follows Lagergren pseudo second order kinetic model. The fluoride ions were surrounded by positively charge surface sites which is bi-metallic cations in acidic phase and involved ligand exchange at pH > 6. De-fluoridation 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.¹⁵ The Langmuir adsorption capacity of AcTAP observed was 8.55 mg/g and it obeyed pseudo second order kinetic. The extreme removal of fluoride was achieved at 6.0 pH and equilibrium time was 180 mins.

Rice husk ash:

The capacity of activated rice husk ash (ARHA) has been investigated.¹⁶ Rice husk ash was prepared by washing and drying rice husk ash from the rice mill at 100°C for 8 hrs in an electric oven, than it was crushed and ground to obtain 250 µm size for the removal of fluoride through batch technique. The Langmuir adsorption capacity of ARHA was 0.402 mg/g obtained and follows the pseudo second order kinetics. The equilibrium was attained in 100 minutes and 88.30% fluoride was removed. The possibility of fluoride removal using rice husk ash coated with aluminium hydroxide has been reported.¹⁷ Rice husk ash was prepared by burning rice/paddy husk which is an abundantly available and is an affordable raw material. The adsorption experiments were carried out at range of 10–60 mg/L initial fluoride concentrations and 0.1 g of adsorbent concentration, while pH value of the initial fluoride solution was maintained at 7. All of the experiments were conducted at 27°C during 1 hr. The adsorption study indicates that the adsorption capacity of modified rice husk ash and column study were found 15.08 and 9.5 mg/g, respectively. The results shows that at strong pH maximum fluoride removal was obtained (pH 5.0), hence removal of fluoride is depend upon strong pH value.

Fly ash:

The calcium hydroxide treated fly ash (CFA) for the removal of fluoride in batch study has been used.¹⁸ More than 80% fluoride was removed from the solution of 10 mg/L by 3 g/L of CFA dosage at 120 mins equilibrium contact time. At pH 7 maximum fluoride removal was obtained. The Langmuir monolayer adsorption capacity was obtained 10.86 mg/g and the chemisorption process follows pseudo second order kinetic. Also this process was endothermic in nature and removal efficiency increases with an increase in temperature. The fly ash filter materials A and S for the removal of high fluoride from drinking water has been introduced.¹⁹ The Freundlich adsorption capacity and quantity for A and S was found to be 1.22, 1.01 mg/g, and 2.46, 2.97 Kg, respectively. It was observed that the high pH of solution resulted into low turbidity of filtered water. The efficiency of de-fluoridation rises with the rising of fluoride concentration of influent and both the quantity of sifted water and effectiveness of the de-fluoridation increases with expansion of temperature.

The study of the batch adsorption capacity of fly ash for fluoride adsorption was observed.²⁰ It was observed that between pH 2 to 12 fluoride adsorption decreases continuously. The effect of pH on fluoride removal in both studies was differ due to the different composition of fly ash and an experimental conditions. The de-fluoridation of groundwater of Agra city with alum treated fly ash (ATF) carried out.²¹ The fly ash was

prepared by soaking it in 1% NaOH, after that dried, finally treated with 2% $\text{Al}_2(\text{SO}_4)_3$ solution for 30 minutes, the white precipitate of $\text{Al}(\text{OH})_3$ was obtained. Then the precipitate of $\text{Al}(\text{OH})_3$ was dissolved in 1:1 HCl at pH 3.5. The fluoride solution concentration ranging from 0.5 to 4.5 mg/L was treated with 3.5 mg/100ml dosage of ATF, resulting 70 to 62.9% removal of fluoride. An alkaline fly ash was employed for the removal of fluoride.²² For this purpose 450 g of alkaline fly ash in packed column (45mm 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 was used. The required time to bring down effluent fluoride concentration to 0 mg/l was achieved in 120 to 168 mins. 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.

Maize ash:

Maize husk fly ash also utilized as an adsorbent for eliminating fluoride from water in batch mode.²³ The greatest fluoride evacuation was seen to be 86% at ideal condition having an agitation rate of 250 RPM at pH 2, and 2.0 g/50 ml of dosage and equilibrium time of 120 mins. It was suggested that the Redlich-Peterson isotherm model ($R > 0.981$) was best fitted than Langmuir, Freundlich and Temkin model.

Red Mud:

Red mud has been used for defluoridation of water, and samples were collected from Sitapura Industrial area, Jaipur (Rajasthan).²⁴ 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. A zirconium hydroxide modified red mud porous material (RMPM) has been reported for removal of fluoride from aqueous solutions.²⁵ 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. A modified red mud with AlCl_3 (MRMA) and further modified by heat activated red mud (MRMAH) as adsorbent have been utilized for removal of fluoride from water.²⁶ The adsorption capacities of MRMA and MRMAH were 68.07 and 91.28 mg/g, respectively, which were much higher as compared to red mud (13.46 mg/g). The highest fluoride adsorption was achieved at range 7-8pH. The Langmuir isotherm was best fitted for isotherm study.

The fluoride evacuation limit of granular red mud in batch and column studies have been reported²⁷. 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 6hrs, while the column study shows 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. The defluoridation by using red mud as such and acid treated red mud by 5.5 M HCl for drinking have been purposed.²⁸ The maximum fluoride removal was obtained at pH 5.5 and the time required to attain equilibrium was 2hrs. The most extreme fluoride adsorption limits were observed to be 3.12 and 6.29 mg/g, respectively.

Bauxite:

A bauxite for defluoridation of water has been used.²⁹ The optimum adsorbent dose was observed to be 1.8 g/50ml and equilibrium was reached in 90 mins with the optimum pH of 6. The fluoride removal of 94% was obtained at optimum conditions and the experimental data fitted well with Langmuir isotherm model. A high alumina (81.5%) content bauxite has been reported for the removal of fluoride for the contaminated water.³⁰ The fluoride percentage removal by 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 R^2 value of 0.986.

Mud pot:

The raw pots are subjected to heat treatment as in the case of brick production. Hence the mud pot also will act as an adsorbent media. As per treatability-study results a marginal reduction in water fluoride level from 1.8 ppm to 1.5 and 1.4 ppm at the end of 2 days and 4 days respectively, which is practically not significant. The water pH was raised from 7.7 to 8.11 and 8.14 the end of 2 and 4 days, respectively, which is beyond the acceptable limits of alkalinity. The fluoride removal capacity will vary with respect to the alumina

content present in the soils used for pot production, which is beyond the control of manufacturer. So, in a practical sense the use of mud pot for defluoridation is not promising. However, people can be advised to use mud pots to store water that is treated by other techniques, which results in partial defluoridation. The major advantages of mud pots are they are economic and readily acceptable for the rural communities.³¹

Leaves:

The Sal (*Shorea Robusta*) leaf powder of particle sizes 0.3 and 1.0 mm have been introduced for defluoridation of water.³² 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 7.5 and dose of 1g/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 defluoridation capacity of Sal powder (0.3mm) was found to be 1.28 mg/g. The adsorption process obeyed Freundlich isotherm model. The lanthanum modified carbon (LMC) derived from *Sargassum* sp. has been prepared for fluoride removal from water.³³ The optimum pH range was 3-9. Where adsorption reaction was high and 90% of adsorption occurred in first 1 hr and reached to equilibrium within 4 hrs. The maximum adsorption capacity of LMC was 94.34 mg/g at neutral pH which was more than other commercial adsorbent. The adsorption mechanism was mainly controlled by outer-sphere complex, electrostatic attraction and ion-exchange. It was suggested that the LMC had awesome prospective in industrial application.

A novel, cheap, easily available and eco-friendly adsorbent obtained from treated *Citrus limonum* (lemon) leaf has been employed with the aim of fluoride ion removal from aqueous environment.³⁴ Batch experiments were performed to study the influence of various experimental variables such as pH of aqueous solution (2–8), adsorbent dose (1–10 g/50 mL fluoride solution), contact time (5–145 mins), initial fluoride concentration (2–15 mg/L) and the presence of few competing anions on the adsorption of fluoride on *C. limonum* (lemon) leaf adsorbent. The most efficient fluoride removal was at pH 2, and that the tested adsorbent shown the maximum defluoridation capacity of 70% of 2 mg/L fluoride ion. The experimental data revealed that both the Langmuir and Freundlich isotherm models fitted with the fluoride sorption process but followed a Freundlich isotherm model very well. The Tulsi (Holy Basil) leaves have been reported for removal of fluoride from groundwater.³⁵ The fluoride removal of 95% from groundwater was achieved within 20 mins. It was 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.

The Silikha (*Terminalia chebula*) leaf powder has been utilized for the defluoridation of aqueous solution.³⁶ The fluoride removal of 74% was obtained at the natural pH of 6.8 at 303K temperature. The defluoridation measurements fitted well with the pseudo-second-order kinetic model. The equilibrium time of 120 mins for defluoridation process. It indicated the high degree of affinity for fluoride sorption. Silikha leaf powder was used as a cost effective biosorbent for treating fluoride bearing water. Similarly the Devdaru (*Polyalthia longifolia*) leaf powder (DLP) as bisorbent also used for removal of fluoride from aqueous solution in batch process.³⁷ 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.

The fluoride removal capacity from aqueous solution by *Ficus religiosa* (peepal) leaves powder of size less than 196 μm has been examined.³⁸ 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 mins of the equilibrium time at 30°C. The Freundlich isotherm model was 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. The defluoridation capability of Basil (*Ocimum sanctum*, Lamiaceae) or Tulsi leaves have been investigated by stem and extract of fresh leaves from aqueous solution in batch process.³⁹ 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 mins, respectively. Thus, it was suggested that 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).

The defluoridation of drinking water samples has been investigated by using drum stick leaves (DSL), drum stick bark (DSB), black clay soil (BCS), alluvial soil (AS), millet husk (MH) and wheat husk (WH).⁴⁰ The samples were taken from hand pumps of 15 villages of Rajgarh (Block), Madhya Pradesh (India) containing 2.5 to 4.0 ppm of fluoride. 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. The peoples living in fluoride infected areas were addicted to take drum stick vegetable in their diet and used pitcher cultivated from Black clay and alluvial soil for storing drinking water. The defluoridation capacity from a fluid arrangement by thermally initiated neem (*Azadirachta indica*) leaves carbon (ANC) and kikar (*Acacia arabica*) leaves carbon (AKC) has been examined in electric furnace at 400 °C.⁴¹ 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.

The leaf powder of neem (*Azadirachta indica*), pipal (*Ficus religiosa*) and khair (*Acacia catechu* wild) trees with and without chemical treatment have been utilized as adsorbents to remove fluoride from aqueous solution.⁴² 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 mins at 29±0.5°C. The experimental data was 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.

Barks:

A thermally treated Babul bark powder in a muffle furnace at 700 °C for 2 hrs has been used for defluoridation of aqueous solution.⁴³ 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 and an equilibrium time achieved in 8 hrs at 303K. The experimental results of 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. The activated carbon prepared by carbonization of *Acacia Auriculiformis* scrap wood char at 750°C under nitrogen atmosphere followed by microwave heating for 5 mins has been reported for removal of fluoride from water.⁴⁴ 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 30-40°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 and 19.022 J/mol-K, respectively as per thermodynamic study.

The defluoridation of water by using low-cost pine wood and pine bark chars (derived as a by-product from bio-oil production unit) that were obtained as a by-product from fast pyrolysis in an auger reactor at 400 and 450 °C have been presented.⁴⁵ The optimum pH was 2.0 and optimum equilibrium time was 48 hrs 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 and 9.77 mg/g at 25 °C. The rate of fluoride adsorption followed pseudo-second-order kinetic model. The pine biochars (SBET 2-3 m²/g) removed more fluoride than activated carbon (SBET 1000 m²/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 waste water then used for water treatment due to low pH of 2.0. The Moringa indica bark activated carbon has been employed for defluoridation of aqueous solution.⁴⁶ The minimum contact time for maximum fluoride removal was 25 mins. The maximum removal of 80% was achieved for 3 mg/L initial fluoride concentration solution of 3g/L dose at pH 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.

Coir:

The defluoridation capability of thermally treated betel nut coir charcoal (BNC) powder has been investigated.⁴⁷ BNC was synthesized at 200-300°C for 2-3 hrs 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 mins. The ideal pH for most extreme fluoride evacuation was accomplished at pH 6.0. The isotherm was fitted well for both Langmuir and Freundlich isotherms. The kinetic study revealed that result obeyed pseudo-second order for adsorption.

Tamarind (*Tamarindus indica*):

Tamarind is an economically important tropical evergreen tree which grows abundantly in the dry tracts of Central and South Indian States. The hard pod shell is removed and discarded when the fruit is ripe, and the fruit is the chief acidulant used in the preparation of foods. Tamarindus indica fruit shells were activated by ammonium carbonate and then carbonized. This material with a BET surface area of 473 m²/g was used for defluoridation.⁴⁸ The removal of fluoride ions from aqueous solution was highly dependent on the pH of the solution in many cases, as it alters the surface charge on the adsorbents. The experimental results revealed that for pH values from 3.0 to 7.0, the fluoride uptake capacity of ammonium carbonate activated Tamarindus indica fruit shells in shaking and stirring experiments increased from 1.84 mg/g to 16.0 mg/g and from 3.12 mg/g to 19.5 mg/g, respectively. Fluoride uptake capacity falls below 7.0 pH and declines above 12.0 pH with 3.12 mg/g and 5.14 mg/g for shaking and stirring dynamic studies respectively. In both the shaking and stirring dynamic experiments, the increase in the concentration of co-ions increased their inhibiting ability. The defluoridation capacities of activated and MnO₂-coated tamarind fruit shell, using batch and column sorption techniques investigated by the fluoride removal capacity of the sorbents was found to be 1990 mg/kg after the contact time of 30 min, at an optimum pH value 6.5.⁴⁹

Grass:

The iron oxide based nanocomposite (IBNC), titania based nanocomposite (TBNC) and micro carbon fibre by using Bermuda grass based nanocarbon carbon fibre upon warmth treatment at 800°C in nitrogen atmosphere in the presence of metal oxides were used for defluoridation.⁵⁰ The defluoridation capacity of IBNC, TBNC and micro carbon fibre was nearly to 97, 92 and 88% respectively 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 information fitted well with Freundlich isotherm model and the adsorption process was found to be spontaneous in nature. Alkali-steam treated water hyacinth and elephant grass used for defluoridation of aqueous solution.⁵¹ 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 mins, 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 (-ΔG) as well as exothermic (-ΔH) in nature and negative values of entropy (-ΔS) 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.

The cynodon dactylon (Burmuda grass) based thermally activated carbon studied for defluoridation of water.⁵² 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 (qm) obtained for cynodon 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.

Saw dust:

The adsorption capacity of sawdust from kail wood examined for defluoridation of aqueous solution in batch process.⁵³ More than 70% maximum removal of fluoride was achieved under optimum condition, including pH of 7.0, contact time of 120 mins 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. The defluoridation potential of brick powder, coal, saw dust and mixture of adsorbents from aqueous solution was investigated.⁵⁴ 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 mins 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 and Langmuir 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.

Root:

The defluoridation capacity of Vetiver root powder was investigated as an adsorbent from water.⁵⁵ The Vetiver had removed 80 to 90% of fluoride from water at pH range 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.

Seeds:

The low cost activated carbon from pitacelobium dulce carbon (PLDC) has been utilized for defluoridation of water and compared it with commercial activated carbon (CAC).⁵⁶ 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% respectively at pH 9. 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. 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. The *Moringa oleifera* (MO) raw seed cake used as natural coagulant and prepared composite coagulant by adding alum and starch with MO seed cake for removal of fluoride from aqueous solution.⁵⁷ In both 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.

The chemically activated (CaCl_2) 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. And fluoride removal efficiency of 93, 93.5 and 94.5%, respectively.⁵⁸ The defluoridation capacities of lignite (L) and restructured surface of lignite (RSL) using a biomaterial called Cuminum cyminum has been investigated.⁵⁹ The RSL has BET surface area 3.12 times greater than lignite and the carbon content was increased by 13%. The fluoride removal capacities of RLA and L adsorbents were 15.8 mg/g and 13.8 mg/g at pH 7.93 ± 0.03 respectively, with particle sizes of 150-90 μm and 20g/L of dose. The experimental data well fitted for pseudo-second-ordered kinetic model along with the Langmuir isotherm model.

The defluoridation capacity of Strychnos Potatorum (SP) from aqueous solution in batch mode have been studied.⁶⁰ 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 and Freundlich isotherms. 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 has been examined.⁶¹The 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.

The removal of fluoride from aqueous solution by mechanically modified guava seeds (MGS) for water in batch mode has been reported.⁶²The experimental data well fitted 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 2g 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. The defluoridation efficiency of alkali and acid treated drumstick (*Moringa oleifera*) seed powder from aqueous solution has been reported.⁶³The 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 and 600 μ particle size adsorbents at pH of 8 and contact time of 2 and 2.5 hrs, respectively.

The 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 has been reported.⁶⁴The maximum removal was found at pH range of 5-8. The experimental results fitted well with the pseudo-second-order model and Langmuir isotherm. 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* and chemical like Manganese Sulphate and Manganese Chloride have been studied.⁶⁵Rice 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.

The defluoridation capacity of Pristine, purified and polyaniline coated tamarind seed (TS) from water was investigated.⁶⁶ 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 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 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.

The potential of tamarind seed, a household waste that was left after removing the tamarind pulp for food preparation that mainly contains polysaccharide has been evaluated.⁶⁷The 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 L of water containing fluoride concentration of 5 mg/l. Thus, for the treatment of 10 litter 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.

Plants:

The potential of *Cissus Quadrangularis* (CQ) powder for removal of fluoride from water in batch process has been investigated.⁶⁸ 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 and Freundlich adsorption isotherms were fitted well as per the study. The biomass of *Tinospora cordifolia* plant powder has been prepared of 1.18 μm particle size after washing and drying in the sun and hot air oven at 60°C.⁶⁹ 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. The Pseudo-first-order kinetic model fitted well as compared to second-order kinetic model.

The activated Dolichos lablab carbon (NDLC) was reported 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 HNO₃.⁷⁰ 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.

Stems:

The nitric acid activated carbon has been prepared from the stem of an *Abutilon Indicum* plant (NAbIC) and utilized for defluoridation of water.⁷¹ The maximum removal of more than 80% was achieved at pH 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°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 physisorption. The effect of co-ions was found in the order of PO₄[>]HCO₃[>] SO₄²⁻> NO₃³⁻> Cl⁻. The phosphate ions reduced the fluoride removal from 83 to 68.7% with 50 mg/L concentration.

The potential studied 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 hrs in muffle furnace.⁷² 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 bisorption equilibrium was achieved within 180 minutes with 94% removal. The 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 has been synthesized for defluoridation of water.⁷³ The 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 m²/g and 81%, for AGAC was 1065 m²/g and 83% and for TBAG was 365 m²/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 than the Langmuir isotherm model. 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.

The study of fluoride removal capability of a *Khimp* plant (*Leptadenia pyrotechnica*) stem powder, having sufficient positive (calcium) ions that adsorbed the negatively charged fluoride ions has been reported.⁷⁴ The fluoride removal mechanism was mainly governed by precipitation and adsorption (CaF₂) onto khimp powder. The maximum fluoride removal of 97% was achieved at pH 6.7 \pm 0.1 with an adsorbent dosage of 6.0g/L of biomass with a contact period of 60 minutes. The employed equilibrium adsorption data obeyed both Langmuir and Freundlich isotherms. A heat activated neem stem charcoal for defluoridation of aqueous solution has been utilized.⁷⁵ 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.

Agricultural Waste:

The feasibility of activated bagasse carbon (ABC), sawdust raw (SDR) and wheat straw raw (WSR) has been investigated for water defluoridation and compared them with commercial activated carbon (CAC).⁷⁶ 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. The fluoride removal capacity of zirconium impregnated walnut shell carbon (ZIWSC) has been studied.⁷⁷ 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 μm 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%.

The capability of bagasse, modified bagasse with 1 M of NaHCO_3 and chitosan has been investigated for removal of fluoride from water.⁷⁸ 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. The Langmuir adsorption capacity of modified bagasse, bagasse and chitosan were 9.033, 2.034 and 1.463 mg/g, respectively. The fluoride removal capability of zirconium impregnated lapsi seed stone activated carbon (ZILSSAC) also reported.⁷⁹ The optimal condition of fluoride removal was achieved at pH 3-4, contact time of 180mins 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.

The fluoride removal capacity of the carbon obtained from pecan nut shells have been reported.⁸⁰ The modified calcium solution extracted from egg shells (CMPNS) was 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 (R²) 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 hydrogen carbonate 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 ground water. The capability of zirconium loaded garlic peel (Zr-GP) as adsorbent has been reported for removal of fluoride from water.⁸¹ The Langmuir maximum adsorption capacity of Zr-GP at equilibrium pH 2 and 6 were 1.10 and 0.89 ml F/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.

The potential of zirconium impregnated cashew nut shell carbon (ZICNSC) has been studied for defluoridation of water.⁸² 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 53 μm 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 mins. similarly, the fluoride removal capacity of zirconium impregnated groundnut shell carbon (ZIGNSC) from water also investigated.⁸³ 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 303 and 333K,

respectively. The kinetic study followed the pseudo-second-order equation. It was concluded the reported the bicarbonate ions was responsible for decrease of fluoride removal from 84 to 74.6%.

The applicability of zirconium impregnated coconut fibre carbon (ZICFC) as adsorbent has been reported for defluoridation of water.⁸⁴ 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. The combinations of chemisorption and physisorption processes with intraparticle diffusion were responsible for the high defluoridation capacity of ZICFC. The potential of zirconium impregnated coconut (ZICSC) shell carbon has been investigated for fluoride removal from water.⁸⁵ The 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.

The fluoride removal capacity of zirconium impregnated groundnut shell, coconut shell coconut fibre and activated charcoal have been studied from water in continuous down flow column at the constant rate of 0.6-0.7 L/hr.⁸⁶ The zirconium ion impregnated coconut fibre, charcoal (ZICFC) showed maximum fluoride uptake after that the groundnut shell and coconut shell carbon showed its effect in decreasing order. The ZICFC was treated in 21 litre of (8.0 mg F⁻/L) test solution and 6 L of (2.47 mg F⁻/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. The regeneration of the ZICFC was accomplished by elution with 0.02 M of NaOH solution.

The potential of KMnO₄ modified activated carbon derived from steam pyrolysis of rice straw (RS₂/KMnO₄) as adsorbent has been investigated for fluoride removal from water.⁸⁷ 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 hrs, 25°C temperature and 20 ppm of initial fluoride concentration. The kinetic study followed the pseudosecond-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 sulphate and to 94 % in case of bromide but chloride had no significant effect on fluoride adsorption. The defluoridation capacity of untreated and aluminium chloride and calcium chloride treated powdered corn cob has been investigated as an adsorbent for removal of fluoride from drinking water.⁸⁸ The 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 mins. 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.

The 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 have been reported.⁸⁹ 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.

Conclusions:

This paper describes the review on the various low cost adsorbents used for the effective removal of fluoride from water. Fluoride in groundwater has been a potential problem to human society.

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