

## Defluoridation of water using adsorbents - A concise review

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REVIEW ARTICLE

### ABSTRACT

Fluoride contamination in potable water and ground water streams due to natural and anthropogenic activities has been known as one of the key problems worldwide imposing a serious threat to human health. Amongst the various treatment methods available for fluoride removal, adsorption process is regarded as efficient and practical. A general list of various inorganic, organic and natural adsorbents from literature has been compiled and discussed. The effects of different parameters such as pH, initial fluoride concentration, temperature, contact time, adsorbent surface charge, etc. were also discussed. This review paper includes the entire spectrum of adsorbents used for defluoridation, factors affecting adsorptive defluoridation process, and also discussed the isotherms and kinetics used for the data interpretation.

### KEYWORDS

adsorption; drinking water; characterization; fluoride; isotherm; kinetics

## 1. INTRODUCTION

Presence of fluoride in the potable water is one of the important environmental issues because of its adverse and toxic effects. Fluorine in the form of fluoride anion (F<sup>-</sup>) is found in the organic and inorganic compounds of the environment (Habuda-Stanić et al., 2014). It is a main constituent in minerals such as topaz, fluorite, cryolite, sellaite, theorapatite, fluorapatite and phosphorite. The percent of fluorine in these minerals is listed in Table 1. It enters the soil through weathering of rocks, precipitation or waste run off. Surface water generally does not contain more than 0.3 mg/L of fluoride unless they are polluted from external sources (Meenakshi and Garg, 2002; Meenakshi and Maheshwari, 2006; Singh and Maheshwari, 2001).

Fluoride pollution has been observed not only in various minerals processing but also in some natural water systems over large areas in Asia, Africa, America, and Europe where the fluoride concentration can range

from 0.01 to 3 mg/L in fresh water and 1-35 mg/L in ground water. Occurrence of fluoride in groundwater has drawn worldwide attention due to its considerable impact on human physiology. The assimilation of fluoride into the human body from potable water at the level of 1.0 mg/L enhances bone development and prevents dental caries (Shusheela, 1993; Tripathy et al., 2006).

## 2. HEALTH EFFECTS OF FLUORIDE

Fluoride ions in aqueous solutions converted into HF in acidic environments such as those of the stomach, and up to about 40% of ingested fluoride is absorbed in the stomach as HF. Prolonged and excessive intake of fluoride may result in a serious public health problem called fluorosis, which is characterized by dental mottling and skeletal manifestations such as crippling deformities, osteoporosis, and osteosclerosis. Endemic fluorosis is now known to be global occurrence

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and affecting many millions of people in different continent (Ayoob and Gupta, 2006; Barbier et al., 2010; S. V. Mohan et al., 2007; Susheela et al., 1993).

The maximum tolerance limit of fluoride in drinking water specified by the World Health Organisation (Kawashima et al., 2009) is 1.5 mg/L, but a lower concentration is recommended for children (Kusvuran et al., 2005). According to WHO estimate, excess fluoride concentration in groundwater (>1.5 mg/L) is affecting more than 260 million people around the world (Amini et al., 2008). Even though the upper limit of fluoride concentration in drinking water is 1.5 mg/L, in many tropical countries, where there is a high sweat loss and a high intake of water due to the hot weather, such an upper limit may be unsuitable (Ponds et al., 1988). The Bureau of India Standards (BIS) prescribes a limit between 1.0 and 1.5 mg/L. In India, about 62 million people are at risk of developing fluorosis from drinking fluoride contaminated water (Fink and Lindsay, 1936; Srimurali et al., 1998). Further, the presence of fluoride in drinking water affects elderly males and induces osteosarcoma (Bassin et al., 2006; Fawell and Nieuwenhuijsen, 2003).

**Table 1.** Fluoride bearing minerals (Rao, 2003).

Mineral	Chemical formula	Percentage of fluorine
Sellaite	MgF <sub>2</sub>	61
Villianmite	NaF	55
Fluorite	CaF <sub>2</sub>	49
Cryolite	Na <sub>3</sub> AlF <sub>6</sub>	45
Bastnaesite	(Ce,La)(CO <sub>3</sub> )F	9
Fluorapatite	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>3</sub> F	3-4

Dental fluorosis also termed as mottled enamel is characterized by white and yellow glistening patches on the teeth which may eventually turn brown due to hypo-mineralization of tooth enamel caused by excess ingestion of fluoride. Skeletal fluorosis can also damage the fetus if the mother consumes water and food, with a high concentration of fluoride during pregnancy/breast feeding. Other effects include severe pain in the backbone, joints and hip region, stiffness of the backbone, increased density of bones and paralysis. Non skeletal manifestations include nervousness, excessive thirst, muscle weakness, stiffness, pain in the muscle and loss of muscle power, acute abdominal pain, diarrhea, constipation, blood in stools, head ache and very painful skin rashes (Bulusu et al., 1979; Rao, 2003).

## 3. FLUORIDE REMOVAL METHODS

### 3.1. Conventional methods of fluoride removal

Therefore removal of excess fluoride from potable water is the topic of concern. The conventional method of fluoride removal includes: ion exchange, reverse osmosis, nano-filtration, dialysis and adsorption. Amongst, the ion exchange (Singh et al., 1999) and the membrane separation processes (Sehn, 2008) are relatively expensive. Membrane processes generally saddled with major problems such as fouling of membranes and costlier membrane-damaging antifouling methods. However, most of these methods have high operational and maintenance cost, low fluoride removal capacities, lack of selectivity for fluoride, undesirable effects on water quality, generation of large volumes of sludge and complicated procedures involved in the treatment. Therefore, defluoridation of drinking waters is usually accomplished by either precipitation or by adsorption processes (Aravind et al., 2015). Adsorption is generally regarded as an efficient, cheap and easy to scale-up design process to defluoridate the water. The comparison on different technologies used in removal of fluoride is explained in Table 2.

### 3.2. Adsorption technology for defluoridation

Adsorption is a physiochemical waste water treatment in which dissolved molecules are attached to the surface of an adsorbent by physical/chemical forces. Depending on the nature of the interactions, ionic species and molecular species carrying different functional groups may be held to the surface through electrostatic attraction to sites of opposite charge at the surface or physisorbed due to action of van der Waals forces or chemisorbed involving strong solute-adsorbent bonding. So, it may lead to attachment of solute molecules at specific functional group on adsorbent surface. It is true that choice of adsorbent plays a very important role (Sivarajasekar and Baskar, 2014b). This technique is quite popular due to its simplicity as well as the availability of a wide range of adsorbents and it proved to be an effective and attractive process for the removal of non-biodegradable pollutants from waste water (Panchore, 2016; Telkapalliwar and Shivankar, 2016; Tomar and Kumar, 2013).

**Table 2.** Comparison of fluoride removal technologies.

Technology	Advantages	Disadvantages	References
Coagulation/precipitation using calcium hydroxide/aluminium hydroxide	High efficiency; commercially available chemicals	Expensive, efficiency depends on pH and presence of co-ions in water, adjustment and readjustment of pH is required, elevated residual aluminium concentration, formation of sludge with high amount of toxic aluminium fluoride complex.	El-Gohary et al., 2010
Membrane filtration: reverse osmosis/nano-filtration	High efficiency; removes other contaminants	High capital high running and maintenance costs toxic waste water produced.	Hu and Dickson, 2006; Sehn, 2008
Electrochemical treatments: Dialysis/electrodialysis/Electro-coagulation	High efficiency; high selectivity	High costs during installation and maintenance	Hu et al., 2003; Mameri et al., 1998
Ion exchange: Strong basic anion exchange resin with quaternary ammonium functional groups	High efficiency	Expensive, vulnerable to interfering ions (sulphate, phosphate, chloride etc.) replacement of media after multiple regenerations, used media present toxic solid waste, regeneration creates toxic liquid waste.	Singh et al., 1999; Tor, 2007
Adsorptive materials: activated carbon, activated alumina, other natural and synthetic adsorbents	Great accessibility; low cost; simple operation	High efficiency often demand adjustment and readjustment of pH, some common water ions can interfere fluoride adsorption.	Mohan et al., 2007; Hamdi and Srasra, 2007

### 3.3. Adsorbents used for defluoridation

There were many adsorbents employed by researchers to remove the fluoride from water. Generally, they can be classified into inorganic and organic adsorbents. Inorganic materials like activated alumina (Tripathy et al., 2006), immobilised activated alumina (Rafique et al., 2013), clay (Hamdi and Srasra, 2007), mud (Erso, 2002; Chidambaram et al., 2003), fly ash (Chidambaram et al., 2003) and etc. were employed for fluoride removal. On the other hand, some naturally occurring charcoal (Mohan and Singh, 2002), activated carbon, and biosorbent prepared from bio-based materials also investigated by several researchers.

#### 3.3.1. Chars and charcoal

Activated carbon/charcoal is one of the most widely used adsorbents for the removal of fluoride ions from aqueous solutions. The adsorption capacity of activated carbon depends on various factors, such as surface area, pore size distribution, surface functional groups on the adsorbent, polarity, solubility and molecular size of the adsorbate, solution pH and the presence of

other ions in solution. The most widely used activated carbons are microporous and have high surface areas, and as a consequence, exhibits high efficiency for the adsorption of low molecular weight compounds (Karthik et al., 2016a; Sivarajasekar and Baskar, 2015a; Sivarajasekar and Baskar, 2015b).

Charcoal packed in an adsorbent column was evaluated to remove fluoride. Untreated charcoal seems to have no significant effect on the concentrations of fluoride as it only adsorbed 0.5 mg/L of fluoride (Chidambaram et al., 2003). Powdered activated charcoal was reported to remove the maximum of 85% fluoride ions at pH 2 (Tembhurkar and Dongre, 2006). The reason for better adsorption at low pH values may be attributed to large number of H<sup>+</sup> ions present at these pH values. Maximum dose of 2.4 g/100 mL, stirring rate of 60 rpm and contact time of 120 min were reported optimum in this study.

Activated carbons of different origin such as commercial activated carbon, carbon black and bone char were evaluated for fluoride removal at 30 °C at a fixed contact time of 3 h (Abe et al., 2004). Fluoride removal efficiency was reported as 17 %, 10 %, and

82 % for commercial activated carbon, carbon black, and bone char, respectively. Bone char obtained from animal bones was used as a bio-adsorbent to remove fluoride ions. Batch adsorption tests were conducted at pH 6.8 to 7.1. The surface area of bone char particles of size 0.2 mm was reported as 280 m<sup>2</sup>/g (Ma et al., 2008).

### 2.3.2. Ores and natural materials

Most recently, the ores and inorganic materials such as alumina, clays, mud, fly ash etc. were reported to be unconventional adsorbents for their removal of fluoride ions from aqueous solutions due to their cheap and abundant resources, and higher surface areas (Liu et al., 2015). Furthermore, the regeneration of these low-cost substitutes is not necessary whereas regeneration of activated carbon is essential (Hamdi and Srasra, 2007; Erso, 2002; Chidambaram et al., 2003).

Rafique et al. (2013) prepared immobilised activated alumina using sol gel method was evaluated for the fluoride ions removal from aqueous phase and its maximum adsorption capacity was found to be 0.76 mg/g. Alum-impregnated activated alumina was prepared by impregnating activated alumina with alum at pH 6.5 and at room temperature. The specific surface area of alum-impregnated activated alumina was found to be 176 m<sup>2</sup>/g and found suitable for fluoride ions adsorption (Tripathy et al., 2006). Ma et al., 2008 reported that activated alumina of particle size 0.2 mm could be effectively used for the removal of fluoride from water. High alumina content bauxite was powdered below 1.18 mm of diameter batch and column experiments were performed by (Lavecchia et al., 2012). In this case, the maximum adsorption capacity of bauxite was 3.15 mg/g for removal of fluoride ions.

Naturally occurring clay materials such as kaolinite, bentonite, charfines and lignite were examined for fluoride adsorption at pH 6.8 to 7.1 at room temperature for 5 h. The removal efficiency of the selected materials were: bentonite (33%) > charfines (19%) > kaolinite (18.2%) > lignite (7.9%). Equilibrium time of 4 h was chosen for both bentonite and charfines at pH 5.5 to 7.5 (Srimurali et al., 1998). Batch adsorption tests were conducted using tourmaline at pH range 6.8 – 7.1 and at temperature range 22 – 25 °C (Ma et al., 2008).

The removal rate of fluoride was tested using red soil, brick powder, fly-ash and serpentine (Chidambaram et al., 2003). Fluoride removal was done by passing water through columns. The brick

and fly-ash showed typically a sudden removal of fluoride. Red soil adsorbs fluoride immediately after 15 min, whereas in serpentine the fluoride removal was maximal within 15 min.

Chitosan is a well-known excellent biosorbent for metal cation removal in near neutral solutions because the large number of amine groups (Miretzky and Cirelli, 2011). Chitosan naturally occurs in the form of flakes or powder. Several methods have been used to modify natural chitosan either physically or chemically in order to improve the adsorption capacity. Chitosan has a very low specific area ranging between 2 m<sup>2</sup>/g and 30 m<sup>2</sup>/g. Batch experiments were carried out using natural form of chitosan, chitosan cross linked with glutaraldehyde and chitosan cross linked with magnesia. The maximum adsorption capacity was found to be 1.39, 11.11 and 22.49 mg/L, respectively. Protonated cross linked chitosan beads (Viswanathan et al., 2009) were prepared by crosslinking chitosan by glutaraldehyde and then treating with concentrated HCl. The maximum fluoride adsorption capacity was found to be 12.14 mg/g at 0.25 g of adsorbent dosage, 30 min contact time at pH 7 and 30 °C.

### 3.3.3. Biosorbents

A number of agricultural and forest wastes/by-products and industrial waste products have been proposed by a number of researchers for the fluoride removal from aqueous wastewater. These low-cost adsorbents are abundant in nature, inexpensive, require little processing, and are effective for fluoride removal (Liu et al., 2015; Mohan et al., 2012; Tomar and Kumar, 2013). The reported adsorbents are described below. The fishbone charcoal was prepared and tested to remove fluoride ions with different initial fluoride concentrations at temperature 20 °C and pH 8. The adsorbent dose of 32 g/L reduced the fluoride concentration up to 50% within 5 min (Bhargava, 2000).

The coconut shell (Bandewar et al., 2015) was utilized as precursor to prepare activated carbon of size less than 150 mm and column adsorption studies carried out. The maximum fluoride removal occurred at 6 cm bed height and saturation of flow rate was attained at 4 mL/min. The adsorbent, granular charcoal activated carbon in combination with granular coconut shell activated carbon proved that it can efficiently remove 72% of fluoride from drinking water. Completely carbonized rice husk (Deshmukh et al., 2009) was used as adsorbent and maximum fluoride removal efficiency was observed 50%. The optimum dose, pH, and agitation time for batch studies were found to be

10 g/L, pH 2, and 40 rpm respectively. The maximum fluoride adsorption capacity was reported as 0.505 mg/g.

Thermally activated biosorbents prepared from banana peel and coffee husk were investigated for fluoride adsorption (Getachew et al., 2015). The real water samples having higher concentrations (6.72 mg/L) of fluoride were collected at Hawassa city, Ethiopia. The concentration of fluoride in the water sample was reduced to 1.17 mg/L and 1.14 mg/L by banana peel and coffee husk, respectively. Low cost adsorbent like bagasse dust, alumina treated bagasse fly ash, bone powder and shell powder were used as adsorbent for fluoride removal from ground water (Gupta et al., 2014). Shell powder showed maximum fluoride sorption at pH 6.0, 25 °C, 150 rpm and contact time 5 h comparatively. Defluoridation order was found to be shell powder > bone powder > alumina treated bagasse fly ash > bone powder > bagasse.

Fresh neem leaves and tress (Goswami et al., 2015) were chosen, dried, powdered and further digested by chemical methods. The efficiency of fluoride removal was found to be 80 % at pH 2 and 75% at pH 4. 90 - 95 % efficiency of fluoride removal was observed with smallest particle size of 600 µm for an initial fluoride ion concentration of 10 mg/L. Crude fibers and tress from neem, pipal and khair (Jamode et al., 2004) were examined as adsorbents. Adsorbent dose of 10 g/L of 600 µm was used to remove fluoride ions from 10 mg/L fluoride solution. About 90% adsorption was reported and maximum adsorption capacity was found to be 0.04 mg/g. Lemon peels (Kumar et al., 2016) were charred and utilized to remove fluoride ions from 221 mg/L solution at pH 4, 120 min, adsorbent dose 10 g/L and at 225 rpm. Maximum fluoride removal percentage of 82% was reported. Fluoride ions removal from water using pinewood and pine bark bio-chars prepared via thermal activation method was carried out for various concentrations and best fit of isotherm models were compared using the equilibrium data.

Dry biomass of *Spirulina* algae (Devanand et al., 2014) was employed to adsorb fluoride ions from 20 mg/L. Optimum parameters for batch adsorption was found to be 1 g/100 mL, contact time 90 min, pH 5 at 30 °C. The plant biomass - *Tinospora cordifolia* (Pandey et al., 2012) was used for the removal of fluoride ions from aqueous solutions. About 7 g of the biomass was utilized to remove fluoride from 5 mg/L solution. Maximum percentage adsorption of fluoride ion was found to at pH 7, 120 min at room temperature. The maximum uptake capacity of fluoride was found to be 25 mg/g. White rot fungus *Pleurotus ostreatus* 1804

(Ramanaiah et al., 2007), a hyper laccase producing strain, was evaluated as biosorbent in nonviable form. Batch adsorption experiments were performed at initial concentration of 5 mg/L fluoride concentration at temperature 30 °C and contact time 360 min and biosorbent dosage 0.5 mg/g. The maximum fluoride removal efficiency was found to be 70%.

Black berry, guava leaf, neem leaf, neem bark and rice husk (Suganandam et al., 2010) were used as biosorbents to remove fluoride ions from aqueous solutions. Amongst, guava leaves were found to be good adsorbent than other selected biosorbents. The guava seeds (Valencia-Leal et al., 2012) were used as adsorbent to remove fluoride from 5 mg/L solution at room temperature. Maximum of 30% of fluoride ions removal was obtained at pH 2 and at 60 rpm.

### 3.4. Factors affecting adsorption

Fluoride removal efficiency always depends on raw water quality profile, i.e., initial fluoride concentration, solution pH, environment temperature, contact time and adsorbent dose (Rafique et al., 2013; Tomar and Kumar, 2013; Srimurali et al., 1998; Ma et al., 2008; Devanand et al., 2014; Tripathy et al., 2006). The various parameters which influence fluoride removal analyzed for different adsorbents are listed in Table 3.

The adsorption of fluoride ion by adsorbent depends on the interactions between the solution and the surface of adsorbent. Adsorption process can be assumed to be complete when equilibrium was achieved between the fluoride ions and the adsorbent (Jamode et al., 2004; Kumar et al., 2016). However, specific time was needed to maintain the equilibrium interactions to ensure that the adsorption process is complete (Aeisyah et al., 2014; Panchore et al., 2016).

Adsorption of fluoride ion from the wastewater is mainly influenced by the pH of the solution. pH can influence the surface charge of the adsorbent and the degree of ionization of the fluoride ions (Ma et al., 2008; Srimurali et al., 1998). In a particular pH range, most fluoride ion adsorption was enhanced with pH, increasing to a certain value followed by a reduction when further pH increases. The dependence of the fluoride ion uptake on pH can be associated with both the surface functional groups on the adsorbent and also the chemistry of the solution (Aeisyah et al., 2014; Panchore et al., 2016).

Initial concentration of fluoride ion can alter the fluoride removal efficiency through a combination of factors such as the availability of specific surface functional groups and the ability of surface functional

**Table 3.** Effects of parameters and their range for fluoride removal.

Adsorbent	pH	Temperature (°C)	Contact time (min)	Initial concentration (g/L)	Reference
Algal biosorbent <i>Spirogyra</i> sp.-IO2	2.0	50	300	10	Mohan et al., 2007
Bentonite	5.5-7.5	30	240	50	Srimurali et al., 1998
Charfines	2.8				
Activated tea ash powder	6.0	30	180	5	Mondal et al., 2012
Immobilised activated alumina	7.0	20	60	10	Rafique et al., 2013
Powdered activated charcoal	2.0	30	120	24	Tembhurkar and Dongre, 2006
Bone char	6.8-7.1	22-25	-	-	Ma et al., 2008
Rice husk	2.0	30	120	10	Deshmukh et al., 2009
Shell powder	6.0	25	300	1-20	Gupta et al., 2014
Banana peel	2.0	30	780	96	Getachew et al., 2015
Coffee husk	2.0	30	180	72	
Leaf biomass powder sample	2.0	30	60	10	Jamode et al., 2004
Activated carbon	4.0	30	120	10	Kumar et al., 2016

groups to bind fluoride ions (Gupta et al., 2014). Initial concentration of solution can provide an important driving force to overcome the mass transfer resistance of fluoride ion between the aqueous and solid phases (Aeisyah et al., 2014; Panchore et al., 2016).

Temperature plays a double role in the fluoride adsorption process. Temperature can impact the physical binding processes of fluoride to adsorbent. Most adsorption studies were conducted at room temperature in laboratory settings. As temperature increased, sorption was shown to be less favoured most likely due to increased deprotonation or hydroxylation of the surface causing more negatively charges adsorbent surfaces (Ma et al., 2008). This was an important observation to note when attempting to apply defluoridation methods on site in hot climates, for adsorption capacities attained under room temperature conditions may be higher than in the field as a result of increased temperatures (Bachale et al., 2016; Panchore et al., 2016).

### 3.5. Isotherm modeling of fluoride adsorption

Adsorption isotherms are viable for describing the relationship between solute molecules and adsorbent surface, highlighting the distribution of solute molecules between the liquid and solid phases when

an adsorption process reaches equilibrium state. The analysis of isotherm data by fitting different isotherm models is a significant step to determine the suitable model which can be used for design purposes. Hence, the correlation of equilibrium data using either a theoretical or empirical equation is essential for interpretation and prediction of the extent of adsorption, in deciding the maximum adsorption capacity of adsorbate for a given adsorbent (Sivarajasekar and Baskar, 2014a; Sivarajasekar et al., 2009). The Freundlich and Langmuir isotherms are useful models for the description of adsorption process by different adsorbents. The Freundlich model refers to surface heterogeneity of the adsorbent, whereas the Langmuir model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface (Getachew et al., 2015).

The Freundlich isotherm has the general form,

$$q_e = K_f C^{1/n} \quad (1)$$

The linearised Freundlich adsorption isotherm can be expressed as,

$$\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e) \quad (2)$$

where  $q_e$  (mg/g) is the amount of metal ions adsorbed per unit weight of adsorbents,  $K_f$  and  $1/n$  are the Freundlich constants. If  $1/n < 1$ , bond energies with surface density, if  $1/n > 1$ , bond energy decreases with surface density and if  $1/n = 1$ , all surface sites are equivalent.  $C_e$  (mg/L) is the equilibrium concentration. Linear plots of  $\log q_e$  vs  $\log C_e$  at different adsorbent

doses are applied to confirm the applicability of Freundlich models (Mittal et al., 2007). The constants of Freundlich on reaction with different adsorbent are shown in Table 4.

The Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable

**Table 4.** Freundlich constants for adsorption isotherm.

Sample	Variables	Constant		R <sup>2</sup>	Reference
		1/n	K <sub>f</sub> (mg/g)		
Activated carbon	30 °C	0.53	0.08	0.999	Abe et al., 2004
	25 °C	0.38	4.54	0.900	Daifullah et al., 2007
	45 °C	0.69	1.3	0.900	
	55 °C	0.83	0.6	0.830	
Carbon black	30 °C	0.35	0.07	0.999	Abe et al., 2004
Bone charcoal	30 °C	0.39	1.06	0.998	
Nano hydroxyapatite	30 °C	0.198	1.280	0.970	Sundaram et al., 2009
	40 °C	0.203	1.412	0.992	
	50 °C	0.22	1.423	0.995	
Pumice stone	pH 6	0.31	27.6	0.950	Asgari et al., 2012
	pH 6	0.39	0.521	0.983	
Hydrogen peroxide modified pumice	pH 6	0.44	0.535	0.887	Sepehr et al., 2013
Magnesium chloride modified pumice	pH 6	0.619	0.777	0.952	
La <sup>3+</sup> polyamidoamine grafted chitosan beads	30 °C	0.413	0.385	0.994	Prabhu and Meenakshi, 2015
	40 °C	1.58	1.87	0.998	
	50 °C	0.296	2.68	0.999	
Zr <sup>4+</sup> polyamidoamine grafted chitosan beads	30 °C	0.170	9.582	0.997	
	40 °C	0.197	9.886	0.999	
	50 °C	0.224	10.169	0.998	
<i>Pithacelo biumdulce</i> carbon	pH 9	0.614	0.0204	0.998	Emmanuel et al., 2008
<i>Ipomoea batatas</i> carbon	pH 9	0.747	0.0043	0.997	
<i>Peltophorum ferrugineum</i> carbon	pH 9	0.719	0.0421	0.997	
Guava seeds	25 °C	0.606	2.248	0.980	Valencia-Leal et al., 2012
	35 °C	0.943	0.1663	0.987	
	50 °C	0.827	0.5092	0.982	
Aluminum impregnated coconut fiber	40 °C	1.254	0.301	0.440	Mondal et al., 2015
	60 °C	0.809	5.984	0.155	
	80 °C	3.267	0.004	0.914	
Treated banana peel	pH 2	0.253	0.1775	0.973	Getachew et al., 2015
Treated coffee husk	pH 2	0.217	0.2256	0.993	
Assimilation of chitin with tin	30 °C	0.493	2.20	0.998	Shekhawat et al., 2016
	40 °C	0.544	1.67	0.989	
	50 °C	0.625	1.14	0.984	

of adsorbing one molecule. Thus, the adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir equation is commonly written as,

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

where  $q_e$  is the amount adsorbed (mg/g) and  $C_e$  is the equilibrium concentration of adsorbate (mg/L),  $q_m$  and  $b$  are the Langmuir constants related to capacity and energy of adsorption, respectively. The linear form of the Langmuir isotherm can be expressed as,

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b q_m C_e} \quad (4)$$

**Table 5.** Langmuir constants for adsorption isotherm

Adsorbent	Variables	$q_{max}$ (mg/g)	$R_L$	B	References
La <sup>3+</sup> polyamidoamine grafted chitosan beads	30 °C	10.37	0.625	0.040	Prabhu and Meenakshi, 2015
	40 °C	11.36	0.571	0.050	
	50 °C	11.45	0.455	0.080	
Zn <sup>4+</sup> polyamidoamine grafted chitosan beads	30 °C	16.377	0.018	2.782	
	40 °C	16.903	0.024	2.877	
	50 °C	17.483	0.025	3.891	
Pumice stone	pH 6.0	41.65	0.163	0.255	Asgari et al., 2012
Pithacelobiumdulce carbon	pH 9.0	0.0700	0.4202	0.276	Emmanuel et al., 2008
Ipomoea batatas carbon	pH 9.0	0.0710	0.4485	0.246	
Peltophorumferrugineum carbon	pH 9.0	0.571	0.4884	0.209	
Alum impregnated activated alumina	pH 4.0	192.65	$3.69 \times 10^{-4}$	0.670	Tripathy et al., 2006
	pH 6.0	40.68	$9.04 \times 10^{-3}$	0.600	
	pH 9.5	19.8	$6.60 \times 10^{-5}$	0.500	
Hydrogen peroxide modified pumice	pH 6.0	11.76	0.297	0.173	Sepehr et al., 2013
Magnesium chloride modified pumice	pH 6.0	5.56	0.312	0.285	
Nano hydroxyapatite Chitosan composite	30 °C	2.04	0.0801	1.260	Sundaram et al., 2008
	40 °C	2.247	0.077	1.337	
	50 °C	2.320	0.078	1.306	
Nano hydroxyapatite chitin composite	pH 3	8.41	-	-	Sundaram et al., 2009
Hydrotalcite/chitosan composite	pH 3	1.876	-	-	Davila-Rodriguez et al., 2009
Magnetic chitosan particle	pH 7	23.98	-	-	Ma et al., 2007
Guava seeds	25 °C	116.5	0.0051	0.997	Valencia-Leal et al., 2012
	35 °C	316.5	0.003	0.998	
	50 °C	413.8	0.007	0.996	
Aluminum impregnated coconut fiber	40 °C	1.128	0.183	-	Mondal et al., 2015
	60 °C	5.60	12.273	-	
	80 °C	5.827	12.636	-	
Treated banana peel	pH 2	0.395	0.426	0.998	Getachew et al., 2015
Treated coffee husk	pH 2	0.416	0.789	0.998	
Assimilation of chitin with tin	30 °C	12.47	0.12	0.160	Shekhawat et al., 2016
	40 °C	13.44	0.21	0.090	
	50 °C	14.77	0.35	0.060	



When  $1/q_e$  is plotted against  $1/C_e$ , a straight line with slope  $1/bq_m$  is obtained which shows that the adsorption follows the Langmuir isotherm. The Langmuir constants  $b$  and  $q_m$  are calculated from the slope and intercept with Y-axis. The essential characteristics of a Langmuir isotherm can be expressed in terms of dimensionless separation factor, and describe the type of isotherm defined by,

$$R_L = \frac{1}{(1+bC_o)} \quad (5)$$

where  $C_o$  is the initial concentration of fluoride (mg/L) and  $b$  is the Langmuir constant (in g/L). The value of separation factor  $R_L$ , indicates the isotherms shape and the nature of the adsorption process as unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) and irreversible ( $R_L = 0$ ) (Mittal et al., 2007). The constants of Langmuir for different adsorbent are shown in Table 5.

### 3.6. Kinetic modeling of fluoride adsorption

Adsorption kinetics describes the solute uptake rate (chemical reaction), which in turn governs residence time of the adsorption process (Karthik et al., 2016b; Sivarajasekar et al., 2008). Throughout recent years, three kinetic models have been widely used in the literature for adsorption processes, namely the pseudo-first-order kinetic model (Lagergren model), pseudo-second order kinetic model (Ho and McKay model) and intra-particle diffusion model (Weber and Morris model). Parameters of the kinetic constants are identified by linearization followed by both linear and non-linear regression analysis.

The Lagergren's first order rate equation is one of the most widely used rate equation to describe the adsorption of adsorbate from the liquid phase. When adsorption is preceded by diffusion through a boundary, the kinetics in most systems follow the pseudo-first-order rate equation. The linear form of pseudo first-order rate expression of Lagergren is given as,

$$\log(q_e - q_m) = \log(q_e) - \frac{k_1 t}{2.303} \quad (6)$$

where,  $q_e$  and  $q_t$  are the amounts of fluoride adsorbed on adsorbent (mg/L) at equilibrium and at time  $t$  (min), respectively, and  $k_1$  is the rate constant of pseudo first-order kinetics. The good correlation coefficients from the plot  $t$  vs  $\log(q_e - q_m)$  will indicate the applicability of pseudo first-order model. The pseudo first-order

rate constant  $k_1$  and  $q_e$  values were determined for each adsorbent from the slope and the intercept of corresponding plot (Rao, 2010). The values of the constants from the model with the use of different adsorbents are listed in Table 6.

Contrary to the other model, the pseudo-second-order equation predicts the behavior over the whole time of adsorption, with the adsorption (chemisorption) mechanism being the rate controlling step (Sivarajasekar and Baskar, 2015a; Sivarajasekar and Baskar, 2015b) which involves valency forces through electrons sharing or exchange (between adsorbate and adsorbent). The model has the advantage that without knowing any parameters beforehand, adsorption capacity, pseudo-second-order rate constant, and initial adsorption rate can be determined from the equation. The pseudo-second kinetic equation is:

$$\frac{t}{q_m} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (7)$$

where,  $q_e$  and  $q_m$  have the same meaning as mentioned previously and  $k_2$  is the rate constant for the pseudo second-order kinetics. The correlation coefficients ( $> 0.9$ ) from the plot ( $t/q_m$ ) vs  $t$  will indicate the significance of pseudo second-order model and in the determination of the values  $q_e$  and  $k_2$  from the slope and intercept of the corresponding plot (Rao, 2010). The values of the constants from the model with the use of different adsorbents are listed in Table 7.

## 4. ADSORBENT CHARACTERIZATION

The adsorbents used for fluoride ions removal were characterized using various methods. The BET surface area was generally used to characterize the specific surface area of the adsorbent (Pathak et al., 2016). The BET surface areas of the adsorbents used in this study are listed in Table 8. Proximate and ultimate analyses were carried out to determine the ash percentage and contents of moisture, fixed carbon and volatile matter (Ma et al., 2008; Ramanaiah et al., 2007). Fourier transform infrared spectra (FTIR) was used to find the functional groups present in the adsorbent surface and to identify the functional groups responsible for fluoride ions adsorption (Bhaumik et al., 2012; Viswanathan et al., 2009). Scanning electron microscope (SEM) was utilized to understand the morphology of adsorbent surface such as pores development (Goswami et al., 2015; Parlikar and Mokashi, 2013). Thermo gravimetric

**Table 6.** Kinetic parameters of Pseudo first order model

Adsorbent	Initial concentration (mg/L)	Maximum adsorption capacity (mg/g)	Average $k_1$ ( $\times 10^{-2}$ ) ( $\text{min}^{-1}$ )	Average correlation coefficient ( $R^2$ )	Reference
Natural pumice	5 – 20	1.132	2.650	0.969	Sepehr et al., 2013
Hydrogen peroxide modified pumice	5 – 20	1.147	2.258	0.931	
Magnesium chloride modified pumice	5 – 20	1.039	2.530	0.970	
Guava seeds	5	0.148	4.895	0.959	Valencia-Leal et al., 2012
Nanohydroxyapatite chitosan	9 – 15	1.778	0.199	0.949	Sundaram et al., 2008
Tamarind fruit shell carbon	2 – 8	82.160	4.243	0.885	Sivasankar et al., 2012
aluminum impregnated coconut fiber	1	2.337	0.739	0.825	Mondal et al., 2015
Treated banana peel	10	-	0.084	0.953	Getachew et al., 2015
Treated coffee husk	10	-	0.072	0.878	

**Table 7.** Kinetic parameters of Pseudo second order model

Adsorbent	Initial concentration (mg/L)	Maximum adsorption capacity (mg/g)	Average $k_2$ ( $\times 10^{-2}$ ) (g/mg min)	Average correlation coefficient ( $R^2$ )	References
Natural pumice	5 - 20	1.732	4.535	0.996	Sepehr et al., 2013
Hydrogen peroxide modified pumice	5 - 20	1.822	5.885	0.998	
Magnesium chloride modified pumice	5 - 20	1.764	5.310	0.997	
Guava seeds	5	0.170	39.000	0.984	Valencia-Leal et al., 2012
Nanohydroxyapatite chitosan	9 -15	-	0.231	0.999	Sundaram et al., 2008
Tamarind fruit shell carbon	2 - 8	58.313	3.063	0.866	Sivasankar et al., 2012
Aluminum impregnated coconut fiber	1	1.607	2.032	0.987	Mondal et al., 2015
Treated banana peel	10	0.3123	3.202	0.984	Getachew et al., 2015
Treated coffee husk	10	0.2946	3.394	0.981	
Treated coffee husk	10	0.2946	3.394	0.981	

weight loss (TG) and Derivative of thermo gravimetric (DTG) studies were conducted in order to understand the thermal stability of the material (Mohan et al., 2012; Shekhawat et al., 2016).

The point of zero charge (pH<sub>zpc</sub>) of adsorbent was also calculated to know the neutral point of pH of the adsorbent surface (Viswanathan and Meenakshi, 2008; Daifullah et al., 2007). X-ray diffraction (EDX) analysis was performed for elemental composition of the adsorbent (Shekhawat et al., 2016).

**Table 8.** BET surface area of different adsorbent used for fluoride removal (Pathak et al., 2016)

Adsorbent	BET Surface Area ( $\text{m}^2/\text{g}$ )
Pomegranate peel	1.28
Pineapple peel	1.00
Watermelon peel	1.44
Garlic peel	1.40
Green pea peel	1.02
Pigeon pea peel	1.04

## 5. CONCLUSIONS

Fluorosis is an important public health problem in India due to fluoride contaminated drinking water. The first and foremost preventive measure of fluoride-free drinking water supply can be accomplished by defluoridation of potable water. Evidently, the cheapest and abundantly available adsorbents have demonstrated outstanding removal capabilities for fluoride removal and can be exploited commercially, contributing to the sustainability of the environment. Metal ores, naturally occurring materials, charcoal and bio-based adsorbents were widely examined for the defluoridation of water. Process parameters such as initial fluoride concentration, adsorbent dose, pH, temperature, and contact time were found to significantly influence the defluoridation process. The adsorption data were generally analyzed using the Langmuir and Freundlich isotherms extensively, whereas the kinetics data were explained by pseudo first order and second order models. This review also covered the essential characterizations required for the adsorbents. From this review, it is concluded that plant products and waste materials not requiring any further modifications can be promising adsorbents for environmental and purification purposes.

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