REMOVAL OF FLUORIDE FROM AQUEOUS SOLUTION BY USING INEXPENSIVE BARK AND WOOD BASED BIO-ADSORBENTS: A COMPREHENSIVE REVIEW

N. G. Telkapalliwar[1,*] and V. M. Shivankar[2]

[1,2]*Department of Chemistry, Dr. Ambedkar College, Deekshabhoomi, Nagpur, Maharashtra, India*

ABSTRACT

Fluoride is a persistent and non-biodegradable pollutant that accumulates in soils, plants, animals and human being. Fluoride in drinking water has a profound effect on teeth and bones in human. This review article is aimed at providing precise information on efforts made by various researchers in the field of fluoride removal for drinking water by using bark and wood as low cost bio-adsorbents. The most important results of extensive studies on various factors such as pH, contact time, initial fluoride concentration, temperature fluctuate removal of fluoride efficiency of adsorbents along with the various isotherm models and kinetic model reported by researcher are reviewed.

1.   Introduction

Water is an essential natural resource for sustaining life and environment that is thought to be available in large quantity as a free gift of nature. However, over the past few decades, the ever-increasing population, urbanization, industrialization and unskilled utilization of water resources have led to the degradation of water quality, causing its reduction in per capita availability in various developing countries [1]. Thus there is a substantial shortfall in the availability of potable water in less developed or developing countries, primarily due to water contamination and pollution [2–4]. It has also been reported that about 80% of the diseases in the world are due to poor quality of drinking water, and the fluoride contamination in drinking water is responsible for 65% of endemic fluorosis in the world which affects the teeth, bone and soft tissues [2,5,6].

Fluorine (F_2) is a pale, yellow-green, corrosive gas which almost cannot be found in natural environment in elemental form due to its high electronegativity and reactivity. Fluoride (F^-) is a fluorine anion characterized by small radius, great tendency to behave as ligand and easiness to form a great number of different organic and inorganic compounds in soil, rocks, air, plants and animals. Some of those compounds are quite soluble in water, so fluoride is present in surface and groundwater as an almost completely dissociated fluoride ion [7,8].

It exists in the form of fluorides in various minerals such as sellaite (MgF_2), fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($Ca_5(PO_4)_3F$). Thus fluorides are also found in rocks, soil, plants, animals, humans and fresh as well as ocean water [9,10]. Therefore fluoride occurs naturally in public water systems as a result of runoff from weathering of fluoride-containing rocks and soils and leaching from soil into ground water [9–12]. In addition to water, fluoride is present naturally in almost all foods and beverages but levels vary widely. However, fluoride has both beneficial and harmful effects on human health depending on its level. Among the beneficial effects of fluoride in the human body, strengthening of bones and prevention from tooth decay are significant [12]. Compared to its beneficial effect fluoride is more detrimental. Thus fluoride is a toxic chemical and it is a risk factor for thyroid hormone production in children when the exposure to fluoride occurs during intrauterine growth period [13]. A report during 2008 in Scientific American on 'second thoughts about fluoride was a warning to all concerned as it revealed the risk of fluoride causing disorders affecting the teeth, bone, brain and thyroid gland [13,14]. It has also been reported that thyroxine and triiodothyronine in serum decreased with increasing urinary fluoride in cattle. Cattle affected with fluorosis developed hypothyroidism and anemia [13]. In addition, it has been confirmed that

there is significant positive relationship between fluoride intake by water and the prevalence of dental fluorosis [9,15–18]. For the general population the intake of fluoride is mainly from drinking water and to a much lesser extent from foodstuffs i.e. drinking water is the major source of daily intake of fluoride [1,9,19].

Due to fluoride pollutions and health problems that it causes, the World Health Organization (WHO) has specified the tolerance limit of fluoride content of drinking water as 1.5 mg/L [20]. Various technologies available to remove fluoride from water, such as coagulation and precipitation [21,22–26], membrane processes [27–35], electrochemical treatments [36,37–46], ion-exchange and its modification [47–53], but the adsorption process is generally accepted as the cheapest and most effective method for removal fluoride from water [1,54,55,56–59].

## 2.	Removal of different pollutants by adsorption:

Adsorption is a surface phenomenon with common mechanism for organic and inorganic pollutants removal. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, liquid–solid intermolecular forces of attraction cause some of the solute molecules from the solution to be concentrated or deposited at the solid surface. The solute retained (on the solid surface) in adsorption processes is called ad- sorbate, whereas, the solid on which it is retained is called as an adsorbent. This surface ac- cumulation of adsorbate on adsorbent is called adsorption. This creation of an adsorbed phase having a composition different from that of the bulk fluid phase forms the basis of separation by adsorption technology. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physicsorption (characteristic of weak Van Der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction.

The term pollutant, in a broad sense, refers to a substance/material that changes the natural quality of the environment by physical, chemical, or biological means. Thus, we may have pollution in air, water, and soil. The three main activities that mankind indulges in are domestic, agricultural, and industrial. In all of these activities, a large amount of fresh water is used, which is discharged as wastewater containing different pollutants depending on the type of activity. These may be various inorganic, organic chemicals and biological agents as well as heat and radiations The removal of these pollutants such as dyes, heavy metals, phenols, pyridine, nitrobenzene, pesticides, biological active agents, dissolved and non-dissolved chemicals, radioactive substances, detergents, polychlorinated biphenyls and other organic hazardous chemicals by different adsorbents (Alumina, Bauxite, Silica gel, Zeolites, ion exchange resins, animal/plant/tree based biosorbents, Carboneous materials, natural soils, clays, alloys, bone char, chitosan, geomaterials, agricultural wastes, industrial products/by-products/wastes, metal oxides/hydroxides, nanomaterials, nanocomposit materials, carbon materials, etc.) has been discussed by Gupta V. K., et al., 2009 [60], George z. Kyzas et al. 2014 [61], M. Mohapatra et al. 2009[62], Vaishali Tomar et al., 2013[63] and Mirna Habuda-stanic et al., 2014 [64] in their review articles.

## 3.	Chemical composition of bark and Wood:
### 3.1.	Bark:

Bark is the outermost layers of stems and roots of woody plants. Plants with bark include trees, woody vines, and shrubs. Bark refers to all the tissues outside of the vascular cambium and is a nontechnical term.[65] It overlays the wood and consists of the inner bark and the outer bark. The inner bark, which in older stems is living tissue, includes the innermost area of the periderm. The outer bark in older stems includes the dead tissue on the surface of the stems, along with parts of the innermost periderm and all the tissues on the outer side of the periderm. The outer bark on trees which lies external to the last formed periderm is also called the rhytidome. Bark tissues make up by weight between 10-20% of woody vascular plants and consists of various biopolymers, tannins, lignin, suberin, suberan and Polysaccharides[66]. Up to 40% of the bark tissue is made of lignin which forms an important part of a plant providing structural support by crosslinking between different polysaccharides, such as cellulose [66]. Condensed tannin, which are in fairly high concentration in bark tissue, is thought to inhibit decomposition [66]. It could be due to this factor that the degradation of lignin is far less pronounced in bark tissue than it is in wood. It has been proposed that, in the cork layer (the phellogen), suberin acts as a barrier to microbial degradation and so protects the internal structure of the plant [66,67].

### 3.2.	Wood:

Wood is a porous and fibrous structural tissue found in the stems and roots of trees, and other woody plants. It has been used for thousands of years for both fuel and as a construction material. It is an organic material, a natural composite of cellulose fibers (which are strong in tension) embedded in a matrix of lignin which resists

compression. Wood is sometimes defined as only the secondary xylem in the stems of trees [68]. In a living tree it performs a support function, enabling woody plants to grow large or to stand up by themselves. It also conveys water and nutrients between the leaves, other growing tissues, and the roots. Wood may also refer to other plant materials with comparable properties, and to material engineered from wood, or wood chips or fiber. Wood is a heterogeneous, hygroscopic, cellular and anisotropic material. It consists of cells, and the cell walls are composed of micro-fibrils of cellulose (40% – 50%) and hemicellulose (15% – 25%) impregnated with lignin (15% – 30%) [69]. The chemical composition of wood varies from species to species, but is approximately 50% carbon, 42% oxygen, 6% hydrogen, 1% nitrogen, and 1% other elements (mainly calcium, potassium, sodium, magnesium, iron, and manganese) by weight [70]. Wood also contains sulfur, chlorine, silicon, phosphorus, and other elements in small quantity.

Bark and wood materials contain proteins, polysaccharides and lignin with their functional groups which are responsible for adsorption [71]. The large occurrence and presence of high amount of surface functional groups make various tree barks good alternatives to expensive synthetic adsorbents [72]. In recent years, many researcher widely studied removal of fluoride from waste water by using bark and wood as low cost biosorbents.

4.   Literature review on removal of fluoride by different bark and wood based adsorbents:

In recent years, many researcher widely studied removal of fluoride from waste water by using bark and wood as low cost biosorbents. Tree bark wood remains the most widely studied adsorbent, and it has been found to adsorb a variety of materials such as metals, dyes, phenols, and a host of other organic compounds and bio-organisms, and is therefore used for the removal of fluoride from wastewaters by adsorption. The design and operation of the process is convenient and can be handled easily, and the operational costs are therefore comparatively low. As a result, the cost of the adsorbent, and the additional costs of regeneration if required, can be a significant fraction of the overall process costs. These materials have been used as such and sometimes after some minor treatment, and are widely known as low-cost adsorbents. In this review article, a summary of some relevant published data with some of the latest important results and giving a source of up-to-date literature on the adsorption properties of tree bark and wood adsorbents is presented in Table 1, and some of the results are discussed here.

4.1   Bark based adsorbents:

Patil Satish et al. 2012, described the process of removal of excess fluoride from water by using Almond tree bark powder (ATBP). He prepared almond tree bark adsorbent by treating with 1 N nitric acid for 3 days. He has studied the effect of pH, contact time, adsorbent dose, fluoride ion concentration, temperature, particle size of adsorbent and agitation speed on removal efficiency of fluoride along batch adsorption experiment. The adsorption kinetics has been found to follow first order rate mechanism and adsorption isotherm followed Freundlich, Langmuir and Temkin models for ATBP [73].

Suneetha et al., 2015 has reported the removal of fluoride from polluted waters using active carbon derived from barks of Vitex negundo plant. He has synthesized nitric acid activated carbon derived from barks of Vitex negundo (NVNC) plant which is found to be an effective adsorbent for the de-fluoridation of waters. The activated carbon is characterized adopting various physicochemical methods and surface morphological studies are carried out using FT-IR and SEM-EDX techniques. The adsorption process is satisfactorily fitted with Langmuir adsorption isotherm with good correlation coefficient value and it indicates monolayer adsorption. The adsorption kinetics is found to follow pseudo-second-order kinetics. The Dubinin-Radushkevich mean free energy and Temkin heat of sorption confirm the physisorption nature as these are lower than 20kJ/mol. De-fluoridation is maximum at the pH: 7.0, adsorbent dosage: 4.0g/lit; equilibrium time: 50 min, Particle size: 45μ and temperature: 30 ± 1°C. The correlation coefficient values for the adsorption isotherms: Freundlich, Langmuir, Temkin and Dubinin-Radushkevich are 0.929, 0.998, 0.980 and 0.946 respectively and for kinetic models: pseudo-first-order, pseudo-second-order, Weber and Morris intraparticle diffusion, Bangham's pore diffusion and Elovich equations are 0.989, 0.994, 0.874, 0.902 and 0.912 respectively. The Temkin heat of sorption, B, and the Dubinin-Radushkevich mean free energy, E, for the activated carbon adsorbent are 0.196 J/mol and 7.07 kJ/mol respectively. The procedure developed is remarkably successful in de-fluoridation of real ground water samples [74].

The applicability of drumstick (Muringa odecifera) bark as adsorbent for the removal of fluoride from water was investigated by D. Santhi [75]. The treatment of dry drumstick bark reduced the fluoride concentration from 5 ppm to 2.4 ppm within an hour. After 24 hours the value of fluoride is slightly reduced than 1 hour treatment but pH of the solution is 8.69, after treatment, the solution becomes acidic ie pH=6.15. After 24 hours treatment, the solution became pale yellow and smell of the solution was changed.

Bhagyashree M. Mamilwar et al. [76] reported result of water defluoridation using a bark of babool (Acacia nilotica tree bark) as adsorbent. The effects of controlling parameters like optimum dose, contact time, pH,

temperature etc. were study. The result shows that activated carbon of bark of babool of 5g/L accomplished a removal of 77.04% of Fluoride from a 5mg/L of Fluoride concentration at normal pH of 8.0 requiring an equilibrium time of 8 hours. The experimental adsorption data fitted with Langmuir and Freundlich adsorption isotherms. The pseudo-second-order kinetic model fitted well as compared to pseudo first-order model. The effects of co-existing ions present in groundwater were also studied.

Dinesh Mohan et al.[77] synthesized a Low-cost pine bark (PB) chars, obtained as a by-product from fast pyrolysis in an auger reactor at 400 and 450 °C, were characterized and used as received for water defluoridation. Sorption studies were performed at different temperatures, pH values, and solid to liquid ratios in the batch mode. Maximum fluoride adsorption occurred at pH 2.0. A kinetic study yielded an optimum equilibrium time of 48 h with an adsorbent dose of 10 g/L. Sorption isotherm studies were conducted over a concentration range of 1–100 mg/L. Fluoride adsorption decreased with an increase in temperature. The char performances were evaluated using the Freundlich, Langmuir, Redlich–Peterson, Toth, Temkin, Sips, and Radke adsorption models. Based on average percent error, the best isotherm fits follow the orders for pine bark: $PB_{Toth} > PB_{Radke-Prausnitz} \approx PB_{Freundlich} > PB_{Redlich-Peterson} > PB_{Langmuir} > PB_{Sips} > PB_{Temkin}$. The pinebark chars successfully treated fluoride-contaminated groundwater at pH 2.0. The chars swelled in water due to their high oxygen content (8–11%), opening new internal pore volume. Fluoride could also diffuse into portions of the chars' subsurface solid volume promoting further adsorption.

Sutapa Chakrabarty et al. [78] investigated removal of fluoride using a neem charcoal as a adsorbent. In the study, Neem stem charcoal (Azadirachta indica) have been used as adsorbing media showed that the adsorbent were highly influenced by temperature, pH of the solution, and initial fluoride concentration. The biosorbent was successful in removal of fluoride ions from aqueous solution of 10mg/l fluoride concentration with about 94% efficiency. Biosorption equilibrium was achieved within 180 minutes. The adsorption was pH dependent with maximum adsorption achieved at pH 5.0. Both Langmuir and Freundlich isotherm models fits well to the adsorption mechanism. The regression coefficient of both pseudo first order and pseudo second order plot indicates adherence of both the rate laws but higher regression value of second order plot than the pseudo first order reaction indicates that the adsorption follows the second order rate law. The Webber and Morris plot reveals an initial curved path indicating boundary layer effect followed by a linear path indicating pore diffusion.

Jain J. K. et al. [79] prepared carbonised Neem bark powder (NB) at 500^0C for removal of fluoride by adsorption. The experiment has followed batch process. The effect of contact time has been studied in detail. The adsorption kinetics has been to follow first order rate mechanism and adsorption isotherm process followed Freundlich and Langmuir models. The adsorbent used in the study have proved to be very efficient and economical for removing fluoride from water.

G. Karthikeyan et al. [80] synthesized acid treated activated carbon of Morringa Indica bark for removal of fluoride from aqueous water. Batch adsorption experiments using activated carbon prepared from Morringa Indica bark were conducted to remove fluoride from aqueous solution. A minimum contact time of 25 min was required for optimum fluoride removal. The influence of adsorbent, dose, pH, co-ions (cations and anions) on fluoride removal by the activated carbon has been experimentally verified. The adsorption of fluoride was studied at 30°C, 40°C and 50°C. The kinetics of adsorption and adsorption isotherms at different temperatures were studied. The fluoride adsorption obeyed both Langmuir and Freundlich isotherms and followed a pseudo first order kinetic model. The thermodynamic studies revealed that the fluoride adsorption by Morringa Indica is an endothermic process indicating an increase in sorption rate at higher temperatures. The negative values of $\Delta G°$ indicate the spontaneity of adsorption. SEM and XRD studies confirmed the surface morphological characteristics of the adsorbent and the deposition of fluoride on the surface of the material.

4.2.   Wood based adsorbents:

K. A. Emmanuel et al. [81] investigated the removal of fluoride on commercial activated carbon (CAC) and indigenously prepared activated carbons (IPACs) from Pithacelobium dulce(PLDC) and Peltophorum ferrugineum(PFC). The effects of various experimental parameters like pH, dose of the adsorbent, adsorbate concentration and contact time have been investigated using a batch adsorption technique. The extent of fluoride removal increased with decrease in the initial concentration of fluoride and particle size of the adsorbent and also increased with increase in contact time, amount of adsorbent used and the initial pH of the solution. Adsorption data were modeled using the Freundlich and Langmuir adsorption isotherms. Kinetic experiments follow first order kinetic equation. The experimental data produced a straight line fit with a relatively good correlation coefficient (R^2) indicating the acceptability of the model for the studied indigenously prepared activated carbons (IPACs) fluoride system. The kinetics of adsorption was found to be first ordered with regards to intra-particle diffusion rate. The adsorption capacities of PLDC (78.96 mg/L) and PFC (74.48mg/L) have been compared with that of the CAC (39.20) in drinking water treatment for removal of fluoride.

Laura R. Brunson et al. [82] presents the results from amending eucalyptus wood char with the following metal salts: aluminum sulfate, aluminium chloride, iron (II) chloride, and iron (III) nitrate. The results show that amending wood char with metal salts, which precipitate from the solution as metal oxides and amend the char surfaces, increases the ability of the wood char to remove fluoride from drinking water. Wood char alone has a $Q_{e1.5}$ value of 0.04 mg/g, whereas the $Q_{e1.5}$ values of the metal-amended wood chars range from 0.14 to 2.06 mg/g. Iron oxide amendments resulted in greater improvements in fluoride removal capacity than aluminum oxide amendments, with $Q_{e1.5}$ values of 2.06 and 0.76 mg/g for the iron oxide–amended chars and 0.57 and 0.14 mg/g for the aluminum oxide–amended chars. Pretreating wood char with the oxidizing agents potassium permanganate and hydrogen peroxide increased the metal loading and fluoride removal capacities in select instances. When wood char was pretreated with potassium permanganate and amended with aluminum sulfate, the $Q_{e1.5}$ value increased from 0.14 to 0.40 mg/g and the metal loading increased from 0.05 to 0.27%. This work offers several conclusions that provide new insights into increasing the fluoride removal capacity of wood char by amending it with metal oxides and using oxidation pretreatment processes. This research demonstrates that using aluminum oxide amendments and the less studied iron oxide amendments is effective at increasing fluoride removal by wood char. Although all four metal amendment methods showed statistically significant increases in fluoride removal above that of wood char alone, the iron oxide amendments actually resulted in higher fluoride adsorption than aluminum for all cases. The iron (III) nitrate showed a $Q_{e1.5}$ value that was over 50 times higher than that of wood char alone. Wood char amended with iron (III) nitrate exhibited the highest metal loading and the largest fluoride updates, but also demonstrated an inefficient use of iron when fluoride removal was normalized by metal loading. This result can likely be attributed to the reduced specific surface area caused by iron oxides blocking the pore spaces in the wood char and preventing full use of pore space and iron content. In contrast, the aluminum chloride–treated wood char showed the lowest metal loading but the highest efficiency when normalized by metal content. In all cases, pretreatment with oxidizing agents decreased the point of zero charge, and in most cases, potassium permanganate pretreatment increased metal loading and fluoride removal. Additionally, wood char, when treated with hydrogen peroxide or nitric acid, which was done in preliminary testing, was found to be less robust through the oxidation process than activated carbon used in oxidation tests conducted by other researchers. Therefore, the specific surface area decreased significantly with the stronger oxidation, i.e., pretreatment with hydrogen peroxide, but less with the potassium permanganate pretreatment. This suggests the weaker oxidation pretreatment is preferable for wood char. This work is one of the first to systematically study one starting material with several oxidizing agents and metal amendment processes. The conclusions from this work suggest that iron oxide amendment processes should be further explored for increased fluoride removal, particularly in geographic areas where iron amendment materials are readily available. Before any implementation of these materials, leaching studies and assessment of metal concentrations in the treated water should be conducted to ensure safe water consumption and disposal of used materials.

Monal Dutta et al. [83] prepared activated carbon by carbonization of Acacia Auriculiformis scrap wood char followed by microwave heating. A batch study on fluoride sorption was carried out at various experimental conditions, including different pH, initial fluoride concentrations, adsorbent concentrations, competitive anion chloride and different temperatures. Fluoride adsorption was found to be pH dependent and the maximum removal of fluoride was obtained at pH of 4.4. On the other hand, the fluoride adsorption was reduced in the presence of chloride ions. The percentage removal of fluoride was found to be increased with increase in temperature and adsorbent dose and a maximum removal of 97.2% was obtained with an adsorbent dose of 2 g/l. On the other hand, the adsorption of fluoride was also increased with decrease in particle size and the maximum removal occurred at a particle size of 58 μm. In order to investigate the mechanism of fluoride removal, various adsorption isotherms such as Langmuir, Freundlich, Tempkin and Herkin-Jura were fitted at 293, 303, and 323 K . The experimental data revealed that the Langmuir isotherm gave more satisfactory fit for fluoride removal. The monolayer adsorption capacity according to Langmuir isotherm was found to be 19.92 mg/g. The adsorption process was observed to follow a pseudo-second-order kinetic model. Thermodynamic parameters were also determined and change in enthalpy and entropy were found to be 6.094 kJ/mol and 19.022 J/mol-K respectively.

Mohammad Ali Zazouli et al.[84] investigated the performance of bicarbonate treated sorghum and canola as cheap natural adsorbents in fluoride (F) removal from water. The effect on adsorbent performance of various parameters, such as pH, adsorbent dose, contact time, and F concentration, were investigated. The F concentration was measured by spectrophotometer at λmax=570 nm. The isotherms and kinetics of adsorption were determined. The results indicated that F removal by both adsorbents increased with increasing contact time and adsorbent dose. However, the removal rate reached a constant amount with an 10 g/L dose of canola and sorghum after 90 and 60 min respectively. For an initial F concentration of 10 mg F/L, the F removal efficiency by the activated stalks of sorghum and canola was 94% and 79%, respectively. Maximum F removal was obtained at pH=5. The adsorption

data followed the type 2 Langmuir isotherm and the pseudo-second-order kinetic. The studied adsorbents can potentially be used as low-cost media for removal of F from, for example, industrial effluents.

Suman Mann et al. [85] studied the adsorption behaviour of sawdust of Kail wood has been studied in order to consider its application for fluoride removal. Batch adsorption and effects of various experimental parameters, such as pH (3-11), adsorbent dosage (0.5-2.5 g/l), particle size (90μm to 300μm), contact time (30-150 min) and initial concentration (5 to 30mg/l) were investigated. The equilibrium data have been analyzed by the Langmuir, Freundlich and Tempkin isotherm models, the experimental data were better fitted to the Langmuir equation. The adsorption kinetics also investigated by the pseudo-first-order, pseudo-second-order, intraparticle diffusion and Elovich model. The deflouridation process followed pseudo second order model.

5. Conclusion :

This review has attempted to cover a wide range of adsorbents which have been used so far for the removal of fluoride from the water.The fluoride removal have been broadly divided in two sections dealing with removal of fluoride by bark based and wood based bioadsorbents. The most important results of extensive studies on various factors such as pH, contact time, initial fluoride concentration and temperature fluctuates removal of fluoride efficiency of adsorbents along with the various isotherm models and kinetic model reported by researcher are reviewed. The review results indicated that very few research performed by using bark and wood based adsorbents which have potential for removal of fluoride from water than removal of other pollutants such as organic, inorganic, heavy metals, dyes, etc.

Table 1. : Comparative details of various bark and wood based adsorbents for removal of fluoride.

Adsorbents	pH range	Temperature Range (K)	Contact Time range (Min)	Concentration range (mg/L)	Isotherm model used	Kinetics model used	Maximum % Removal	Maximum adsorption capacity(mg/g)	Reference
Almond tree (Terminialia cattapa) bark powder (ATBP) (Nitric acid treated)	2-9	298-318	10 - 90	2 - 6	F,L,T	PF, PS, ID, E	--	0.166	[73]
Vitex negundo (NVNC) plant bark (Activated carbon with nitric acid treatment)	2-11	303-323	10-100	1-12	F, L, T, D-R	PF, PS, ID, E, BPD	99.2 %	1.150	[74]
Drumstick (Muringa odecifera) tree bark		RT	60	5	--	--	52 %	--	[75]
Bark of babool (Acacia nilotica tree bark) (Activated carbon)	2-12	293-313	60-600	1-15	F, L	PF, PS	77.04 %	1.891 at 293 K	[76]
Neem stem charcoal (Azadirachta indica)	2-10	RT	30-180	2-10	F,L	PF, PS, ID	94 %	1.27	[78]
carbonised Neem bark powder (NB)	--	298	10-90	--	F, L	PF, PS, ID	--	--	[79]
Acid treated activated carbon of Morringa Indica bark	2-12	303-313	5-35	2-6	F,L	PF, PS, ID	--	--	[80]
Nitric acid treated carbonized Pithacelobium dulce(PLDC)	4-10	303 ± 1	10-120	1-8	F,L	PF, PS, ID	89 %	78.96	[81]
Nitric acid treated carbonized Peltophorum ferrugineum(PFC)	4-10	303 ± 1	10-120	1-8	F,L	PF, PS, ID	78 %	74.48	[81]
Activated carbon of Acacia Auriculiformis scrap wood char	2.7-7	303-323	20-120	5-20	F,L,T, H-J Herkin-Jura	PF, PS, ID	97.2	19.92	[83]
Bicarbonate treated stalks of Sorghum	3-11	RT	10-180	20-100	F,L,T	PF, PS	94	7.8	[84]
Bicarbonate treated stalks of canola	3-11	RT	10-180	20-100	F,L,T	PF, PS	79	8.24	[84]
Sawdust of Kail wood	3-11	RT	30-150	5-30	F,L,T	PF, PS, ID, E	75.6	--	[85]

[*] RT-Room temperature.

[@] L: Langmuir, F: Freundlich, T: Tempkin, D-R : Dubinin-Radushkevich , R-P : Redlich–Peterson, H-J: Herkin-Jura isotherms.

[#] PF: Pseudo first order, PS: Pseudo second order, ID: Intraparticle diffusion model, E: Elovich model, BPD: Bangham's Pore diffusion kinetic models **.**

6. References :

[1]   Meenakshi, R.C. Maheshwari, Fluoride in drinking water and its removal, J. Hazard.Mater. 137 (2006) 456–463.

[2]   G. Viswanathan, A. Jaswanth, S. Gopalakrishnan, S.S. Ilango, G. Aditya, Determining the optimal fluoride concentration in drinking water for fluoride endemic regions in South India, Sci. Total Environ. 407 (2009) 5298–5307.

[3]   I.A. Shiklomanov, Appraisal and assessment of world water resources, Water Int.25 (2000) 11–32.

[4]   N.C.R. Rao, Fluoride and environment— a review, in: M.J. Bunch, V.M. Suresh, T.V. Kumaran (Eds.), Proceedings of the Third International Conference on Environment and Health, Chennai, India 15–17 December 2003, 386–399.

[5]   A.J. Felsenfeld, M.A. Robert, A report of fluorosis in the United States secondary to drinking well water, J. Am. Med. Assoc. 265 (1991) 486–488.

[6]   World Health Organization, Environmental Health Criteria 227: Fluorides, 2002.(Geneva)

[7]   Fluoride and Fluorides: Environmental Health Criteria 36, World Health Organization (WHO), Geneva, Switzerland, 1984.

[8]   Fluorides—Environmental Health Criteria 227, World Health Organization (WHO), Geneva, Switzerland, 2002.

[9]   Z. Mandinic, M. Curcic, B. Antonijevic, M. Carevic, J. Mandic, D. Djukic-Cosic, C.P. Lekic, Fluoride in drinking water and dental fluorosis, Sci. Total Environ. 408 (2010) 3507–3512.

[10]   N. Gandhi, D. Sirisha, S. Asthana, A. Manjusha, Adsorption studies of fluoride on multani matti and red soil, Res. J. Chem. Sci. 2 (2012) 32–37.

[11]   N. Chen, Z. Zhang, C. Feng, M. Li, D. Zhu, R. Chen, N. Sugiura, An excellent fluoride sorption behavior of ceramic adsorbent, J. Hazard. Mater. 183 (2010) 460–465.

[12]   A. Rafique, M.A. Awan, A. Wasti, I.A. Qazi, M. Arshad, Removal of fluoride from drinking water using modified immobilized activated alumina, J. Chem. 2013 (2013), http://dx.doi.org/10.1155/2013/386476 (Article ID 386476, 7 pages and references cited therein).

[13]   A.K. Susheela, M. Bhatnagar, K. Vig, N.K. Mondal, Excess fluoride ingestion and thyroid hormone derangements in children living in Delhi, India, Fluoride 38 (2005) 98–108.

[14]   D. Fagin, Second thoughts about fluoride, Sci. Am. 298 (2008) 74–81.

[15]   W. Binbin, Z. Baoshan, Z. Cheng, Y. Guangquian, L. Xiaojing, Relationship between fluorine in drinking water and dental health of residents in some large cities in China, Environ. Int. 30 (2004) 1067–1073.

[16]   G. E. J. Poinern, M.K. Ghosh, Y.-J. Ng, T.B. Issa, S. Anand, P. Singh, Defluoridation behavior of nanostructured hydroxyapatite synthesized through an ultrasonic and microwave combined technique, J. Hazard. Mater. 185 (2011) 29–37.

[17]   G. Viswanathan, A. Jaswanth, S. Gopalakrishnan, S.S. Ilango, Mapping of fluoride endemic areas and assessment of fluoride exposure, Sci. Total Environ. 407 (2009)1579–1587.

[18]   Z. Mandinic, M. Curcic, B. Antonijevic, C.P. Lekic, M. Carevic, Relationship between fluoride intake in Serbian children living in two areas with different natural levels of fluorides and occurrence of dental fluorosis, Food Chem. Toxicol. 47 (2009) 1080–1084.

[19]   N. Viswanathan, C.S. Sundaram, S. Meenakshi, Removal of fluoride from aqueous solution using protonates chitosan beads, J. Hazard. Mater. 161 (2009) 423–430.

[20]   Guidelines for Drinking-Water Quality, 3rd ed.; World Health Organization (WHO): Geneva, Switzerland, 2008; Volume 1.

[21]   Khatibikamal V., Torabian A., Janpoor F., Hoshyaripour G., Fluoride removal from industrial wastewater using electrocoagulation and its adsorption kinetics. J. Hazard. Mater. 2010, 179, 276–280.

[22]   Turner B.D., Binning P., Stipp S.L.S., Fluoride removal by calcite: Evidence for fluorite precipitation and surface adsorption. Environ. Sci. Technol., 39(2005)9561–9568.

[23]   El-Gohary F., Tawfik A., Mahmoud U., Comparative study between chemical coagulation/precipitation (C/P) versus coagulation/dissolved air flotation (D/DAF) for pre-treatment of personal care products (PCPs) wastewater. Desalination,252(2010)106–112.

[24]   Saha S., Treatment of aqueous effluent for fluoride removal. Water Res., 27(1993)1347–1350.

[25]   Reardon E.J., Wang Y., A limestone reactor for fluoride removal from wastewaters. Environ. Sci. Technol., 34(2000)3247–3253.

[26]   Gong W.-X., Qu J.-H., Liu R.-P., Lan H.-C., Effect of aluminum fluoride complexation on fluoride removal by coagulation. Colloids Surf. A Physicochem. Eng. Asp., 395(2012)88–93.

[27] Ndiaye P.I., Moulin P., Dominguez L., Millet J.C., Charbit F., Removal of fluoride from electronic industrial effluent by RO membrane separation. Desalination,173(2005)25–32.

[28] Karabelas A.J., Yiantsios S.G., Metaxiotou Z., Andritsos N., Akiskalos A., Vlachopoulos G., Stavroulias S., Water and materials recovery from fertilizer industry acidic effluents by membrane processes. Desalination, 138(2001)93–102.

[29] Sehn P., Fluoride removal with extra low energy reverse osmosis membranes: Three years of large scale field experience in Finland. Desalination, 22392008)73–84.

[30] Guo L., Hunt B.J., Santschi P.H., Ultrafiltration behavior of major ions (Na, Ca, Mg, F, Cl and SO$_4$) in natural waters. Water Res., 5(2001)1500–1508.

[31] Lhassani A., Rumeau M., Benjelloun D., Pontie M., Selective demineralization of water by nanofiltration Application to the defluoridation of brackish water. Water Res. 35(2001) 3260–3264.

[32] Hu K., Dickson J.M., Nanofiltration membrane performance on fluoride removal from water. J. Membr. Sci. 279(2006)529–538.

[33] Malaisamy R., Talla-Nwafo A., Jones K.L., Polyelectrolyte modification of nanofiltration membrane for selective removal of monovalent anions. Sep. Purif. Technol., 77(2011)367–374.

[34] Ghosh D., Sinha M.K., Purkait M.K., A comparative analysis of low-cost ceramic membrane preparation for effective fluoride removal using hybrid technique. Desalination,327(2013)2–13.

[35] Chakrabortty S., Roy M., Pal P., Removal of fluoride from contaminated groundwater by cross flow nanofiltration: Transport modeling and economic evaluation. Desalination, 313(2013)115–124.

[36] Shen F., Chen X., Gao P., Chen G., Electrochemical removal of fluoride ions from industrial wastewater. Chem. Eng. Sci., 8(2003)987–993.

[37] Tahaikt M., Achary I., Menkouchi Sahli M.A., Amor Z., Taky M., Alami A., Boughriba A., Hafsi M., Elmidaoui A., Defluoridation of Moroccan groundwater by electrodialysis: Continuous operation. Desalination,189(2006)215–220.

[38] Piddennavar R., Review on defloridation techniques of water. Int. J. Eng. Sci., 2(2013)86–94.

[39] Menkouchi Sahli M.A., Annouar S., Tahaikt M., Mountadar M., Soufiane A., Elmidaoui A., Fluoride removal for underground brackish water by adsorption on the natural chitosan and electrodialysis. Desalination, 12(2007)37–45.

[40] Zuo Q., Chen X., Li W., Chen G., Combined electrocoagulation and electroflotation for removal of fluoride from drinking water. J. Hazard. Mater.,159(2008)452–457.

[41] Ergun E., Tor A., Cengeloglu Y., Kocak I., Electrodialytic removal of fluoride from water: Effects of process parameters and accompanying anions. Sep. Purif. Technol., 64(2008)147–153.

[42] Kabay N., Arar O., Samatya S., Yüksel U., Yüksel M., Separation of fluoride from aqueous solution by electrodialysis: Effect of process parameters and other ionic species. J. Hazard. Mater., 53(2008)107–113.

[43] Mameri N., Lounici H., Belhocine D., Grib H., Piron D.L., Yahiat Y., Defluoridation of Sahara water by small plant electrocoagulation using bipolar aluminium electrodes. Sep. Purif. Technol., 24(2001)113–119.

[44] Arar O., Yavuz E., Yuksel U., Kabay N., Separation of low concentration of fluoride from water by electrodialysis (ED) in the presence of chloride and sulfate ions. Sep. Purif. Technol., 44(2009)1562–1573.

[45] Cui H., Qian Y., An H., Sun C., Zhai J., Li Q., Electrochemical removal of fluoride from water by PAOA modified carbon felt electrodes in a continuous flow reactor. Water Res., 49(2012)3943–3950.

[46] Tezcan Un U., Savas Koparal A., Ogutveren U.B., Fluoride removal from water and wastewater with a bach cylindrical electrode using electrocoagulation. Chem. Eng. J., 223(2013)110–115.

[47] Kodama H., Kabay N., Reactivity of inorganic anion exchanger BiPbO$_2$(NO$_3$) with fluoride ions in solution. Solid State Ion.,141–142(2001)603–607.

[48] Chubar N.I., Samanidou V.F., Kouts V.S., Gallios G.G., Kanibolotsky V.A., Strelko V.V., Zhuravlev I.Z., Adsorption of fluoride, chloride, bromide and bromate ions on a novel ion exchanger. J. Colloid Interface Sci.,291(2005)67–74.

[49] Hänninen K., Kaukonen A.M., Murtomäki L., Hirvonen J., Mechanistic evaluation of factors affecting compound loading into ion-exchange fibers. Eur. J. Pharm. Sci.,31(2007)306–317.

[50] Liu R.X., Guo J.L., Tang H.X., Adsorption of fluoride, phosphate, and arsenate ions on a new type of ion exchange fiber. J. Colloid Interface Sci., 248(2002)268–274.

[51] Meenakshi S., Viswanathan N., Identification of selective ion-exchange resin for fluoride sorption. J. Colloid Interface Sci., 308(2007)438–450.

[52] Paudyal H., Pangeni B., Inoue K., Kawakita H., Ohto K., Ghimire K.N., Alam S., Preparation of novel alginate based anion exchanger from Ulva japonica and its application for the removal of trace concentrations of fluoride from water. Bioresour. Technol., 48(2013)221–227.

[53]   Guo Q., Tian J., Removal of fluoride and arsenate from aqueous solution by hydrocalumite via precipitation and anion exchange. Chem. Eng. J., 231(2013)121–131.

[54]   Sujana M.G., Thakur R.S., Das S.N., Rao S.B., Defluorination of Waste Water. Asian J. Chem., 4(1997)561–570.

[55]   Bhatnagar A., Kumar E., Sillanpää M., Fluoride removal from water by adsorption—A review. Chem. Eng. J., 71(2011)811–840.

[56]   Leyva Ramos R., Ovalle-Turrubiartes J., Sanchez-Castillo M.A., Adsorption of fluoride from aqueous solution on aluminum-impregnated carbon. Carbon, 37(1999)609–617.

[57]   Sarkar M., Banerjee A., Pramanick P.P., Sarkar, A.R., Use of laterite for the removal of fluoride from contaminated drinking water. J. Colloid Interface Sci., 302(2006)432–441.

[58]   Oguz E., Adsorption of fluoride on gas concrete materials. J. Hazard. Mater., 117(2005)227–233.

[59]   Alagumuthu G., Veeraputhiran V., Venkataraman R., Adsorption isotherms on fluoride removal: Batch techniques. Arch. Appl. Sci. Res., 2(2010)170–185.

[60]   V. K. Gupta, P.J.M. Carrott, M.M.L. Ribeiro Carrott, Suhas, Low-Cost Adsorbents: Growing Approach to Wastewater Treatment—a Review, Critical Reviews in Environmental Science and Technology, 39(2009)783–842.

[61]   George Z. Kyzas, Margaritis Kostoglou, Green Adsorbents for Wastewaters: A Critical Review, Materials, 7(2014)333-364; doi:10.3390/ma7010333.

[62]   M. Mohapatra, S. Anand, B.K. Mishra, Dion E. Giles, P. Singh, Review of fluoride removal from drinking water, Journal of Environmental Management, 91 (2009) 67–77

[63]   Vaishali Tomar, Surendra Prasad, Dinesh Kumar, Adsorptive removal of fluoride from water samples using Zr–Mn composite material, Microchemical Journal, 111 (2013) 116–124.

[64]   Mirna Habuda-Stanić , Maja Ergović Ravančić, Andrew Flanagan, A Review on Adsorption of Fluoride from Aqueous Solution, Materials, 7(2014)6317-6366; doi:10.3390/ma7096317,

[65]   Peter H. Raven, Ray F. Evert, Helena Curtis , Biology of Plants, New York, N.Y.: Worth Publishers, (1981) 641

[66]   Christopher H. Vane, Trevor C. Drage, Colin E. Snape, Bark decay by the white-rot fungus Lentinula edodes: Polysaccharide loss, lignin resistance and the unmasking of suberin, International Biodeterioration & Biodegradation, 57,1(2006)14–23

[67]   Kolattukudy P.E., Biochemistry and function of cutin and suberin, Canadian Journal of Botany, 62 (1984)2918–2933; doi:10.1139/b84-391.

[68]   Hickey M., King C., The Cambridge Illustrated Glossary of Botanical Terms, Cambridge University Press, (2001).

[69]   https://en.wikipedia.org/wiki/Wood

[70]   Jean-Pierre Barette; Claude Hazard et Jérôme Mayer, Mémotech Bois et Matériaux Associés. Paris: Éditions Casteilla., (1996) 22.

[71]   Wase J., Forster C. ,Biosorbents for Metal Ions, Taylor & Francis Ltd.,(1997).

[72]   Bulut Y., Tez Z. Adsorption studies on ground shells of hazelnut and almond. J. Hazard. Mater. 149(2007)35–41.

[73]   Patil Satish, Renukdas Sameer, Patel Naseema, Defluoridation of Water Using Biosorbents: Kinetic and Thermodynamic Study, Int. J. Res. Chem. Environ., 3,1(2013)125-135.

[74].   Mekala Suneetha, Bethanabhatla Syama Sundar and Kunta Ravindhranath, Removal of fluoride from polluted waters using active carbon derived from barks of Vitex negundo plant, Journal of Analytical Science and Technology, 6,15(2015)1-19.

[75]   D. Santhi, Removal of fluoride in drinking water by drumstick bark and its leaves, Jr. of Industrial Pollution Control, 26,1(2010) 119-120.

[76]   Bhagyashree M. Mamilwar , A.G.Bhole , A.M.Sudame, Removal Of Fluoride From Ground Water By Using Adsorbent, International Journal of Engineering Research and Applications, 2,4 (2012)334-338.

[77]   Dinesh Mohan, Rupa Sharma, Vinod K. Singh, Philip Steele, and Charles U. Pittman Jr, Fluoride Removal from Water using Bio-Char, a Green Waste, Low-Cost Adsorbent: Equilibrium Uptake and Sorption Dynamics Modeling, Ind. Eng. Chem. Res., 51,2(2012)900–914

[78]   Sutapa Chakrabarty, H.P.Sarma, Defluoridation of contaminated drinking water using neem charcoal adsorbent: Kinetics and equilibrium studies, International Journal of ChemTech Research, 4(2012) 511-516.

[79]   Jain J. K., Gupta Nidhi, Defluoridation of Water Using Bioadsorbents : Kinetic Study, International Journal of Scientific Research, 2, 12 (2013) 71-175

[80]   G. Karthikeyan, S. Siva Ilango, Fluoride sorption using Morringa indigo-based activated carbon, Iranian Journal of Environmental Health Science & Engineering, 4,1(2007)21-28

[81]   K. A. Emmanuel ,K.A.Ramaraju, G.Rambabu, A.Veerabhadra Rao, Removal of fluoride from drinking water with activated carbons prepared from HNO_3 activation-A comparative study, Rasayan J. Chem., 1,.4(2008)802-818.

[82]   Laura R. Brunson, David A. Sabatini, Methods for Optimizing Activated Materials for Removing Fluoride from Drinking Water Sources, Journal of Environmental Engineering, 142, 2 (2016); 10.1061/(ASCE)EE.1943-7870.0001044, 04015078.

[83]   Monal Dutta, Tanumoy Ray, Jayanta Kumar Basu, Batch adsorption of fluoride ions onto microwave assisted activated carbon derived from Acacia Auriculiformis scrap wood, Archives of Applied Science Research, 4, 1(2012)536-550.

[84]   Mohammad Ali Zazouli, Amir Hossein Mahvi, Yousef Mahdavi, Davoud Balarak,Isothermal and kinetic modelling of fluoride removal from water by means of the natural biosorbents Sorghum and Canola, Fluoride 48,1 (2015)37–44.

[85]   Suman Mann, Anubha Mandal, Removal of Fluoride from Drinking Water Using Sawdust, Int. Journal of Engineering Research and Applications, 4, 7(2014)116-123.