Defluoridation using adsorption: a review on batch analysis parameters, kinetics, isotherms, activation energy and thermodynamics

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Abstract

Fluoride is one of the common contaminants present in groundwater and in waterbodies in general. It can create serious health hazards if ingested more (>1.5 mg/L). Scientists understands that removing fluoride from ground water is a difficult task. Several techniques like coagulation, membrane filtration, etc. are available for treatment but because of the high processing costs, such technologies are not always suitable for developing countries. As a result, environmentally friendly and low-cost technology like adsorption is one such method that can be successfully employed for fluoride removal. Fluoride was removed using a variety of low-cost adsorbents such as tamarind seed, tamarind gel, and duck weed etc. by defluoridation using adsorption and can be considered as one of the efficient and practical technique. This review article reports for the successful and efficient use adsorption and various adsorbents for the defluoridation of contaminated water. Observations have been reported for batch studies done by several researchers for effect of various parameter like initial concentration, temperature, contact time, pH, stirring rate on defluoridation from aqueous solution which can be supported from the fact that most of the researches done follows Pseudo second order kinetic model which suggests that the rate of adsorption is substantial and adsorption is an effective tool for the removal of fluoride from contaminated

water. Isotherm studies reveal that most of the adsorption follows either Langmuir or Freundlich models. Overall, the research analyses suggests that adsorption technique can be regarded as one of the important techniques for defluoridation of contaminated waters.

Keywords

Adsorption, Defluoridation, Adsorption equilibrium, Activation Energy, Adsorption kinetics, Point of zero charge (pH$_{pzc}$)

1. Introduction

Fluorine (F$_2$) is a corrosive, pale yellow-green gas that is almost impossible to find in elemental form in the natural environment due to its high electronegativity and reactivity. Fluoride (F) is a fluorine anion with a small radius, a high proclivity for acting as a ligand, and the ability to produce a wide range of organic and inorganic compounds in soil, rocks, air, plants, and animals.Fluoride is present in surface and groundwater as a nearly totally dissociated fluoride ion [1,2]. Fluoride is the 13th most abundant naturally occurring element which is reactive and electronegative. Althoughfluoride concentration in surface water and groundwaterdepends on various contributing factors, including as total dissolved solid, pH, hardness, alkalinity and the geological makeup of aquifers [1, 3-8] high fluoride concentrations are a result of fluorine tainted waste water discharges in many nations across the world. The superphosphate fertiliser business is frequently the source of such waste streams [9,10] coal fired power station [11], oil refineries[12] etc.

FRRDF report found that a total of 17 out of 32 States in India are reported to have endemic fluorosis in India [13],from which 70-100% affected state are Rajasthan, Gujarat and Andhra Pradesh. 40-70% affected state are Maharashtra, Madhya Pradesh, Assam, Jharkhand, Bihar, Uttar Pradesh, Karnataka, Chhattisgarh, Haryana, Delhi, Punjab, Uttaranchal, TamilNadu. 1-40% Jammu & Kashmir, West Bengal, Orissa, Kerala. In 1987 it is estimated that 25 million people were suffering from fluorosis.

Fluoride is beneficial to human body for the classification of dental enamel and maintenance of healthy bones. Intake of fluoride in body is through drinking water, food products. As per WHO, the maximum permissible limit for fluoride in drinking water is 1.5 mg/l [1,14], but a lower concentration is recommended for children and as per BIS 10500 (2012), the maximum permissible limit of fluoride in drinking water is 1.5 mg/l[15], but if the consumption of fluoride exceeds above permissible limit for a long period of time it can cause dental

fluorosis, cancer, skeletal fluorosis and non-skeleton fluorosis change in the DNA-structure. People exposed to large amount of fluoride (>1.5 mg/l) show dental skeletal fluorosis [16-23]. Dental fluorosis affects children and discolours and disfigures teeth. Skeletal fluorosis affects the bones and major joint of the body like neck, backbone, shoulder, hip and knee joints resulting in severe pain, rigidity or stiffness in joints. Severe forms of skeletal fluorosis results in marked disability. Non-skeletal forms of fluorosis are earlier manifestations, which develop long before onset of typical change in teeth and skeletal bones. These are seen as gastro-intestinal symptoms and may overlap with other diseases leading to misdiagnosis. It affects men, women and children of all age group.
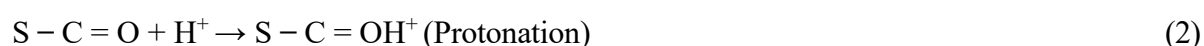
2. Materials and Methods

2.1 Fluoride and its adsorption chemistry

Fluoride is an inorganic, monatomic fluorine anion with the chemical formula F, whose salts are typically white or colourless. Fluoride salts are usually colourless and have a characteristic bitter flavour. Its salts and minerals are essential chemical reagents and industrial chemicals, mostly used to make hydrogen fluoride for fluorocarbons.Although fluorine is categorised as a weak base because it only interacts partially in solution, pure fluoride is corrosive and can cause skin irritation. The simplest fluorine anion is fluoride. The fluoride ion is similar to the hydroxide ion in charge and size. Fluoride ions are found in various minerals on Earth, including fluorite, but in nature only in trace amounts in water bodies.

Removal of fluoride using cellulosic based adsorbents [8, 24] are in wide practice and hence its important to understand the chemistry of fluoride adsorption by an adsorbent consisting cellulosic material.

Cellulosic adsorbents mainly consist of cellulose, hemicellulose and lignin components with functional groups primarily responsible for uptake of adsorbate from an aqueous solution are hydroxyl and carboxyl groups [25-42]with symbols OH, COOH, NH-O and C=O. Also, there are hetero atoms i.e., O and H, which undergo protonation and they release a lone pair of electrons. These lone pair electrons develop a positive charge and they participate in the adsorption of fluoride. Reactions involved during adsorption can be summarized as:

$$S-OH + H^+ \rightarrow S-OH_2^+ (+F \text{ electrostatic attraction}) \tag{1}$$

$$S-C=O + H^+ \rightarrow S-C=OH^+ (\text{Protonation}) \tag{2}$$

$$S - HN + H^+ \rightarrow S - H_2N^+ \text{ (+F electrostatic attraction)} \tag{3}$$

After that electrostatic physisorption between ions and dipoles will take place and subsequently electrostatic attraction between positive poles of partial bonds of OH, NH and CO groups of adsorbents and fluoride will occur as:

$$S \text{-}O^{-S} - H^{+S} + F \rightarrow S - O^- \tag{4}$$

$$-H^{+S} - \ldots\ldots F \rightarrow S - N^{-S} - H^{+S} \tag{5}$$

For adsorption by soil minerals, adsorbents in soils, such as calcareous minerals, aid in pH-dependent fluoride solubility, as shown by the mass balance equation:

$$CaCO_3 + H^+ (aq)\, 2F^- (aq) \leftrightarrow CaF_2(s) + HCO_3^- (aq) \tag{6}$$
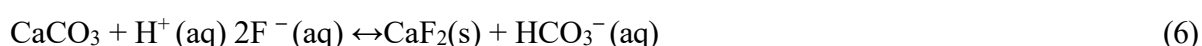
The above equation corelates fluoride and calcite when both salts come into contact with water in natural soil condition. As a result, rising pH and HCO_3^- concentrations raise water fluoride levels, and vice versa. Furthermore, anionic adsorption onto soil adsorbents can be done in two ways: specific and non-specific. The former is based on ligand-exchange processes, in which anions remove OH^- and H_2O from soil surfaces. The latter is based on the pH of zero net charge (pH_{zpc}) of the adsorbent soil surface and involves electrostatic coulombic forces. The soil surface becomes positively charged above pH_{zpc}, but below net positive surface charge persists.For example, ligand exchange happens in the selective adsorption of fluoride by metal oxyhydroxide surface sites, according to equation 7 and 8 as follows for protonated and non-protonated sites:

$$SOH_2^+ + F^- \leftrightarrow SF + H_2O \tag{7}$$

$$SOH + F^- \leftrightarrow SF^- + H_2O \tag{8}$$

As a result, the pH of the aqueous media is the primary determinant of fluoride uptake by soil surfaces.Importance of pH_{zpc} in relation to adsorption is also discussed later in section 3.2 of this article.

According to many studies,bagasse fly ash (BF) has a high carbon content, according to [43] agro cum industrial waste bagasse dust, which contains functional groups associated with sucrose, lignin, cellulose, and proteins as key ingredients.Anion adsorption on such materials is attributable to the presence of aquo groups (—M—OH_2—) and hydroxo groups (—M—OH), as well as the large surface area and charge on their tiny particles.Deprotonation or a hydroxyl ion association reaction determine the surface chemistry of an oxide in contact with an aqueous solution to a great extent [44]. However, some evidence suggests that even if the

surface is neutral, an anion like F$^-$ can be adsorbed by an ion exchange mechanism as shown below.

$$—M—OH + F^- ———————> —M—F + OH^-$$
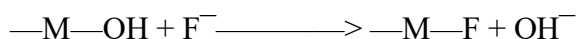
Defluoridation methods may broadly be classified in two categories namely Additive methods and Adsorptive methods. In additive methods, certain reagents are added and optimum conditions for the defluoridation are maintained. Fluoride ion present in water reacts with the reagents added and forms an insoluble complex and is being removed as ad flocs. In adsorptive methods, a bed of greater surface activity is chosen and water is passed through the bed. Due to surface activity, fluoride ions get preferentially adsorbed on the bed surface thereby causing a reduction of fluoride ion in the exit stream. To remove fluoride from water, a variety of technologies are currently available, as shown in Table 1, including coagulation and precipitation [12, 45-49], membrane procedures [50-58], electrochemical treatments [59-69], and ion-exchange and its modification [70-76]. However, the adsorption process is often regarded as the most cost-effective and efficient approach for removing fluoride from water [8, 24, 25, 26, 77-80].Advantages and disadvantages of different defluoridation techniques are highlighted in Table 1.

Table 1. Comparison of different defluoridation techniques in use [8, 25, 46, 58, 61, 81, 82]

Processes	Technology	Advantages	Disadvantages
	Coagulation Flocculation	Simple, economically feasible	High sludge production, handling and disposal problems
Conventional treatment processes	Biodegradation	Economically attractive, publicly acceptable treatment	Slow process, necessary to create an optimal favourable environment, maintenance and nutrition requirements
	Adsorption on activated carbons	The most effective adsorbent, great, capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
	Membrane	Removes all dye	High pressures, expensive,

	Separations	types, produce a high-quality treated effluent	incapable of treating large volumes
Established Recovery processes	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dyes
	Oxidation	Rapid and efficient Process	High energy cost, chemicals required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective bio-sorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganisms	Slow process, performance depends on some external factors (pH, salts)

2.2 Adsorption process

Any removal of pollutants using adsorption is primarily achieved by determining the adsorption capacity of adsorbents for the removal of adsorbates. This is conventionally done by using mass balance equation which is given as:

$$q_{max} = \frac{c_i - c_f}{m} \times V \qquad\qquad (9)$$

Where, q_{max} = Maximum adsorption capacity of adsorbent (mg/g); c_i =Initial fluoride

concentration (mg/L); C_f= Finalfluoride concentration in the solution (mg/L); V = Solutionvolume (L); m=massofadsorbent (g)

The following equation was used to calculate the percent (%) dye removal:

Removal percentage (%) = $\frac{C_i - C_e}{C_i} \times 100$

Where, C_e is equilibrium concentration of dye in the solution.

For defluoridation, adsorption is a commonly employed method.Several researches involved various materials as adsorbent for defluoridation, such as use of alumina in activated form [83-86], bauxite [33, 34, 85, 87-96], brick powder [94], activated carbons [27-32], hematite [91, 97-99], use of resins from polymers [74, 92, 93, 100], pumice stone [95, 101, 102], use of charcoal, serpentine, brick, red soil, fly ash [96, 103, 104], granular ceramics [105], extract of seeds from *Moringaoleifera* [33], use of chitin, chitosan, alginate [91, 106-112], rice husk in activated form [29, 33-35], treated hydroxide/ferric oxide [113-119], HAP (hydroxyapatite) [35, 100, 120-122], cerium and zirconium treated materials [123-134], sorbents derived from titanium [135-137], use of schwertmannite [138], cellulosic substances in modified form [36, 37], different form of clays [139-143], zeolite [81, 144-150] and magnesium treated adsorbent [121, 134, 151]. Studies revealed that among different metal oxides and hydroxides, especially those synthesised in nano-form, provide the greatest results and better adsorption capabilities among all of the above-mentioned adsorbents.

However, as fluoride concentrations fall, many adsorbents lose their fluoride removal capacity; the lowest limit for fluoride reduction by most adsorbents is 2 mg/L; as a result, they are not suitable for drinking water, especially since some of them can only work at extreme pH values, such as activated carbon, which is only effective for fluoride removal at pH< 3.0 [152].

The process of solute molecules attaching to the surface of an adsorbent is known as adsorption. The adsorption process can be done in a batch or in a column. Physical adsorption (physisorption) and chemical adsorption (chemisorption) are the two main processes involved in adsorption. Physical adsorption is caused by weak forces of attraction (van der Waals), whereas chemisorption is caused by the development of a strong bond between the solute and the adsorbent, resulting in electron transfer [153-156]. Researchers now a days has focused

on various type of inexpensive and effective adsorption media. Apart from the use for defluoridation, adsorption is also widely used for removal of harmful synthetic dyes and heavy metals from aqueous solution [153-156]. For defluoridation using adsorption technique, important batch studies include analysis of effect of various parameters like pH, adsorbent dose, contact time, initial concentration, temperature, effect of RPM etc. To understand adsorption mechanism, studies required are analysis of adsorption kinetics, adsorption isotherm equilibrium studies, study of activation energy and thermodynamic parameters.

2.2.1 Adsorption isotherm studies

Adsorption isotherms are useful in explaining the distribution of adsorbate molecules between the liquid and solid phases when an adsorption process is at equilibrium [157]. Quantity of adsorbate adsorbed on the surface of an active adsorbent and the representation of equilibrium concentration for liquid adsorbate achieved during the adsorption process at constant temperature is scientifically presented by adsorption isotherm models. For any pollutant removal using adsorption, isotherm equilibrium studies are as important as kinetic studies if not more. Isotherm studies are used to quantitatively describe adsorbate-adsorbent interactions and to investigate the absorbent's efficacy for a specific adsorbate. Some of the renowned isotherms which are in use by various researchers for defluoridation using adsorption are discussed as below:

Langmuir isotherm:

The Langmuir isotherm [160]is based on the premise that there is a point of valence on the adsorbent's surface and that each adsorption site may adsorb one molecule. The adsorbed layer will be one molecule thick as a result. In addition, it is considered that all of the adsorption surface for molecules of the adsorbate is homogeneous, monolayer adsorption and that the presence of adsorbed molecules at one site has no effect on the adsorption of molecules at nearby sites. The Langmuir equation is conventionally represented like:

$$q_e = \frac{Q_m b c_e}{1 + b c_e} \tag{12}$$

q_e = quantity adsorbed (mg/g), C_e = adsorbate concentration at equilibrium in mg/l, and Q_m and b = Langmuir isotherm constants linked to adsorption capacity and energy, respectively.

Rearranging equation 3 provide the linearized form of Langmuir model as-

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b\,q_m\,C_e}$$

This equation is in the form of straight-line y = mx + c, Where

$Y = \frac{1}{q_e}$, $x = \frac{1}{c_e}$, m = slope of the straight line $= \frac{1}{Q_m\,b}$, c = intercept $= \frac{1}{Q_m}$

In order to determine whether the adsorption system is favourable or not ‗R_L' name as dimensionless separation factor, which is obtained from Langmuir model is defined by the following equation:

$$R_L = \frac{1}{(1 + bc_0)}$$

Where, the starting fluoride concentration is C_0, and the Langmuir constant is b. The value of R_L is used to explain the reactions' feasibility.

If $R_L > 1$ then the adsorption is unfavourable

If $R_L = 1$ then it is linear

If $0 < R_L > 1$ then the adsorption process is favourable

If $R_L = 0$ indicate process is irreversible

Freundlich isotherm:

Freundlich [161] presumed the heterogeneity of the surface of adsorbent where there is exponential distribution of adsorption site at the surface of the adsorbent and also the exponential variation of the energy of adsorption. On this presumption he proposed the isotherm model. It is empirical and very widely used. It is expressed as-

$$q_e = K_F \times C_e^{1/n} \tag{13}$$

Where 1/n and K_F are system specific constants or Freundlich constants.

K_F is an indicator of adsorption capacity. Higher value of K_F indicates the higher adsorption capacity of adsorbent. The adsorption intensity is measured by the number n. The better the adsorption, the higher the n value. $2 < n < 10$ value of n shows that adsorption is feasible and favourable

The linearised Freundlich adsorption isotherm can be expressed as,

ln q_e = (1/n) ln C_e + ln K_F

This equation is in the form of straight-line Y = mx + C, where

Y = ln q_e, X = ln C_e, m = slope of the straight line = 1/n, C = intercept = ln K_F

Temkin Isotherm:

The Temkin isotherm model [162] implies that all molecules' adsorption heat reduces linearly as the adsorbent surface is covered more, and that adsorption is characterised by a uniform distribution of binding energies up to a maximum binding energy. The Temkin isotherm is represented as follows:

$$qe = B_T ln K_T + B_T ln\ Ce \tag{14}$$

Where, B_T is Temkin constant and K_T is Temkin adsorption potential

D-Risotherm:

Dubinin Radushkevich (D-R) model [163] is a more general model in which assumption is not based on homogenous surface or constant adsorption potential, it gives insight into the biomass porosity as well as the adsorption energy. The value of adsorption energy further provides information as to whether adsorption process is physical or chemical in nature. According to the Dubinin-Radushkevich (D-R) isotherm model, adsorbent size is equivalent to micropore size, and the adsorption equilibrium relation for a particular adsorbate-adsorbent combination may be represented independently of temperature using the adsorption potential (ε). The D-R isotherm can be represented as follows:

$$ln qe = ln qs - \beta\ \varepsilon^2 \tag{15}$$

Where, q_S denotes theoretical isotherm saturation capacity (mg/g)

β = Dubinin–Radushkevichisothermconstant

$\varepsilon = RTln\ (1 + 1/C_e)$

2.2.2 Adsorption kinetics studies

Kinetic studies are an inseparable part of any adsorption analysis. Any adsorption experimentation is essentially incomplete if it doesn't include analysis of kinetics. Kinetics models can be used to determine the likely dye adsorption mechanism as well as possible

rate-controlling steps[157]. Adsorption kinetics is defined as the rate of retention or release of a solute from an aqueous environment to the solid-phase interface at a particular temperature, pH, flow rate and adsorbent dose. Kinetics studies are of great significance to evaluate the adsorption performance and reveal the underlying mechanisms. Adsorption kinetics hasprime importance indescribing solute uptake rate and time required for adsorption process. Two types of kinetic study are generally done namely, Pseudo first order kinetic[158] and Pseudo second order kinetic[159]. For any adsorption removal of hazardous material, if the analysis reveals that sorption is following Pseudo first order, then it is understood that rate of sorption is less andthus will require more time for adsorption equilibrium to reach whereas if the sorption follows Pseudo second order kinetic then it implies that rate of sorption is more and will require lesser time compared to the former one which is more desirable. Two rate kinetics are discussed as below:

Pseudo-first order kinetic

Pseudo-first order [158] Kinetic equation is given by:

$$\frac{dq}{dt} = K_{pa}\left(q_e - q\right)^a$$

(10)

where q is the amount of adsorbed adsorbate onto the adsorbent at time t in mg/g, q_e is the adsorption capacity at equilibrium in mg/g, and the sorption rate constant in represented by k_1 in minutes.

Putting a= 1 and equating

After integration we get

$$\ln\left(q_e - q\right) = -k_{p1} \times t + \ln q_e$$

This is in the pseudo first order rate equation in the form of straight line

Y= mx + c where, y=ln$\left(q_e - q\right)$; x=t; m= - kp1 and the intercept c = lnq_e here k_{p1} = Pseudo first order rate constant and q_e and q are the amounts of fluoride adsorbed (mg/g) at equilibrium and at time t respectively.

Pseudo-second order kinetic

Ho and McKay [159] presented the Pseudo-second order kinetic as-

$$\frac{d\mathbf{q}}{d\mathbf{t}} = K_{pa} (q_e - q)^a$$

(11)

Putting a= 2 and equating

After integration we get

$$\frac{t}{q} = \frac{1}{K_{p2} \times q_e^2} + \frac{t}{q_e}$$

This is in the pseudo second order rate equation in the form of straight line

q (mg/g) is the amount adsorbed at time t (min) and q_e is the amount adsorbed at equilibrium (mg/g). K_{p2} is the rate constant.

2.2.3 Activation energy and Thermodynamic parameters

The lowest amount of energy required in chemistry to activate atoms or molecules in a condition that allows them to undertake chemical transfer or physical transport is known as activation energy. To begin, all chemical reactions, including exothermic reactions, require activation energy.Although the energy changes caused by a reaction can be positive, negative, or even zero, an energy barrier must be overcome in both cases before the reaction can take place. Reactants need activation energy to move together, overcome repulsion forces, and begin breaking bonds. The adsorption process with negative activation energy is exothermic, meaning it increases at lower temperatures and decreases at higher temperatures. The adsorbate may desorb (leave the surface) when the temperature rises, because unfavourable intermolecular interactions between the adsorbate and the solvent are significantly stronger than those between the adsorbate and the adsorbent.The Arrhenius equation[164] can be used to calculate the activation energy of any chemical interaction. The following is the equation for the same.

$$ln\,K = ln\,A - \frac{E}{RT}$$ (16)

After producing a graph of ln K versus 1/T, the slope of the curve may be used to calculate the activation energy E_a. Where T is the temperature in kelvin, and K is either a pseudo first order rate constant or a pseudo second order rate constant, depending on the kinetic reaction's preferred rate of adsorption. The type (physical or chemical) of adsorption is revealed by

activation energy. Thermodynamic parameters such as ΔG° = Gibbs free energy change, ΔH° = Enthalpy change, and ΔS° = Entropy change must be investigated to determine the temperature suitability of the adsorption, whether the sorption process is endothermic or exothermic, and whether the adsorption is enthalpy or entropy driven. The following equations can be used to conduct the studies.

$$\Delta G° = -RT\ln K_{ad} \tag{17}$$

$$K_{ad} = \frac{C_0 - C_e}{C_e} \tag{18}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{19}$$

The plot of $\Delta G°$ and T can be used to calculate the values of $\Delta H°$ and $\Delta S°$. The initial and equilibrium dye concentrations of the solution are C_o and C_e, respectively. At equilibrium, K_{ad} is the rate constant of the adsorption process. Rate kinetic analysis can be used to determine the value of n by determining which rate model best matches the observed data.


3. Results and Discussions

3.1 Characterization of adsorbents

Apart from batch studies, characterization using SEM [165, 166, 167, 170, 171, 179] images for adsorbents before and after adsorption, scientifically explains about the change in surface morphology and FTIR [165, 166, 167, 170, 172-179, 181] studies reveals about functional groups responsible for defluoridation. Various functional groups which are prominent in modified adsorbents and are responsible for uptake of pollutants like fluoride are shown intable 2. Other Characterization studies involves EDS [167-170] BET [179], EDX [179],TEM, XRD [180], analysis. Singh et. al., 2016 used sugarcane bagasse for the removal of fluoride form aqueous solution, in their analysis they used FTIR study to explain the adsorption phenomenon. Figure 1. Shows their FTIR image.

Table 2: Functional groups and their characteristic absorption frequencies

Functional Group	Characteristic Absorption(s) (cm^{-1})
Alkyl C-H Stretch	2950 - 2850 (m or s)
Alkenyl C-H Stretch Alkenyl C=C Stretch	3100 - 3010 (m) 1680 - 1620 (v)
Alkynyl C-H Stretch Alkynyl C$\equiv$C Stretch	~3300 (s) 2260 - 2100 (v)
Aromatic C-H Stretch Aromatic C-H Bending Aromatic C=C Bending	~3030 (v) 860 - 680 (s) 1700 - 1500 (mm)
Alcohol/Phenol O-H Stretch	3550 - 3200 (broad, s)
Carboxylic Acid O-H Stretch	3000 - 2500 (broad, v)
Amine N-H Stretch	3500 - 3300 (m)
Nitrile C$\equiv$N Stretch	2260 - 2220 (m)
Aldehyde C=O Stretch Ketone C=O Stretch Ester C=O Stretch Carboxylic Acid C=O Stretch Amide C=O Stretch	1740 - 1690 (s) 1750 - 1680 (s) 1750 - 1735 (s) 1780 - 1710 (s) 1690 - 1630 (s)
Amide N-H Stretch	3700 - 3500 (m)
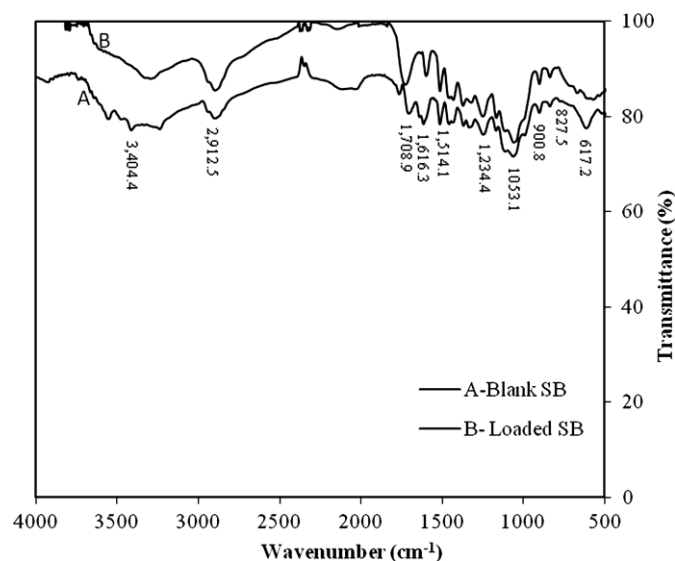
Fig. 1FTIR of virgin and Fluoride loaded sugarcane bagasse [166]

The presence of free and intermolecularly bound hydroxyl groups can be detected in Fig. 1 with an adsorption peak around 3,404.4 cm^{-1}. The stretching vibration of C-H groups is responsible for the peaks detected at 2,912.5 cm^{-1}.Peaks about 1,620 cm^{-1} correspond to C=C, which could be attributable to lignin aromatic groups. The OCH_3 group is responsible for the strong C-O bond at 1,053.1 cm^{-1}, confirming the presence of lignin structures in bagasse.Similar type of results for defluoridation utilising adsorption was reported [182-185]

3.2 Point of zero charge(pH_{pzc})

The pH at which an adsorbent surface has a net neutral charge is known as the point of zero charge (pH_{pzc}). Study of pH_{pzc} for any adsorbent is of much significance which reveals the potentiality of anyadsorbent surface to attract anionic or cationic adsorbates. For e.g.,if a given adsorbent surface have a positivecharge at the solution with pH less than pH_{pzc}then that adsorbent surface will uptake adsorbates which are anionic. On the other hand, ifthat adsorbent surfacehaveanegativechargeatthesolutionwith pHgreaterthanpH$_{pzc}$then the adsorbent will uptake cationic adsorbate[186-188].In other words, the significant factor, the point of zero charge (pH_{pzc}), indicates the surface's adsorption ability and the sort of surface-active centres [189]. The point of zero charge (pzc) is the pH at which the surface charge is zero and is commonly used to quantify or characterise the electrokinetic properties of a surface. Only in systems where H^+/OH^- are the potential determining ions is the pH value utilised to explain

pzc. To better understand the adsorption mechanism, many researchers analyzed the point of zero charge (pH_{pzc}) of various adsorbents made from agricultural solid wastes. At $pH>pH_{pzc}$, cationic dye adsorption is favoured due to the presence of functional groups such as the OH^- group, whereas anionic dye adsorption is favoured at $pH<pH_{pzc}$, where the surface becomes positively charged [189].The above concept can be applied in any adsorption interaction to reveal whether the adsorption favours anionic or cationic sorption depending upon the charge present on the adsorbent surface and pH of the interactive solution. [167] in their analysis evaluated the point of zero charge forprotonated xanthate modified Ficus religiosa (PXFR) andprotonated Ficus religiosa (PFR) which are depicted using figure 2.
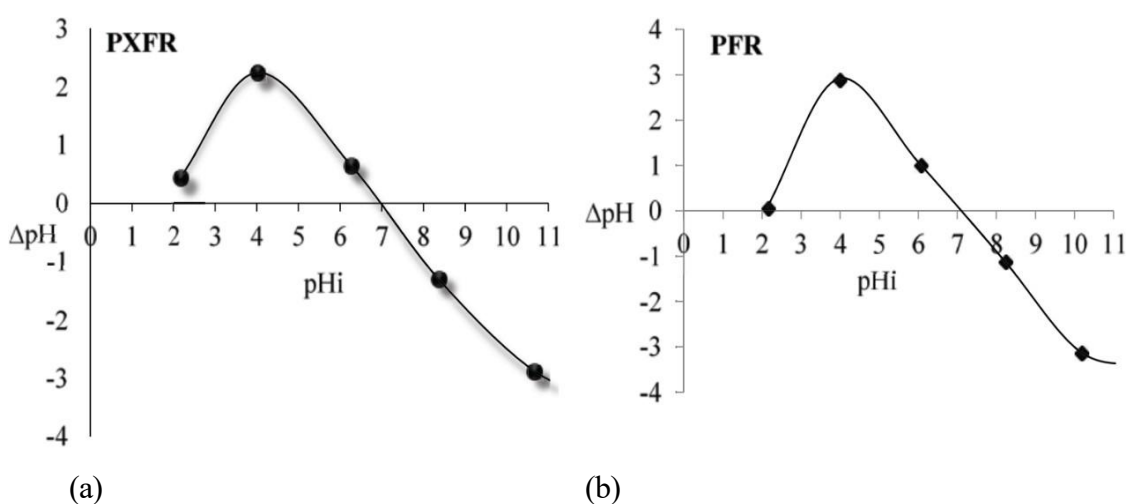

Fig. 2. Point of zero charge pH (pH_{pzc}) for (a) Protonated xanthate modified Ficus religiosa (PXFR) and (b) protonated Ficus religiosa (PFR) [167]

As per their definition [167], a chargeless point,the pH of the solution at which the surface charge of biomass becomes neutral is called point of zero charge (pHpzc). As the pH of the solution rises over pHpzc, the surface of the bio-sorbent becomes negative. The surface, on the other hand, accumulates positive charge and attracts an anion (fluoride) when the pH of the solution falls below pHpzc [190]. As per their analysis (refer figure 2), the pHpzc values of both bio-sorbents (PFR, PXFR) were determined to be 7.1 and 6.9, respectively. The significantly more acidic character of sulphur being connected as a modifier could explain the small reduction in pHpzc of xanthate modified material.

3.3 Review for use of different adsorbents and batch study results

In general, there are two types of adsorbents, namely organic and inorganic. Organic adsorbents like activated carbon prepared from sugarcane, coconut shell, tamarind fruit cover, date palm, neem leaf, rice husk etc, and inorganic materials like activated alumina, immobilised activated alumina, Mukondeni clay soils etc. Different adsorbents (organic & inorganic) used by different researchers to study the removal of fluoride from the aqueous solution and results of batch studies are reported below.

[191] Prepared a mixed Mukondeni clay soils (MMCS) as a cheap adsorbent for the removal of fluoridefrom aqueous solution where they found that the optimum condition for the removal of fluoride using MMCS are 60 min, 1.5 g, 9 mg/L, at pH of 2 and a temperature of 25°C. Freundlich isotherm fitted well for the adsorption with regression parameter (R^2 = 0.95) and Kinetic studies revealed that the adsorption followed pseudo second order kinetics. The BTS surface area of MMCS was found as 35.4613 cm^2/g which is a moderate surface area for fluoride adsorption.

[192] in his study used modified immobilized activated alumina (MIAA) prepared by sol-gel method for the removal of fluoride from aqueous solution. The modification was done by adding a specific amount of alum during the sol formation step. The removal efficiency of fluoride was reported as 1.35 times higher as compare to normal immobilized activated alumina, the maximum removal of fluoride was obtained at pH 7 at a stirring rate of 150 and at a temperature of 20°C with an initial fluoride concentration of 12 mg/l. More than 90% of fluoride was removed within 60 minutes of contact time and maximum fluoride adsorption capacity was found to be 0.76 mg/g. Langmuir adsorption isotherms fitted well for the fluoride adsorption on MIAA with the regression coefficient R^2 of 0.99 which suggested monolayer adsorption.

[193] uses a modified fly ash for the removal of fluoride. Two types of bed were prepared, bed 1 was prepared by treatment with 12M HCL followed by neutralization with 5M NaOH solution. The reaction mass was filtered, washed, dried and crushed to fine powder and bed 1 was mixed with alum and $MgCl_2$ solution and treated with 0.9M Na_2CO_3 until pH reached to 4.5. Mass was again filtered, washed, dried at 120°C for 4 hours and crush to the fine powder which was taken as bed 2 material. Among them, bed 1 was used to maintain pH and bed 2 was used for defluoridation. Now initial fluoride concentration of 100ppm was taken with an adsorbent dose of 15g and allowed to passed through bed 2 and were found to contain no

fluoride but the pH was 5.4-5.5 to maintain the pH as per WHO it was again passed through bed 1.

[194] used treated bark of Phyllanthus emblica (amla) tree as an adsorbent where the maximum removal occurred at pH 7 with an optimum dose of 1.5g/l for a concentration of fluoride ion with 5mg/l at an optimum contact time of 60 min. Adsorption model of PTB well fitted in Freundlich model at 30°C.

Coconut shell activated carbon was used by [195], as an adsorbent where the maximum efficiency of 65.9% was obtained with a particle size of 150μ. Coconut shell activated carbon were used at a pH of 2 with an initial fluoride concentration of 14mg/l and adsorbent dose of 160g/l.

[196] used tamarind (Tamarindus indica) fruit cover (TNFC) as a natural adsorbent in virgin and acid treated forms. The maximum adsorption capacity of virgin TNFC and treated TNFC sorbents as obtained from the Langmuir adsorption isotherm was found to be 4.14 mg/g and 6.11 mg/g of fluoride at a pH 6 and both natural and acid treated (TNFC) forms followed pseudo-second-order kinetic model.

[197] demonstrated the potential for selective adsorption of fluoride ions with rice husk. In their analysis, the optimum sorbent dose was found to be 10g/L by varying the dose of adsorbent from 0 to 16g/L; equilibrium was achieved in 120 min for the optimum pH 2 with a fluoride ion concentration of 5 mg/l, maximum fluoride removal was observed to be 75% at optimum conditions.

Custard apple as an adsorbent was used by [198], found that an efficiency of 95% was achieved at optimum parameters of pH 7, contact time 30 min, agitation speed 500 rpm, and adsorbent dosage 1.5g per 50 mL of fluoride water with a concentration of (2-10 ppm), Langmuir isotherm fitted well for the adsorption of fluoride ion on custard apple.

[199], used thermally activated bio-sorbents prepared from banana (Musa paradisiaca) peel and coffee (Coffea arabica) husk as an adsorbent with efficiency ranging from 80 to 84 % with an optimum pH of 2 for both the adsorbents, and the optimum dose was found to be 24 g/ 250 mL at 13-hour contact time for banana peel and 18 g/250 mL at 3 hour contact time for coffee husk. Fluoride concentrations in flour factory, poultry, and Lake Hawassa water samples were found to be 12.54, 11.02, and 6.72 mg/L, respectively. The Langmuir

adsorption model and pseudo second-order reaction kinetics were fitted best to the adsorption process.

Coconut root as an adsorbent was used by [200], for the removal of fluoride. For this analysis, maximum fluoride removal of 93.48% was attained with adsorbent dose of 8 g/L, contact period 90 min, stirring speed 80 rpm and temperature 50 °C when the initial adsorbate concentration was 5 mg/L. The adsorption kinetic data fitted well with the pseudo-second-order kinetic model and adsorption isotherm can be best described by Langmuir isotherm model.

[166] used low-Cost sugarcane bagasse for defluoridation and as per they reported 45% fluoride removal was found at a contact period of 60 min with initial fluoride concentration of 4 mg/l at a adsorbent dose of 1 g/L and maximum uptake of fluoride was found to be 4.12 mg/g. The adsorption kinetic data fitted well with the pseudo-second-order kinetic model and adsorption isotherm was best described by Langmuir isotherm model.

[201], used bio-adsorbent from possotia (Vitex negundo) leaf, their study showed that the PLP can remove more than 70% of fluoride from a 3-ppm aqueous solution on its own at a normal pH range of 7-8, with a contact time of 120 min and 3 g/L of its dose. And adsorption kinetics data were fitted to pseudo second order kinetics.

[202], in their study used several materials as adsorbent which showed maximum fluoride sorption capacity at pH 6.0, temperature 25°C, with rpm of 150 and contact time of 5 hour respectively. When compared for different adsorbents, defluoridation order was found to be as: shell powder > bone powder > alumina treated bagasse fly ash > bone powder > bagasse.

[203], calculated maximum removal efficiency of 85% at pH 2 with a contact time of 120 min and an initial fluoride concentration of 10mg/l at an adsorbate dose of 10g/l using a low-cost bio-sorbent alkali treatment neem leaf as an adsorbent to remove the fluoride from water.

[204], used guava seeds modified with aluminium as bio-sorbent for their research. They collected guava seeds (Psidium guajava) from a local traditional candy factory. In their study, they found that maximum fluoride adsorption capacity was to be 0.3445 mg/g at a optimum pH of 6, contact time 150 min at temperature 30°C with an initial fluoride concentration of 10 mg/l. The adsorption process followed Langmuir adsorption model.

[165], demonstrated the potential for selective adsorption of fluoride ions with tea ash as an adsorbent. It was also shown that tea ash has enough potential to remove fluoride (8.55 mg/g)

from aqueous solution and also found that maximum adsorption occurs in acidic pH and further increase of pH showed less adsorption. This can be attributed to the neutralization of the negative charges at the surface of bio-sorbent by greater hydrogen concentration at lower pH values. The adsorption process observed Langmuir adsorption model and pseudo second-order reaction kinetics.

Activate carbon of Catha edulis was made for the removal of fluoride from aqueous solution by [181]. Their study showed that maximum fluoride removal of 73% was observed at an optimum condition with the corresponding adsorbent dose of 1.5 g in 100 mL, contact time of 60 min and pH of 2 in a 30mg/l of initial fluoride concentration. Freundlich isotherm ($R^2 = 0.98$) was better fitted to the experimental data, which indicated that the adsorption process was multilayer and heterogeneous.

In adsorption, equilibrium time is reached when there is no more substantial adsorption of adsorbate onto the adsorbent after a certain amount of time has passed, or when adsorption is no longer a time-dependent process.Table 3 to table 7 depicts the results for the corresponding equilibrium values achieved during different defluoridation studies done by various researchers for pH, Temperature, contact time, initial fluoride concentration and RPM respectively.

From table 3, it is understood that for most of the analyses, adsorption was favoured at lower pH and in acidic condition, an illustrative example is shown by using figure 3 [165]. That means for maximum of the studies, point of zero charge values for adsorbents were lower than neutral pH before adsorption which indicates that the adsorbent surfaces were positively charged and hence, they were ready to uptake anions as adsorbate and that is perfectly justified from the fact that fluoride is a negative ion of fluorine, Fluoride often is written as F^- which means fluoride is anionic.Also, apart from pH, other parameters that effects the adsorption nature are temperature, flow rate etc.

Table 3. Equilibrium pH values for different defluoridation studies using adsorption

Sl. No	Type of adsorbent	pH at equilibrium adsorption	References
1	Treated amla bark	7	194
2	Activated tea ash Powder	6	165

3	Rice husk	2	197
4	Neem leaf	2	203
5	Banana Peel	2	199
6	Coffee husk	2	199
7	Date palm seed	7	205
8	Sugarcane	5.4	166
9	Coconut root	7	200
10	Catha edulis (Khat)	2	181
11	Custard apple	7	198
12	Mukondenu clay soil	2	191
13	modified immobilized activated alumina	7	192
14	Coconut shell	2	195
15	Tamarind fruit cover	6	196
16	Vitex negundo leaf	8	202
17	Guava seed	6	170
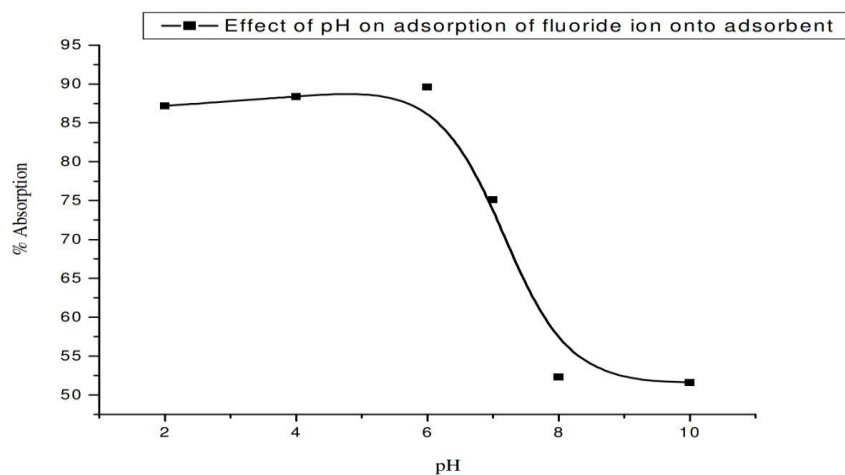
Fig.3. Effect of pH on removal of fluoride onto AcTAP (activated tea ash powder) Operating parameters: stirring speed: 300 RPM, Contact time: 60 minutes, sorbent dose: 0.8 gm/L, Temperature: 303 K, Particle size: 100 μm, Initial fluoride concentration: 5.0 mg/L [165]

Because sorption is an exothermic process, it has traditionally been assumed that increasing the temperature will reduce the adsorbents' sorption capacity. However, because of endothermicity, if the adsorption process is regulated by diffusion (pore diffusion, intraparticle), the sorption capacity will increase as the temperature rises.As the temperature rises, the adsorbate's mobility increases and the retarding forces acting on the diffusing adsorbates decrease. Furthermore, as the temperature rises, the active sites of the adsorbents increase as well. As a result, the adsorptive capacity of the adsorbent is increased [206].Table 4 illustrates for the suitable temperature values obtained by various researches in their study.

Table 4. Favouredtemperaturevalues for different defluoridation studies using adsorption

Sl. No	Type of adsorbent	Favoured temperature (°C) for adsorption	References
1	Treated amla bark	30	194
2	Activated tea ash Powder	30	165
3	Rice husk	30	197
4	Neem leaf	27	203
5	Banana Peel	30	199
6	Coffee husk	30	199
7	Date palm seed	32	205
8	Sugarcane	30	166
9	Coconut root	26	200
10	Catha edulis (Khat)	25	181
11	Custard apple	30	198
12	Mukondenu clay soi	25	191
13	modified immobilized activated alumina	20	192
14	Coconut shell	25	195

15	Tamarind fruit cover	25	196
16	Vitex negundo leaf	30	202
17	Guava seed	30	170

[198] in their defluoridation study using dry and pyrolyzed custard apple powder (refer figure 4) found that adsorption was higher at higher temperature so their process was endothermic. They discovered that when the temperature was raised from 303 K to 333 K, the proportion of dry leaf powder removed increased from 69 to 88 percent. When the temperature was raised from 303 K to 333 K, the proportion of Pyrolyzed leaf powder removed increased from 93 percent to 99 percent. The temperature difference is not noteworthy in this case because the rise is only 6%.The pyrolyzed leaf adsorbent had already reached its saturation point. As a result, temperature had the least impact in this scenario. The fact that the percentage fluoride removed increases significantly as the temperature rises suggests that the adsorption process was endothermic in nature. The solubility and, in particular, the chemical potential of the adsorption are affected when the temperature of the solution rises [192].Rise in temperature leads to increase in diffusivity of fluoride molecules and hence an increase in the adsorption rate. This method may confirm that the rate-controlling stage in this process is diffusion. When compared to Dry leaf powder, Pyrolyzed leaf powder had a higher fluoride removal effectiveness.
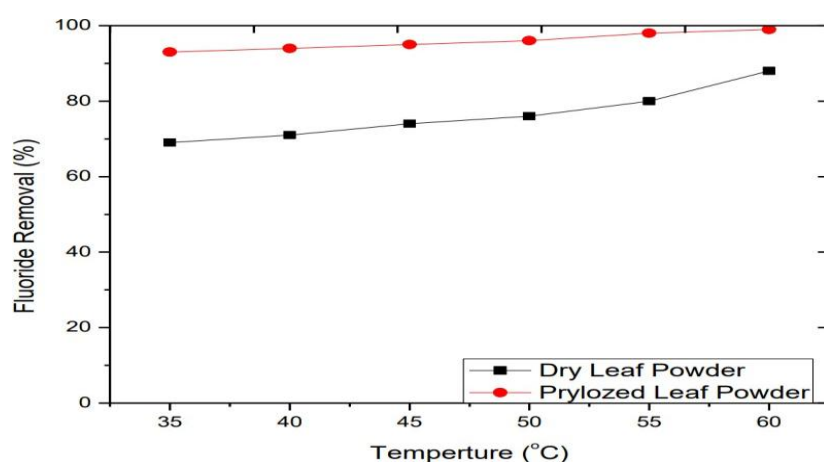
Fig.4. Effect of temperature for fluoride removal by dry leaf and pyrolyzed leaf [198]

It is a general observation in any adsorption process that the reaction is rapid in initial phases and gradually the interaction slows down with time and there is no difference for defluoridation also. In their study, [166], discovered that for an initial fluoride concentration of 4 mg/L, the percent removal of fluoride was very fast at the initial stages, with roughly 45 percent removal occurring within 60 minutes. After 60 minutes, the rate of removal did not significantly rise, and after 5 hours, adsorption processalmost stopped. Fluoride uptake appeared to reach saturation after 60 minutes, indicating fast kinetics.The presence of particular functional groups and active surface locations in the adsorptive removal of fluoride ion may explain the initial fast adsorption [207]. However, as the initial fluoride concentration in the aqueous phase increased from 4 to 8 mg/L, the fluoride removal efficiency decreasedfrom 44 to 24 percent.As a result, during the later stages of adsorption, the adsorption slows down. Similar observation was also reported[208].Table 5 represents for the several equilibrium contact time readings obtained by researchers during their study. An illustrative contact time study has been also been depicted using figure 5 [201].
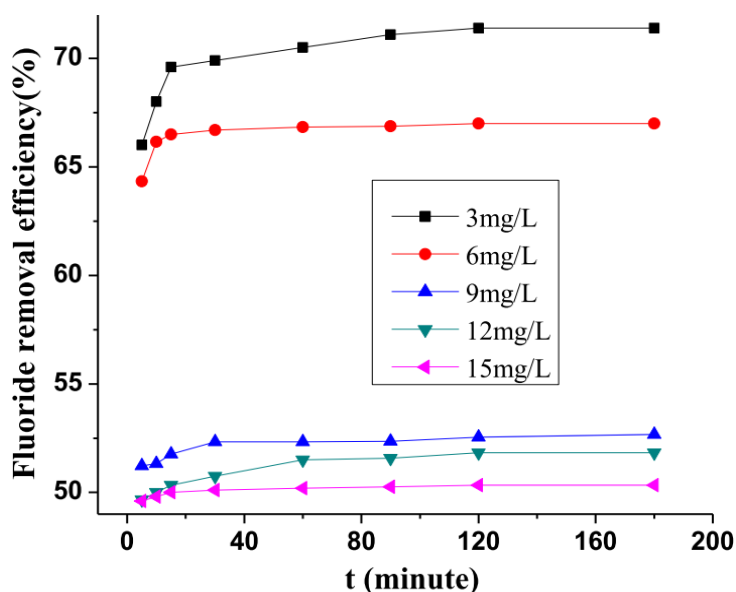
**Fig.5.** Effect of contact time vs fluoride concentration [201]

Table 5. Equilibrium contact time values for different defluoridation studies using adsorption

Sl. No	Type of adsorbent	Contact time (min)at equilibrium adsorption	References
1	Treated amla bark	300	194
2	Activated tea ash Powder	180	165
3	Rice husk	120	197
4	Neem leaf	120	203
5	Banana Peel	780	199
6	Coffee husk	180	199
7	Date palm seed	40	205
8	Sugarcane	60	166
9	Coconut root	90	200
10	Catha edulis (Khat)	60	181
11	Custard apple	30	198
12	Mukondenu clay soi	60	191
13	modified immobilized activated alumina	60	192
14	Coconut shell	-	195
15	Tamarind fruit cover	-	196
16	Vitex negundo leaf	120	202
17	Guava seed	150	170

Through a combination of factors such as the availability of specific surface functional groups and the capacity of surface functional groups to bind fluoride ions, the fluoride removal efficiency can be altered [203].The initial fluoride concentration in the solution can be a powerful driving factor in overcoming the fluoride ion's mass transfer resistance between the aqueous and solid phases [165, 166].Table 6 illustrates the values of initial fluoride concentrations considered by various researchers. Figure 6 illustrates a study on effect of initial fluoride concentration on its removal capacity [179].

Table 6. Initial fluoride concentration considered for different defluoridation studies using adsorption

| Sl. No	Type of adsorbent	Initial fluoride concentration (mg/l) taken	References
1	Treated amla bark	5	194
2	Activated tea ash Powder	5	165
3	Rice husk	5	197
4	Neem leaf	10	203
5	Banana Peel	10	199
6	Coffee husk	10	199
7	Date palm seed	5	205
8	Sugarcane	4	166
9	Coconut root	5	200
10	Catha edulis (Khat)	30	181
11	Custard apple	10	198
12	Mukondenu clay soi	10	191
13	modified immobilized activated alumina	12	192
14	Coconut shell	14	195
15	Tamarind fruit cover	10	196
16	Vitex negundo leaf	3	202
17	Guava seed	10	170
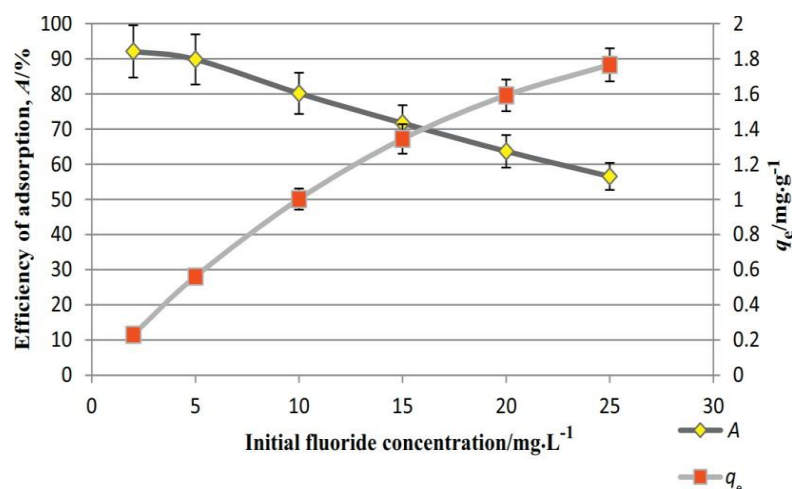
Fig.6. Effect of initial fluoride concentration on its removal capacity [179]

It has been observed that during adsorption, the process of removal of pollutants increases with an increase in the mixing/stirringspeed (RPM), but further increase in speed after a certain value leads to a decrease or reversal in removal of pollutents from solution. The reverse migration of dye molecules from the adsorbent surface to the solution occurs when the shaker's rotating speed increases, i.e., at high RPM values.The rotational speed results in more kinetic energy gain by the dye molecules and it further results in the reduction of effect of boundary layer. Thus, when rotational speed initially increases, adsorption also increases. Due to the difference in masses, a centripetal force ($m\omega^2 r$) acts on the adsorbed dye molecule and adsorbent differently, which may result in the small reduction in removal of dye at rpm more than a optimum value. So, they always tend to readapt radius of their path which results in a development of repulsive force between them. As the rotational speed increases, the magnitude of separative force also increases and becomes greater than the binding force, especially the weaker Vaan der wall force when rpm exceeds a certain value. As a result,removal of dye from solution decreases at very high speed of desorption. Since in physical adsorption the binding force is not as stronger as compared to chemical adsorption, therefore, desorption might get influenced because of increased rotational speed of the shaker. Table 7 depicts for RPM values obtained at equilibrium by various researchers in their defluoridation studies.Figure 7 illustrates for effect of stirring time for fluoride removal capacity [197].

Table 7. RPM observed at equilibrium for different defluoridation studies using adsorption

Sl. No	Type of adsorbent	RPM observed at equilibrium	References
1	Treated amla bark	150	194
2	Activated tea ash Powder	300	165
3	Rice husk	40	197
4	Neem leaf	200	203
5	Banana Peel	200	199
6	Coffee husk	200	199
7	Date palm seed		205
8	Sugarcane	150	166
9	Coconut root	80	200
10	Catha edulis (Khat)		181
11	Custard apple	500	198
12	Mukondenu clay soi	250	191
13	modified immobilized activated alumina	150	192
14	Coconut shell	150	195
15	Tamarind fruit cover	200	196
16	Vitex negundo leaf		202
17	Guava seed	100	170
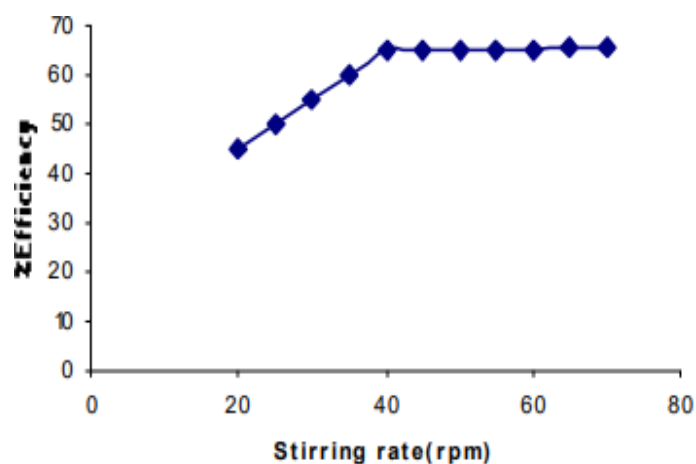
Fig.7. Effect of RPM on fluoride removal capacity [197]

Because more adsorbent sites are available, the percentage removal of fluoride increases with increasing adsorbent dosages at the initial concentration [166]. All active sites are eventually occupied, and the percentage removal gradually becomes constant [187, 208, 209, 210].The same phenomena have been reported by various studies [197, 201]. It has been found that as the adsorbent dose was increased, the percentage of adsorption increased, while loading capacity (amount of fluoride adsorbed per gram of adsorbent) declined, indicating that the number of interaction sites between the adsorbent and adsorbate reduced. This is most likely owing to an increase in the number of adsorption sites [165]. According to another study [179], adsorption capacity increased with increasing adsorbent dose due to higher adsorption area and thus availability of more adsorption sites [211] up to a point, after which further increases in adsorbent dose are actually accompanied by a decrease in adsorption capacity due to a reduction in fluoride/active adsorbent binding site ratio [212]. According to another study [196], the amount of adsorbent used has a substantial impact on the degree of fluoride adsorption. The availability of a greater number of fluoride ions per unit mass of adsorbent, i.e., a larger fluoride/adsorbent ratio, accounts for this increase in loading capacity. It can also be shown that, up to adsorbent doses of 0.7 g, fluoride removal improved significantly due to an increase in the adsorbent site /fluoride ratio; however, subsequent increases in adsorbent dose did not result in any meaningful improvement in fluoride removal. This could be due to the fact that the equilibrium concentration of fluoride is so low that the driving force responsible for adsorption is insignificant. The removal of fluorides begins to decline and stabilise in another research [170], which the authors ascribe to a bigger quantity of active sites not occupied by the F^- ions, both on the surface and in the pores of the bio-sorbent, as

well as bio-sorbent crowding [171, 213, 214].Figure 8 illustrates for the effect of adsorbent dose on fluoride removal [170].
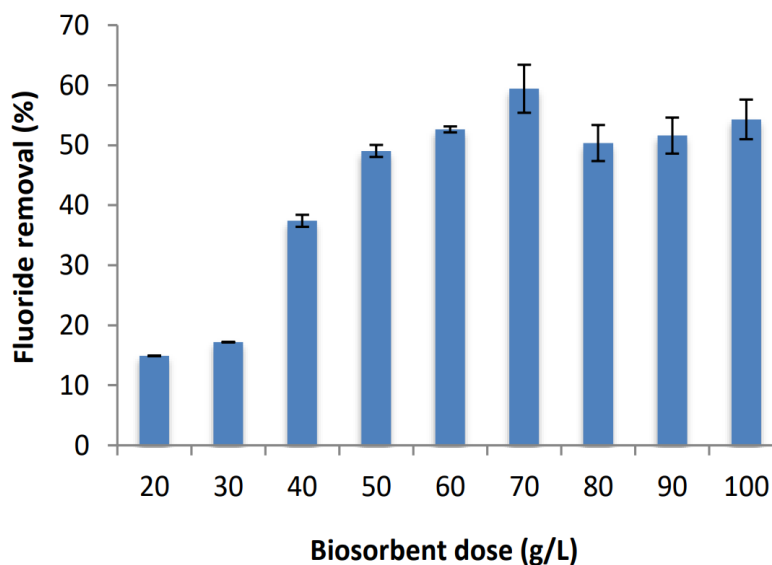
Fig. 8. Effect of adsorbent dose on fluoride removal [170]

3.4 Studies for adsorption kinetics for defluoridation

As discussed in section 2.1.1 of this article, analysis of rate kinetics is very important. Table 8 reports for the various parameters obtained during the Pseudo first and second order kinetic modelling respectively for the same sorbate-sorbent interactions for several separate studies. Suitability of kinetic model (whether Pseudo first order or second order) for all the individual researches can be interpreted by observing the R^2 (coefficient of corelation, best fit value) values for each of the separate studies.Closer the value of R^2 to unity, better the suitability of that kinetic model to the particular adsorption interaction. Q_{max} in the table denotes for maximum adsorption capacity. Also, another table (table 9) is illustrating the suitability of a particular kinetic model (Pseudo first order or second order) found out by various researchers during their experimentations. As reported in table 9 it was observed that apart from some unreported kinetic models, studies done by various researchers supported pseudo second order rate kinetic indicating quick adsorption rate and enhanced adsorption.Also, figure 9 depicts for an illustrative study [166] for Pseudo second order kinetic model for different initial fluoride adsorption.

Table 8. Pseudo first order and second order rate kinetic parameters reported for various defluoridation studies

Type of Adsorbent	Initial fluoride concentration (mg/L)	Q_{max} (mg/g)	Pseudo first order parameters		Pseudo second order parameters		References
			Average k ($x10^{-2}$) 1 (min^{-1})	Average correlation coefficient (R^2)	Average k ($x10^-$) 1 (min^{-1})	Average correlation coefficient (R^2)	
Tamarindfruitshellcarbon	2 –8	82.160	4.243	0.885	3.063	0.866	215
Guavaseeds	5	0.148	4.895	0.959	39.000	0.984	216
Magnesium chloridemodi-fiedpumice	5–20	1.039	2.530	0.970	5.310	0.997	217
aluminum impregnated coconutfiber	1	2.337	0.739	0.825	2.032	0.987	218
Hydrogenperoxidemodi-fiedpumice	5–20	1.147	2.258	0.931	5.885	0.998	217
Nanohydroxyapatite chi-tosan	9 –15	1.778	0.199	0.949	0.231	0.999	219
Treatedbananapeel	10	-	0.084	0.953	3.202	0.984	199
Naturalpumice	5–20	1.132	2.650	0.969	4.535	0.996	217
Treatedcoffeehusk	10	-	0.072	0.878	3.394	0.981	199
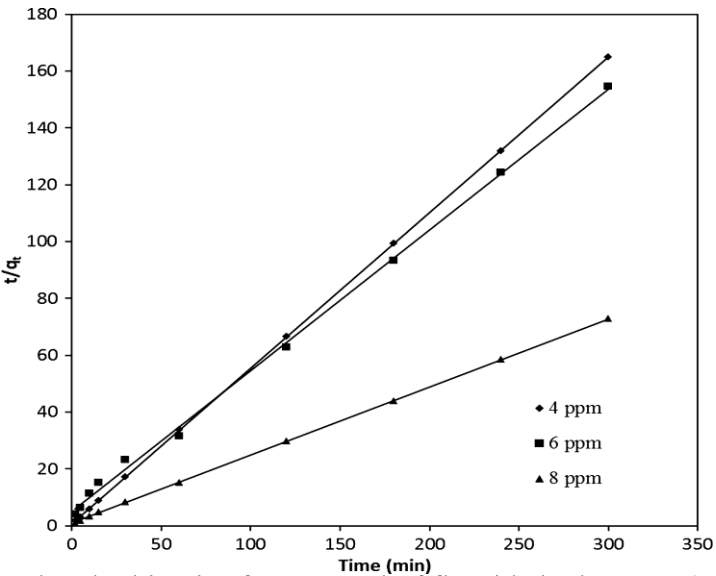
Fig. 9. Pseudo second-order kinetics for removal of fluoride by bagasse (m =1 g/L, pH = 5.4,

T = 303 K[166]

Table 9. Favoured kinetic models reported for various defluoridation studies

Sl. No	Type of adsorbent	Favoured Kinetic model	References
1	Treated amla bark	-	194
2	Activated tea ash Powder	Pseudo-Second-order	165
3	Rice husk	-	197
4	Neem leaf	-	203
5	Banana Peel	Pseudo-Second-order	199
6	Coffee husk	Pseudo-Second-order	199
7	Date palm seed	-	205
8	Sugarcane	Pseudo-Second-order	166
9	Coconut root	Pseudo-Second-order	200

| 10 | Catha edulis (Khat) | - | 181 |
11	Custard apple	-	198
12	Mukondenu clay soi	Pseudo-Second-order	191
13	modified immobilized activated alumina	-	192
14	Coconut shell	Pseudo-Second-order	195
15	Tamarind fruit cover	Pseudo-Second-order	196
16	Vitex negundo leaf	Pseudo-Second-order	202
17	Guava seed	Pseudo-Second-order	170

3.5 Analysis for isothermsduring defluoridation studies

Significance of isotherm equilibrium modelling is discussed in section 2.1.2 of this article. Table10 is illustrating the suitability of particular isotherm models found out by various researchers during their researches. On the other hand, table 11 and table 12 reports for the Freundlich and Langmuir isotherm constant parameter values obtained during several defluoridation studies. Also, figure 10 demonstrates for suitability of experimental data's against different isotherm models for the removal of fluoride [165].

Table 10. Favoured isotherm equilibrium models reported by various defluoridation studies

Sl. No	Type of adsorbent	Favoured Isotherm model	References
1	Treated amla bark	Freundlich	194
2	Activated tea ash Powder	Langmuir	165
3	Rice husk	Freundlich	197
4	Neem leaf	-	203
5	Banana Peel	Langmuir	199

6	Coffee husk	Langmuir	199
7	Date palm seed	-	205
8	Sugarcane	Langmuir	166
9	Coconut root	Langmuir	200
10	Catha edulis (Khat)	Langmuir	181
11	Custard apple	Langmuir	198
12	Mukondenu clay soi	Freundlich	191
13	modified immobilized activated alumina	Langmuir	192
14	Coconut shell	Freundlich	195
15	Tamarind fruit cover	Langmuir	196
16	Vitex negundo leaf	Freundlich	202
17	Guava seed	Langmuir	170
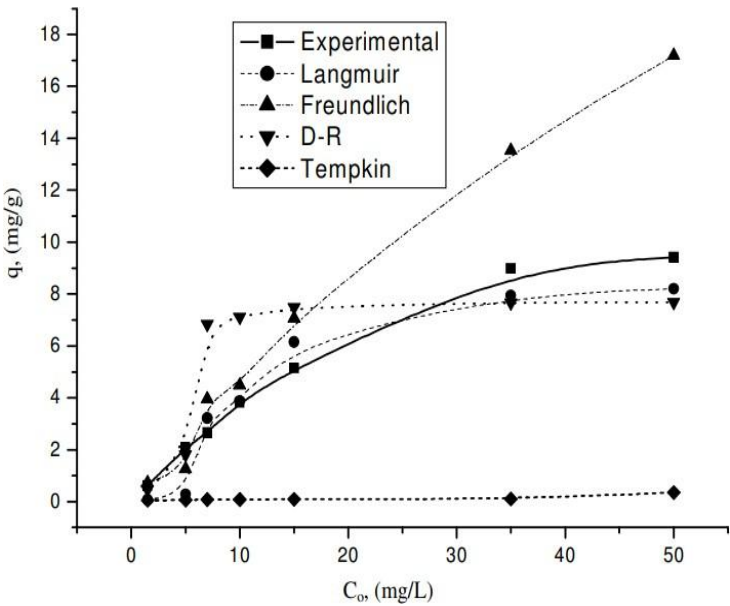
Fig. 10. Experimental vs various isotherm profiles for the removal of fluoride by using AcTAP (activated tea ash powder) for different initial concentration (mg/l). (Operating parameters: sorbent dose: 2.4 mg/L, contact time: 180 minutes, particle size: 50 m, Temperature: 303 K, solution pH: 6.0, stirring speed: 300 RPM) [165]

Table 11. Freundlich constant values obtained during various defluoridation studies

Type of adsorbent	Freundlich constants			References
	1/n	**K_f**	**R^2**	
Aluminumimpregnatedcoconutfiber	1.254	0.301	0.440	218
	0.809	5.984	0.155	
	3.267	0.004	0.914	
*Pithacelobiumdulce*carbon	0.614	0.0204	0.998	220
*Ipomoeabatatas*carbon	0.747	0.0043	0.997	
*Peltophorumferrugineum*carbon	0.719	0.0421	0.997	
Magnesiumchloridemodifiedpumice	0.44	0.535	0.887	217
	0.619	0.777	0.952	
Nanohydroxyapatite	0.198	1.280	0.970	219
	0.203	1.412	0.992	
	0.22	1.423	0.995	
La^{3+}polyamidoaminegraftedchitosanbeads	0.413	0.385	0.994	221
	1.58	1.87	0.998	
	0.296	2.68	0.999	
Activatedcarbon	0.53	0.08	0.999	222
	0.38	4.54	0.900	31
	0.69	1.3	0.900	
	0.83	0.6	0.830	
Carbonblack	0.35	0.07	0.999	222
Bonecharcoal	0.39	1.06	0.998	
Nanohydroxyapatite	0.198	1.280	0.970	219
	0.203	1.412	0.992	
	0.22	1.423	0.995	
Assimilationofchitinwithtin	0.493	2.20	0.998	223
	0.544	1.67	0.989	
	0.625	1.14	0.984	

Zr^{4+}polyamidoaminegraftedchitosanbeads	0.170	9.582	0.997	221
	0.197	9.886	0.999	
	0.224	10.169	0.998	
Treatedbananapeel	0.253	0.1775	0.973	199
Treatedcoffeehusk	0.217	0.2256	0.993	
Pumicestone	0.31	27.6	0.950	101
	0.39	0.521	0.983	
Guavaseeds	0.606	2.248	0.980	216
	0.943	0.1663	0.987	
	0.827	0.5092	0.982	
La^{3+}polyamidoaminegraftedchitosanbeads	0.413	0.385	0.994	221
	1.58	1.87	0.998	
	0.296	2.68	0.999	

Table 12. Langmuir constant values obtained during various defluoridation studies

Type of adsorbent	Langmuir constants			References
	q_{max} (mg/g)	R_L	B	
Alum impregnatedactivated alumina	192.65	3.69×10^{-4}	0.670	224
	40.68	9.04×10^{-3}	0.600	
	19.8	6.60×10^{-5}	0.500	
Treatedbananapeel	0.395	0.426	0.998	199
Treatedcoffeehusk	0.416	0.789	0.998	
Pithacelobiumdulcecarbon	0.0700	0.4202	0.276	
Ipomoeabatatascarbon	0.0710	0.4485	0.246	220
Peltophorumferrugineumcarbon	0.571	0.4884	0.209	
La^{3+}polyamidoaminegraftedchitosanbeads	10.37	0.625	0.040	221
	11.36	0.571	0.050	
	11.45	0.455	0.080	
Pumicestone	41.65	0.163	0.255	101
Guavaseeds	116.5	0.0051	0.997	216
	316.5	0.003	0.998	
	413.8	0.007	0.996	
Assimilationofchitinwithtin	12.47	0.12	0.160	223

	13.44	0.21	0.090	
	14.77	0.35	0.060	
Magnesiumchloridemodifiedpumice	5.56	0.312	0.285	217
Nanohydroxyapatitechitincomposite	8.41	-	-	219
Hydrotalcite/chitosancomposite	1.876	-	-	225
Magneticchitosanparticle	23.98	-	-	226
Zn^{4+}polyamidoaminegraftedchitosanbeads	16.377	0.018	2.782	221
	16.903	0.024	2.877	
	17.483	0.025	3.891	
Aluminiumimpregnatedcoconutfiber	1.128	0.183	-	218
	5.60	12.273	-	
	5.827	12.636	-	
Nanohydroxyapatite Chitosancomposite	2.04	0.0801	1.260	219
	2.247	0.077	1.337	
	2.320	0.078	1.306	
Hydrogenperoxidemodifiedpumice	11.76	0.297	0.173	217

3.6 Studies for activation energy and thermodynamic parameters

[165] used activated tea ash powder as adsorbent for fluoride removal. In their analysis they calculated activation energy $E_a$as 32.01 KJ/mol from the graph of ln k vs. 1/T as per the equation as listed as equation 16 of section 2.1.3 of this article. Magnitude of activation energy indicates for the nature of adsorption as to whether the adsorption is driven by physical or chemical process [227]. The Ea value obtained by [165] implies that the adsorption of fluoride ions is a physical adsorption process. This result is consistent with the D-R isotherm results. Gibb's free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) were determined as thermodynamic parameters connected with the adsorption processas per the equations 17, 18 and 19 described in section 2.1.3 of this article. In their analysis they obtained the values of ΔG^0,ΔH^0 and ΔS^0 as all negative.The fact that ΔG^0 is negative at all temperatures implies that the fluoride ions were adsorbedwith spontaneity. Lower ΔG^0 values with increase in temperature, suggests adsorption was easier at lower temperatures. The negative value of ΔH^0 indicates that the adsorption process is exothermic, and the negative value of ΔS^0 indicates that the process is enthalpy driven.

ΔG^0 values for fluoride removal using sugarcane bagasse were determined to be in the range of −24.696 to −28.056 kJ/mol with a temperature increase from 293 to 323 K [166]. The decrease in ΔG^0 values as temperature rises suggests that the fluoride adsorption process on bagasse becomes more favourable at higher temperatures [78, 228]. Negative ΔG^0 denotes the adsorption's feasibility and spontaneity. The positive ΔH^0 value obtained confirms that the entire sorption process is endothermic, and the value is 8.117 kJ/mol. 0.111 kJ/mol K is found to be the ΔS^0 value. The positive value of ΔS^0 indicates bagasse's fluoride affinity and suggesting that the degree of disorder is increasing. The fact that ΔS^0 is positive indicates that the adsorption process is entropy driven.

Another study [179] looked at the thermodynamics of fluoride adsorption on thermally activated carbon made from coconut tree roots (C. nucifera Linn. Root). Temperature of 20–50 °C, initial fluoride concentration of 5 mg/L, dose of adsorbent of 8 gm/L, contact length of 90 minutes, and agitation speed of 80 RPM were their preliminary input parameters. They discovered that as the temperature rose, the effectiveness of sorption and sorption capacity increased. The most likely reason for this is pore size enlargement [211], which means that as the temperature rises, the surface thickness of C. nucifera Linn. root adsorbent decreased, and the kinetic energy of adsorbate ions rapidly increased, increasing the diffusion rate of adsorbate ions along the exterior border layer and intramural pores of C. nucifera Linn. root adsorbent [229]. The sorption phenomenon's appropriateness and the spontaneous nature of fluoride sorption onto C. nucifera Linn. root adsorbent is highlighted by the negative value of ΔG^0 obtained with respect to different temperatures. With a rise in temperature, the more negative ΔG^0 values become, indicating that higher temperatures favoured sorption. The fact that ΔH^0 (12.728 kJ/mol) is positive in their study implies that the adsorption mechanism is endothermic [230]. The positive value of entropy change ΔS^0 in their research shows that when temperature rises, randomness rises as well.Thermodynamic studies of fluoride adsorption using P. emblica activated carbon [231], activated carbon generated from the Ficus racemosa plant [232], activated biochar from domestic food waste [233], and pumice stone adsorbent [101] all yielded similar results.

Saikia et al., 2017, in their analysis of fluoride removal using treated possotia leaf observed that their ΔG^0 values were all positive for different temperature study and ΔH^0 and ΔS^0 wereall negative. They [234] concluded that the negative values of ΔH^0 suggest the exothermic nature of the adsorption process based on the nature of the values, The negative ΔS^0 values reflect a decrease in randomness at the PLP (possotia leaf powder) surface during

the adsorption process, whereas the ΔG^0 values demonstrate the practicality of adsorption at low temperatures, demonstrating the bio-utility of the sorbent's at room temperature.

3.7 Desorption of fluoride

To develop a meaningful and economical adsorbent for defluoridation, it is critical to desorb the fluoride adsorbed for the reusability of the sorbent media.

[166] investigated the desorption of fluoride from loaded adsorbents (sugarcane bagasse) at various pH levels (2–12). An initial concentration of 4 mg/L, a period of 1 hour, a temperature of 293 K, and an optimum dose of 1 gm/L were used for desorption study. The rate of desorption was determined to be 3–4%. Bagasse desorption efficiency was low, and a significant amount of fluoride could not be removed. According to them,bagasse is also available as a waste material in India,as a result, desorption and regeneration of spent bagasse is not advised. They recommended that the used bagasse be filtered out of the mixture, dewatered, sun dried, and then burned as fuel in a boiler, furnace, or traditional chulha used for cooking in rural India to recover its energy worth.It can also be used as a filler for levelling low-lying regions when mixed with dirt or sand. According to them, it is more cost effective to dispose of low-cost adsorbents rather than regenerate them.

[167] emphasised that desorption of adsorbed fluoride ions is required to investigate the bio-recycling sorbent's capabilities. Fluoride ion, being an anion, was desorbed by raising the pH of the solution above pH_{pzc}, according to their findings. NaOH(0.1M) solution was used to raise the pH.Because IPXFR (immobilised protonated xanthate modified Ficus religiosa) had improved absorption results, the xanthate modified adsorbent was used to investigate desorption. Desorption was also explored in a continuous way. The maximum was reached in about 37 minutes during the first cycle of desorption (75 mL of eluting agent).The column was discovered to regenerate completely in 75 minutes (150 mL of eluting agent). A second adsorption-desorption cycle was performed on the column. The periods for maxima and full regeneration remained unchanged in the second cycle. During this cycle, the column's removal percentage (R%) was reduced from 100 percent to 75.67 percent.The degradation of IPXFR in the presence of a strong alkali solution could be the reason for the drop in percent removal.

[196] stated that the sorbent can be regenerated using a variety of processes such as solvent extraction, thermal desorption, steam washingand so on. Each method has its own set of benefits and drawbacks.Several solvents were explored to rejuvenate the TNFC (Tamarind

fruit cover) adsorption bed in their research. The use of a 0.1 M NaOH solution was shown to be better in desorbing and eliminating fluoride ions from the adsorbent bed quantitatively.The fluoride-saturated fixed bed columns of adsorbents are regenerated by flowing 0.1 M NaOH solution as an eluent at a set flow rate of 1.0 mL/min. Maximum desorption occurred at 100 mL of 0.1 M NaOH solution, while complete fluoride regeneration occurred at 150 mL.

Desorption studies aid in the understanding of adsorption and recycling of wasted adsorbent and adsorbate. [165] carried out a fluoride desorption analysis using different regeneration media, such as 25% NaOH and 1(N) HCl. Adsorbed fluoride desorption on AcTAP (activated tea ash powder) was successful with a high percentage desorption value of 91.68%.

4. Conclusion

In this review article we have reported different organic and in-organic adsorbents used by different researchers for the removal of fluoride from aqueous solution. Study also found that adsorption is influence by various parameters like pH, contact time, temperature, stirring rate, initial concentration. Adsorption kinetic are explained by pseudo first order and second order models and adsorption Isotherm are best explained by either Langmuir or Freundlich isotherms. From this study it can concluded that modification of raw adsorbents into treated or activated carbon form gives better defluoridation using adsorption in aqueous solution.

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