Adsorption of Fluoride (F⁻) from Aqueous Solution by Using Pineapple (*Ananas comosus*) Peel and Orange (*Citrus sinensis)* Peel Powders

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Abstract The ability of the peel powders of *Ananas comosus* and *Citrus sinensis* for removal of fluoride from water through adsorption has been investigated in the present study. All the experiments are carried out by batch adsorption mode. The effect of various parameters viz. contact time, pH effect (pH 3–9), adsorbent dose (0.2–1.2 g/L) and initial fluoride concentration (1–4 mg/L) has been investigated to determine the adsorption capacity of peel powders of *Ananas comosus* and *Citrus sinensis*. The efficacy of peel powders of *Ananas comosus* and *Citrus sinensis* to remove fluoride from water is found to be above 90% at pH 6 for *Citrus sinensis* peel powder and above 90% at pH 4 for *Ananas comosus* peel powder contact time for one hour, dose of 0.6 g/L, when 4 mg/L of fluoride is present in 100 ml of water.

Keywords: *Ananas comosus (Pineapple) peel powder, Citrus sinensis (Orange) peel powder, batch adsorption, isotherm studies, adsorption kinetics, thermodynamic studies*

1. Introduction

Fluoride is the most common element and due to its high reactivity it exists only in a combined state. It is essential element for humans and animals. Excess of fluoride causes toxic effect on the environment. The range of fluoride is 2- 20 ppm in wastewater and industrial effluent. By Indian law the fluoride concentration limit in treated effluent from common sewage treatment plants for discharge is 2 mg/l [1]

There are various commercial and efficient methods available for the removal of fluoride from wastewater streams.

To develop a cost effective efficient and easily employable method for the removal of fluoride bio adsorption is studied in depth [2]. The present study deals with the removal of fluoride from industrial waste water by using *Ananas comosus* and *Citrus sinensis* peel powders. The studies are carried out with respect to contact time, concentration of fluoride, adsorbent dosage and temperature.

2. Materials and Methods

2.1. Selection of Adsorbents

Table 1. Characterization of Adsorbents

S.No	Parameter	Pineapple peel	Orange peel
01	Moisture content	85.3 %	45 %
02	Particle size	250 mic	250 mic
03	Particle density	0.25	0.29
04	Surface area	43.40 cm^2	36.89 cm^2
05	Porosity& void ratio	50	65.1
06	Apparent density	0.25	0.29
07	Real density	0.50	0.83

Pineapple (*Ananas comosus*) is processed as canned fruit and juices. Pineapple is usually discharged before or after bromalin is extracted. Pineapple peel produces 35% wastage. Orange (*Citrus sinensis*) fruits are used as a diet

by humans due to its high nutritional values. Peel of orange fruit also discharges into environment. This wastage produces serious environment problems. From the point of multipurpose utilization and protection of environment, pineapple peel and orange peel powders are used as a bio adsorbent for controlling fluoride from water and wastewater [3-9]. The general characterization of selected adsorbents done by standard methods and listed in Table 1. From the Table 1, it is observed that the moisture content of pineapple is more compare to orange peel powder. The porosity, void ratio, apparent density, real density, partial density of orange peel higher than peel powder of pineapple.

2.2. Selection of Optimum Contact Time

The contact time strongly influences the adsorption process, for this study an 1000 ml of different concentrations of fluoride solutions were taken separately and they were mixed with optimum adsorbent dosage and stirred for different period of contact time i.e. for 1hr and time interval varies as 3,5,10,15……60 min. After completion of 60 mints contact time the samples were filtered through watt man NO.1 filter paper and analyzed for fluoride concentration using spectrophotometer method.

2.3. Determination of Optimum Dosage of Adsorbent

The effect of adsorbent dose on the removal of fluoride, is studied in neutral condition (pH 7), at ambient temperature (25±2°C) and contact time of 60 minutes for initial fluoride concentration of 4 mg/L. The added amount of adsorbent was varied from 0.2 g – 1.2 g. After completion of optimum contact time period the solutions were filtered and analyzed for residual and removal of fluoride concentrations respectively. The dosage which gives minimum residual concentration is chosen as optimum dosage.

2.4. Effect of Initial Concentration of Ion

The adsorption of fluoride onto various selected adsorbents was studied by varying initial fluoride concentration using optimum adsorbent dosage, at ambient temperature (25±2°C) and contact time of 60 minutes. The filtered solutions were analyzed for residual and removal of fluoride concentrations respectively.

2.5. Determination of Optimum pH

A series of conical flasks were taken with 1000 ml of 4 mg/L of fluoride solution to determine the optimum pH by adding optimum adsorbent dosage at different pH. The pH of the flasks was adjusted ranging from 3.0 to 10.0. The flasks were kept at room temperature for optimum contact time. After stirring the samples are filtered and analyzed for the chromium and fluoride concentration. The flask which gives minimum and less concentrations (F) is selected as the optimum pH.

2.6. Effect of Temperature

Temperature has an important effect on the process of adsorption. The percentage of fluoride adsorption is studied as a function of temperature. The batch experiments were performed at temperatures of 0°C, 30°C, 40°C, 50°C, at different initial (1, 2, 3 and 4 mg/L) concentrations of fluoride.

2.7. Adsorption Isotherm Models

The parameters obtained from the different models gives important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. The most widely accepted surface adsorption isotherm models for single-solute systems are the Langmuir and Freundlich models. The correlation with the amount of adsorption and the liquid phase concentration were tested with the Langmuir, Freundlich and Tempkin isotherm equations [11]. Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients.

A) Temkin Adsorption Isotherm Model

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface [12,13,14]. The assumptions made by Temkin are

- Heat of adsorption decreases with surface coverage due to the interactions between adsorbent and adsorbate [15].
- Bonding energies are uniformly distributed up to certain binding energies. Depending upon these two factors Temkin proposed an empirical equation which is represented as follows [16,17]

$$q_e = B_T \ln K_T C_e \qquad \text{(i)}$$

The linear form of temkin equation is as follows (Temkin and Pyzhav)

$$q_e = B_T \ln K_T + B_T \ln C_e \qquad \text{(ii)}$$

Where T is absolute temperature (K), R is universal gas constant (8.314 J/mol.k), K_T is equilibrium binding constant (L/Mg), b_T is Variation of adsorption energy (kJ/mol) B_T is Temkin constant (kJ/mol).The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbates. If the adsorption process follows Temkin adsorption isotherm model the graph between C_e versus q_e has to show a linear relationship.

B) Langmuir Adsorption Isotherm Model

Langmuir adsorption isotherm explains quantitatively the formation of monolayer adsorbate on outer surface of the adsorbent, and after that no further adsorption takes place. The theoretical Langmuir isotherm is valid for adsorption of solute from a liquid solution as monolayer adsorption on a surface containing a large number of identical sites. Langmuir isotherm model [18] explains uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface. The Langmuir isotherm has an assumption that the adsorption occurs within adsorbent at specific homogeneous site. The linear form of Langmuir equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \qquad \text{(iii)}$$

Where q_e is adsorption capacity equilibrium, q_m is the maximum adsorption capacity, C_e is the solution concentration at equilibrium k_L is Langmuir constant.

C) Freundlich Adsorption Isotherm Model

The Freundlich equation is basically empirical but is often useful as a mean for data description. The equation generally agrees with the Langmuir equation and experimental data over moderate ranges of concentration [19]. This is commonly used to describe the adsorption characteristics for the heterogeneous surface [20]. The data often fit the empirical equation proposed by Freundlich.

$$q_e = k_f C_e^{1/n} \qquad (iv)$$

The linear form of Freundlich equation is as follows [21]

$$\log q_e = \log k_f + 1/n \left(\log C_e \right) \qquad (v)$$

Where k_f is the Freundlich adsorption capacity and *n* is the adsorption intensity. A plot of log q_e versus log C_e gives a linear line with slope of 1/n and intercept of log k_f.

2.8. Adsorption Kinetic Models

In order to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, several kinetic models are used to test experimental data. The mechanism of adsorption involves the chemical reaction of functional groups present on the surface of the adsorbent and adsorbate. In present study the experimental data were tested with pseudo first order, pseudo Second order, Elovich model and intra particle diffusion models [22].

(i). Pseudo first order equation:

Pseudo-first-order kinetic model**,** the Lagergren rate equation, has been the most widely used rate equation for assigning the adsorption of an adsorbate from a liquid phase since 1898 [23]. A simple kinetic analysis of adsorption is the pseudo-first-order equation in the form [24,25].

$$dq_t / dt = k_1 \left(q_e - q_t \right) \qquad (vi)$$

Where k_1 is the rate constant of pseudo-first-order adsorption and q_e denotes the amount of adsorption at equilibrium. After definite integration by applying the initial conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the linear equation is as follows

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} Xt \qquad (vii)$$

The plot of log $(q_e - q_t)$ versus t should give a straight line with slope of $-k/2.303$ and intercept log q_e. Pseudo first-order kinetic equation differs from a true first-order equation in following ways

- The parameter, k $(q_e - q_t)$ does not represent the number of available sites,
- The parameter, log (q_e) is an adjustable parameter and often it is found that it is not equal to the intercept of the plot of log $(q_e - q_t)$ versus *t*, whereas in a true first order model the value of log q_e should be equal to the intercept.

Hence, pseudo first order kinetic model is used for estimating *k* alone, which is considered as mass transfer coefficient in the design calculations [26].

(ii). Pseudo second-order kinetics

As pseudo first-order kinetic model gives only *k* and as q_e cannot be estimated using this model, applicability of the pseudo second-order kinetics has to be tested for the estimation of q_e with the rate equation given by Ho 1995, [27]. The pseudo second order kinetic order equation expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (viii)$$

Where k_2 is the rate constant of pseudo second order adsorption (g/mg/min) and q_e is the equilibrium adsorption capacity (mg/gm) [28]. The plot of *t/qt* versus *t* should give a linear relationship which allows the computation of a second-order rate constant, k_2 and q_e. The pseudo-second order model is based on the assumption that the rate limiting step may be chemical adsorption involving valence forces through sharing or exchange of electrons between the adsorbent and adsorbate [29].

(iii). Elovich Model

Elovich equation is also used successfully to describe second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate–adsorbent [30,31]. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation [32]. The Elovich or Roginsky–Zeldovich equation is generally expressed as follows [14,33,34,35]

$$\frac{dq_t}{d_t} = \alpha \exp(-\beta q_t) \qquad (ix)$$

Where, α is the initial adsorption rate (mg/g/min), β is the desorption constant (g/mg). If the adsorption fits to the Elovich model, a plot of q_t versus ln (t) should give a linear relationship with a slope of $(1/\beta)$ and an intercept of $1/\beta$ In (αβ).

(iv). Intraparticle Diffusion Model

In adsorption studies it is mandatory to find out the rate limiting step. Therefore the results obtained from the batch adsorption experiments were used to study the rate limiting step. The rate limiting step might be film or intraparticle diffusion which was tested by plotting a graph between amount of ion adsorbed and square root of time [36].

$$q_t = K_{id} t^{1/2} + I \qquad (x)$$

Where q_t is the amount of chromium and fluoride adsorbed (mg/g) at time t (min), and I is the intercept (mg/g). k_{id} and I values are obtained from the slopes and intercept of the linear plot. If the postulated mechanism is correct, then a linear plot passing through the origin is obtained. Additionally, the value of the rate constant for diffusion is obtained from the slope of the line. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process. In general, a mass transfer process is diffusion controlled and its rate is dependent upon the rate at which components diffuse towards one another. The intra-particle diffusion model has been applied in three different forms:

(i) The amount of adsorption at any time, q_t is plotted against $t^{1/2}$ to get a straight line pssing through origin. This

means that A is equal to zero which implies that the rate is not limited by mass transfer across the boundary layer. This occurs when a system is agitated and mixed to a sufficient extent (high turbulence);

(ii) Multi-linearity in qt versus $t^{1/2}$ plot is considered (that is, two or three steps are involved). In this form, the external surface adsorption or instantaneous adsorption occurs in the first step; the second step is the gradual adsorption step, where intra-particle diffusion is controlling; and the third step is the final equilibrium step, where the solute moves slowly from larger pores to micro pores causing a slow adsorption rate. The time required for the second step usually depends on the variations of the system parameters such as solute concentration, temperature, and adsorbent particle size;

(iii) qt is plotted against $t^{1/2}$ to obtain a straight line but does not necessarily pass through the origin; that is, there is an intercept [37]. This implies that the rate is limited by mass transfer across the boundary layer. This occurs in a slowly stirred batch adsorption process.

2.9. Thermodynamic Parameters

Thermodynamic parameters were calculated from the variation of the equilibrium constant, K, at different temperature by using following equation.

$$K_c = \frac{q_e}{C_e} \qquad \text{(xi)}$$

K_c (L/g) values were obtained using the Khan and Sing method [38] by plotting ln (q_e/C_e) versus q_e and extrapolating to zero. The intercept of the straight line with the vertical axis gives the values of K_c. The Gibbs free energy change of the adsorption process is related to K_c as in equation given below [39].

$$\Delta G° = -RT\ln K_c. \qquad \text{(xii)}$$

The changes in enthalpy (ΔH^o) and entropy (ΔS^o) for chromium and fluoride adsorption were calculated from the slope and intercept of the plot of ln Kc against $1/T$ according to the van't Hoff equation [39,40].

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad \text{(xiii)}$$

Where $\Delta S°$ is change in entropy, $\Delta H°$ is change in enthalpy $\Delta G°$ is change in free energy. Plotting ln K_c versus $1/T$ shows straight lines. From their slope and intercept, ΔH^o and ΔS^o are determined. The negative values of ΔG^o indicate a favourable and spontaneous process [40].

2.10. Equilibrium Parameter

In order to find out the efficiency of adsorption process, the dimensionless equilibrium parameter, R_L is calculated by using following equation [11,41].

$$R_L = \frac{1}{1+bC_o} \qquad \text{(xiv)}$$

Where C_o = Initial concentration (mg/L), b is Langmuir isotherm constant. Values of the dimensionless equilibrium parameter explain the differences in the shapes of the isotherm. The R_L values lies between 0 and 1 indicate favourable adsorption. The R_L value above 1 indicates unfavourable.

2.11. Non-linear Regression Analysis

In this experimental study, a non-linear regression analysis was conducted to determine the isotherm and kinetic constants and statistical comparison values such as determination coefficient (R^2), standard error of the estimate (SEE) and Absolute sum of squares (ASS). The batch adsorption data was evaluated using Graphpad prism scientific software. As regression models were solved, they were automatically sorted according to the goodness-of-fit system into a graphical interface. To determine the statistical significance of the predicted results 95 % confidence was used in the non-linear regression analysis.

3. Results & Discussion

3.1. Effect of Contact Time between Fluoride & Adsorbents

The data measures the effect of contact time on the batch adsorption of fluoride at initial concentration of 10 mg/l indicated that increase in contact time from 2 to 45 minute the percentage removal of fluoride is increasing significantly (Figure 1). The variation in the percentage removal of fluoride by the orange peel and pineapple peel can be explained on the basis of certain components presence. The pineapple waste consists of 19% cellulose, 22% hemicelluloses, 5% lignin content. Orange peel waste consists of 13.3% fiber, lignin content is 1.5 – 1.8 % and cellulose content is 37-39%. As there is a variation in cellulose content the adsorption capacity is more initially incase of pineapple peel than orange peel. As time increases the percentage removal is high in case of orange peel than pineapple peel [3,9].

3.2. Effect of Initial Fluoride Concentration

The adsorption data of fluoride at different initial concentration ranging from 1-4 mg/l. however the experimental data is measured after 60 minutes of contact time to make sure that full equilibrium was attained. From the data the percentage removal is high at lower concentration [41,42,43,44]. At higher concentration percentage of removal is low in case of both adsorbents (Figure 2).

3.3. Effect of Adsorbents Dosage

To study the effect of adsorbents dosage on the uptake of fluoride, experiments were done with 100 ml of 2 mg/l solution. Figure 3, showed that the percentage removal of fluoride from waste water increased with the adsorbent does and reached a optimum at 0.4 gm of adsorbent in case of pineapple peel and 0.6 gm in case of orange peel. The increase in ion removal was due to increase in the available sorption surface area [45,46,47,48].
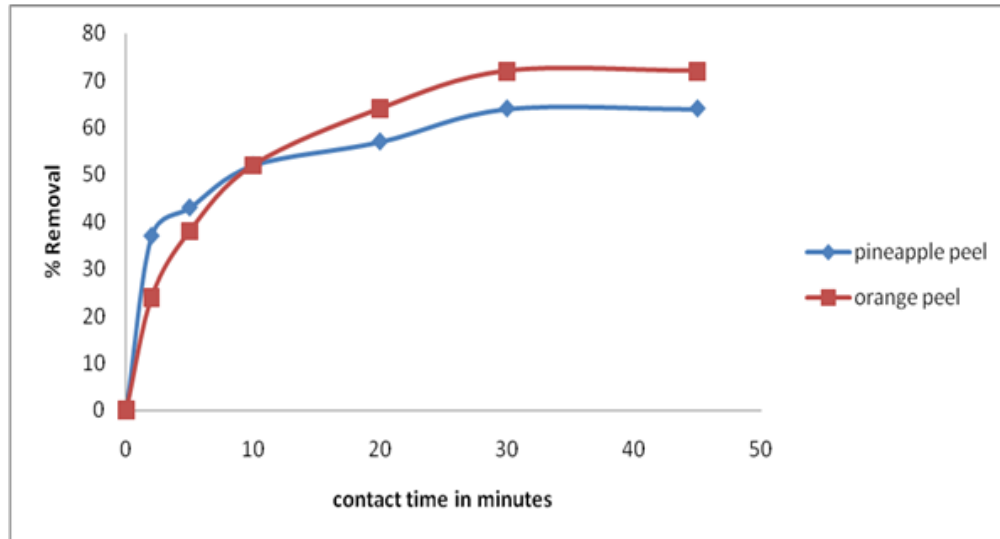
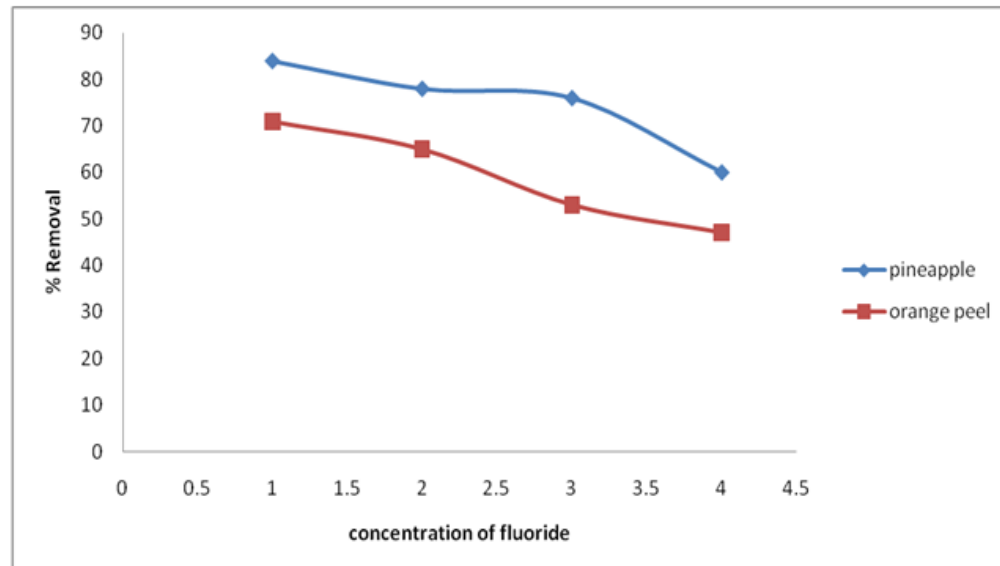**Figure 1.** Variation of contact time between fluoride and Adsorbents

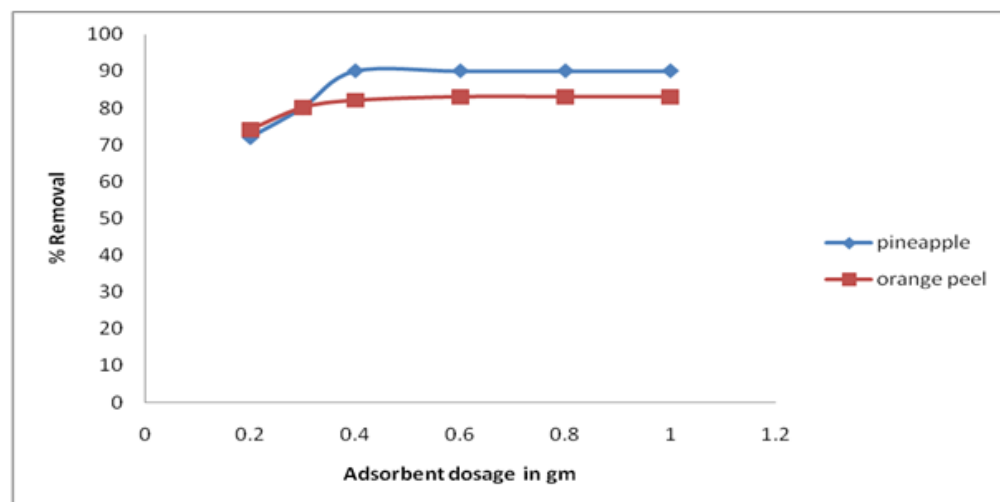**Figure 2.** Variation of initial fluoride concentration on adsorbents

Figure 3. Variation of adsorbent dosage on fluoride

3.4. Effect of pH

The pH influences the adsorbent surface properties and ionic forms of fluoride in the solution. The influence of pH on the adsorption of fluoride ions is shown in Figure 4. From the figure it is observed that the both adsorbents shown high percentage removal in acidic conditions. The maximum percentage removal of fluoride was at pH 4 for

pineapple peel powder, where as the maximum percentage removal of fluoride observed at pH 6 in case of orange peel powder as an adsorbent [49,50,51,52].

3.5. Effect of Temperature on Adsorption of Fluoride:

Figure 5 indicates the effect of temperature on the removal efficiency of fluoride ions from waste water using activated orange peel powder and pineapple peel powder. Five different temperatures were considered in this study (0, 40, 60, 80 and 100°C). The figure showed that the removal efficiency increased by increasing the temperature, where the maximum adsorption (85-92 % approx.) is achieved at 80°C in both cases [53,54,55,56,57]. The adsorption process does not usually operate at low temperature (less than 60°C).
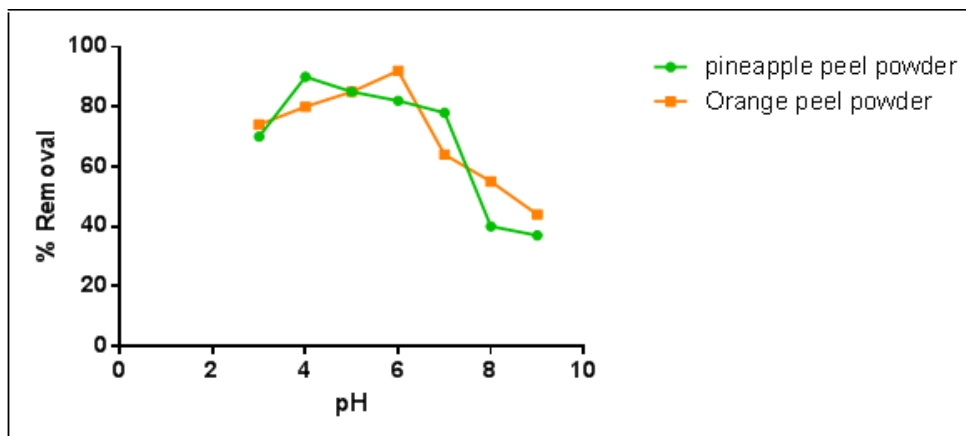

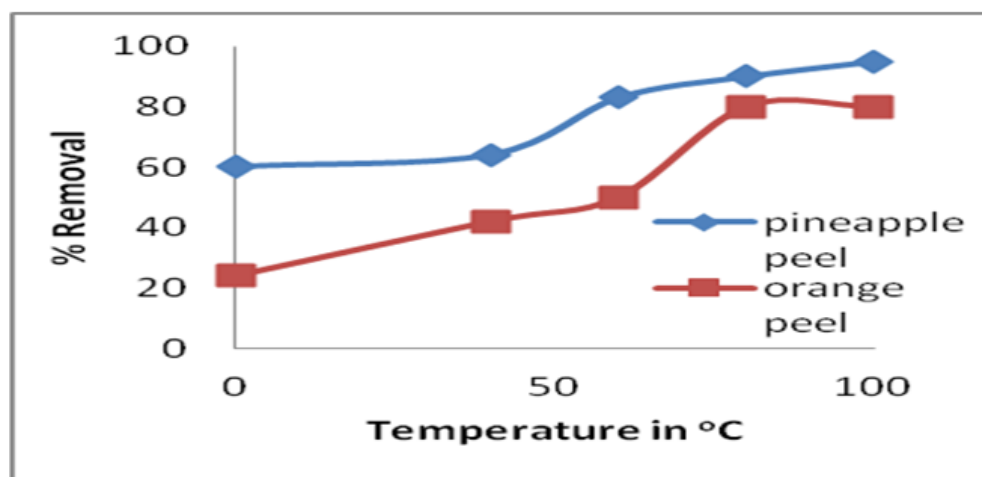**Figure 4.** Effect of pH on adsorption of fluoride

Figure 5. adsorption capacity of pineapple peel and orange peel at different temperature

3.6. Adsorption Isotherm Models

Isotherm study on adsorption provides information on the efficiency of the adsorbent. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for adsorbate molecules. Equilibrium data can be analyzed using commonly known adsorption systems. Several mathematical models can be used to describe experimental data of adsorption isotherms. The freundlich, Langmuir and Temkin models were employed to analysis adsorption occurred in the experiments [53-58].

A) Temkin Adsorption Isotherm:

The Figure between x/m on Y- axis and concentration of fluoride on X-axis of orange peel shows 3 parts. The initial steep and strait line of curve shows that adsorption is directly proportional to concentration due to vacant surface area of the adsorbent. The horizontal part of the graph indicates that the surface area is completely covered or it indicates the saturation. The central part of the curve indicates the intermediate stages of adsorption. For pineapple peel the curve only shows one part. The initial steep and strait line of curve indicates the adsorption phenomena increases with increases in concentration and surface of pineapple peel. It may stable at higher temperature also. High concentrated solution of fluoride can be utilized to check the surface area coverage of pineapple peel.

B) Freundlich Adsorption Isotherm:

In the case of freundlich isotherms ranging between 0°C to 80°C foe fluoride indicates that the value of slope is increasing at 0°C and becoming constant at 40°C, Indicating that the optimum temperature is 40°C. As the temperature rises the quantity of equilibrium adsorption decreases and as a result the isotherms at higher temperature are below the isotherms at lower temperature. The temperature is the limiting factor for the adsorption process and it is dependent on adsorption molecules. The results are shown in Figure 8 & Figure 9.
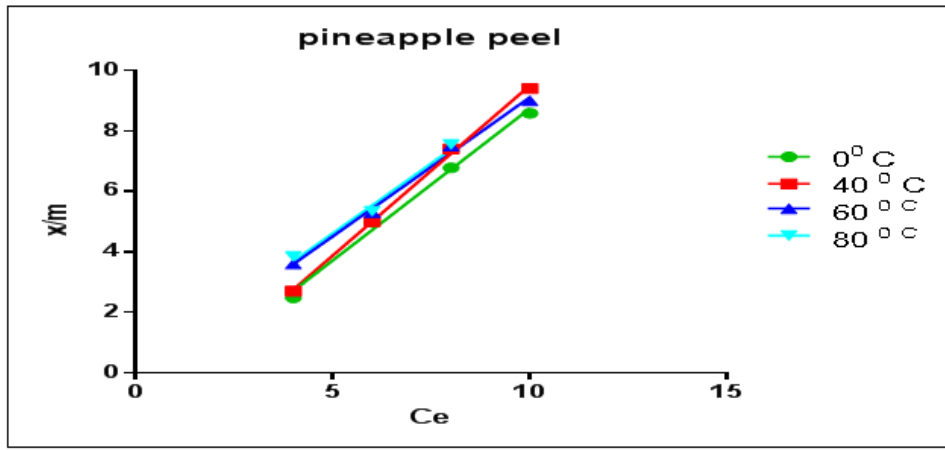
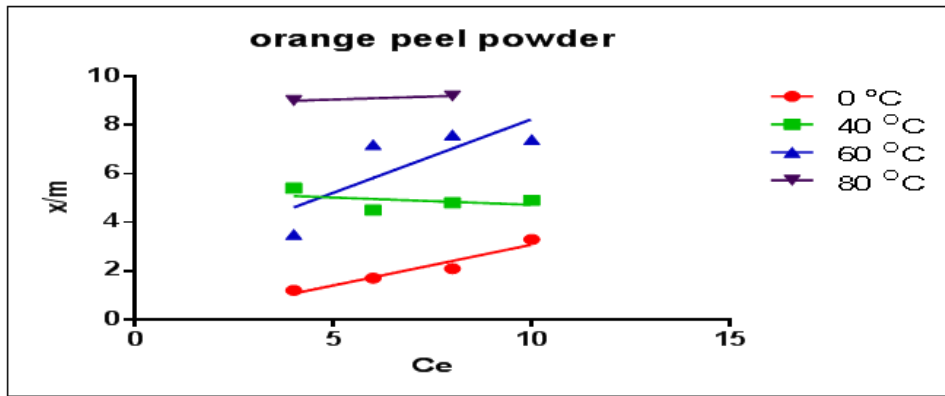**Figure 6.** Temkin isotherm for removal of fluoride by pineapple powder

Figure 7. Temkin isotherm for removal of fluoride by Orange peel powder
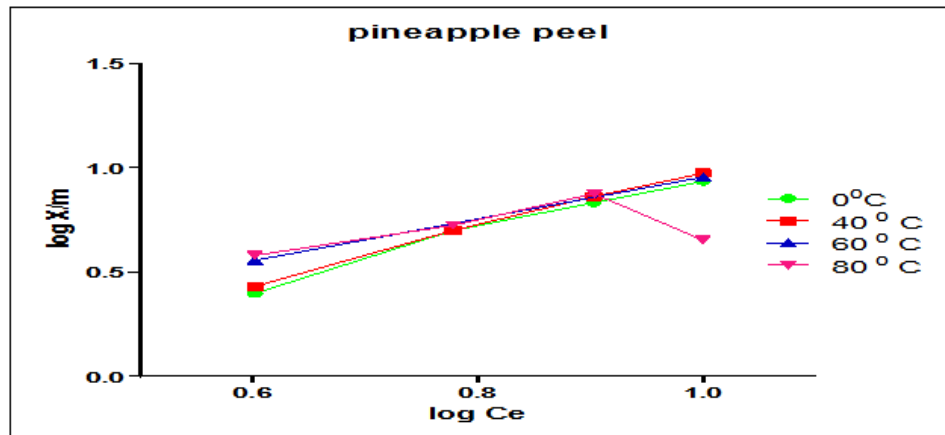

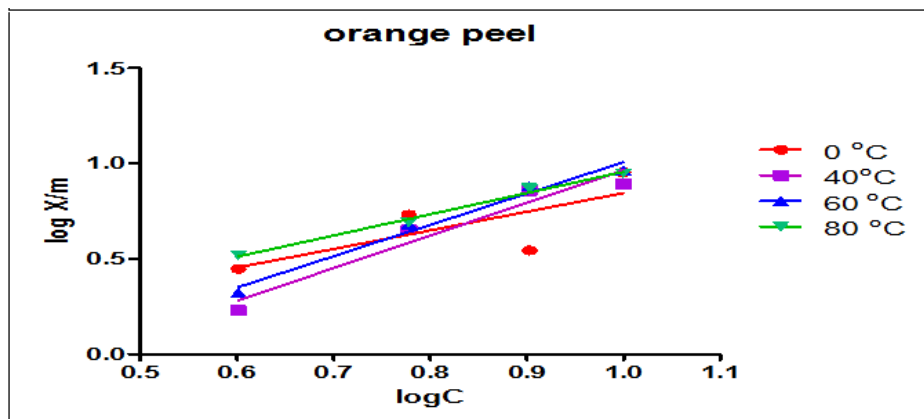**Figure 8.** Freundlich adsorption isotherms for removal of fluoride by pineapple peel powder

Figure 9. Freundlich adsorption isotherms for removal of fluoride by orange peel powder

C) Langmuir Adsorption Isotherm:

The Langmuir isotherms are useful for determine the efficiency of adsorbent at higher temperature. The freundlich isotherms are applicable only at lower temperatures to get an idea about the adsorption phenomena and monolayer coverage of the adsorbent. The intercept values for fluoride are 0.3, 0.35, 0.45 and 0.55 this indicates that the adsorption capacity increases up to 80°C. Increasing of temperature is favorable for removal of fluoride.
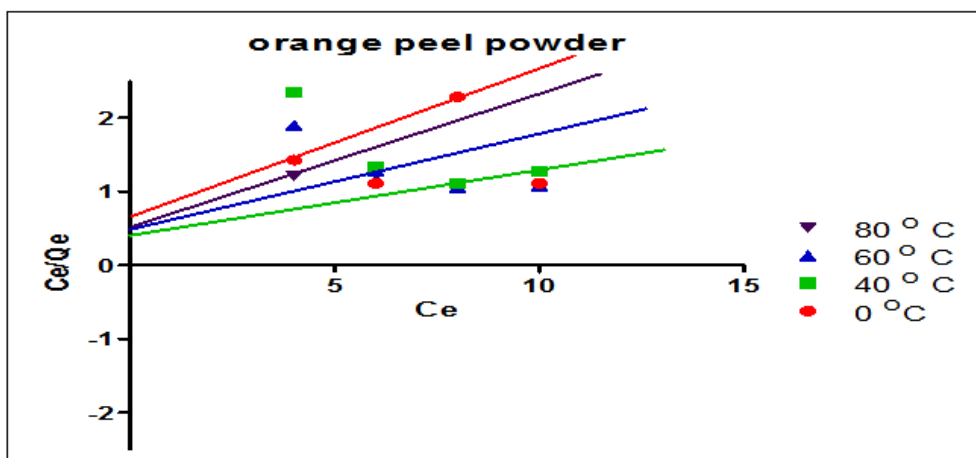

Figure 10. Langmiur adsorption isotherms plots for removal of fluoride by using orange peel powder
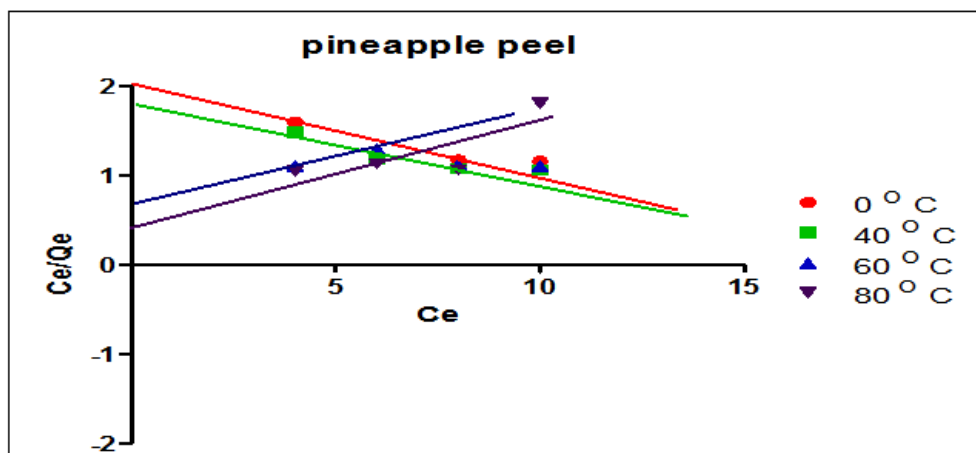
Figure 11. Langmiur adsorption isotherms plots for removal of fluoride by using orange peel powder

3.7. Thermodynamic Parameters

A plot of ln Kc vs 1/T was found to be linear ΔH^o and ΔS^o (i.e. enthalpy change and entropy change) are calculated from the slope and intercept. ΔS^o is 2.4 and 2.0 for pineapple peel and orange peel respectively which indicates adsorption is exothermic. The positive values of ΔS^o show the increased randomness at the solid surface during the interaction solid with the fluoride ions. The negative value of ΔG^o indicates the feasibility of process and spontaneous nature of adsorption process [59,60].

Figure 12. Relationship between 1/T and ln k

3.8. Adsorption Kinetic Models:

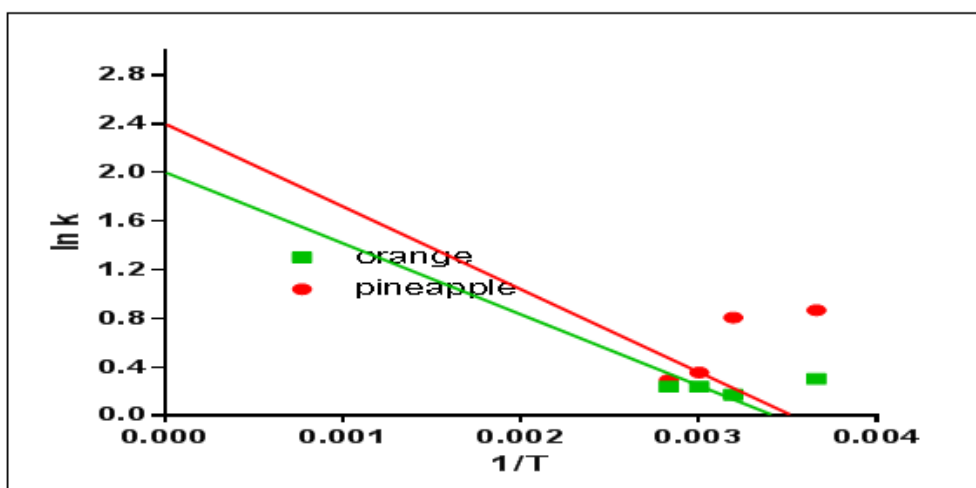Figure 13 (a) and Figure 13 (b) shows a plot of the lagergren (Pseudo first order) equation for the results of adsorption of fluoride on pineapple peel and orange peel powder. The pseudo first order model can be used to describe the kinetics of sorption of fluoride on pineapple peel but not suitable for orange peel. The results of sorption of fluoride on both adsorbents are represented by Elovich pseudo first order equations (Figure 14 (a) & 14 (b)). These results showed can be approximated using Elovich equation. The same data are shown as pseudo second order equations. The value of q_e and the pseudo second order rate constant k_2 can be calculated from the slop and intercept of the straight line obtained from the plot. Increasing the initial concentration from 4 to10 mg the amount absorbed increases with increase of contact time. These graphs indicate more sorption driving force [58,59,60,61].
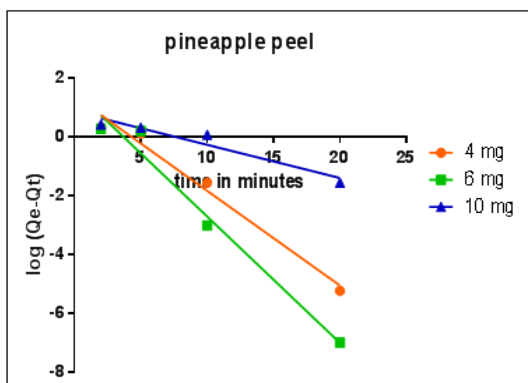

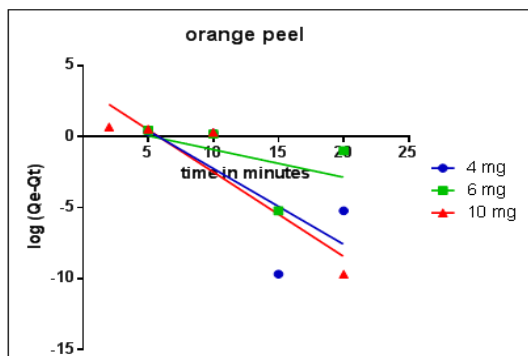**Figure 13** (a). Lagergren (Pseudo First Order Equation) Model for pineapple peel

Figure 13 (b). Lagergren (Pseudo First Order Equation) Model for orange peel
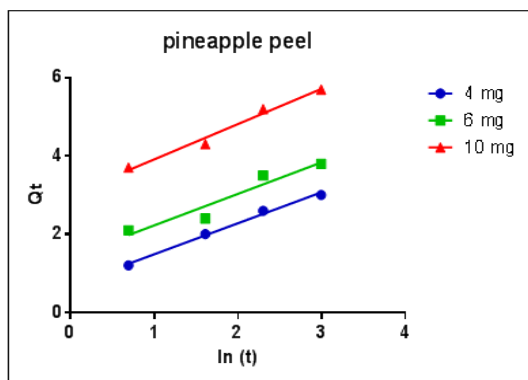
Figure 14 (a). Elovich Model for removal of fluoride using pineapple peel powder
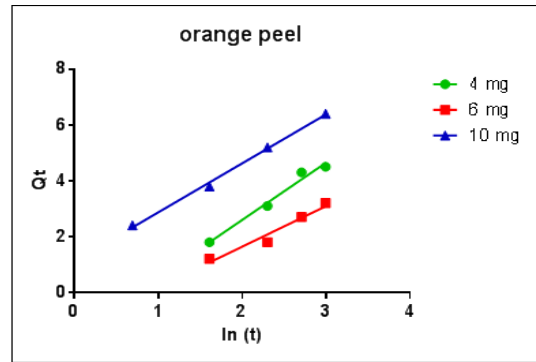
Figure 14 (b). Elovich Model for removal of fluoride using orange peel powder
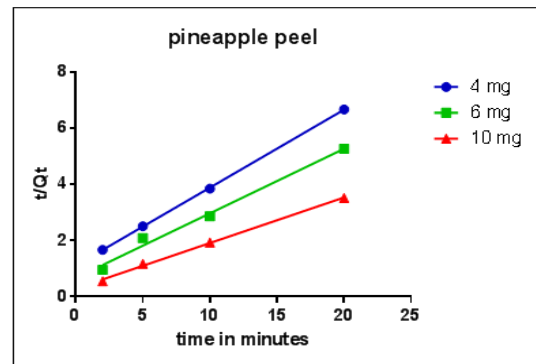
Figure 15 (a). Pseudo Second Order Model for removal of fluoride pineapple powder
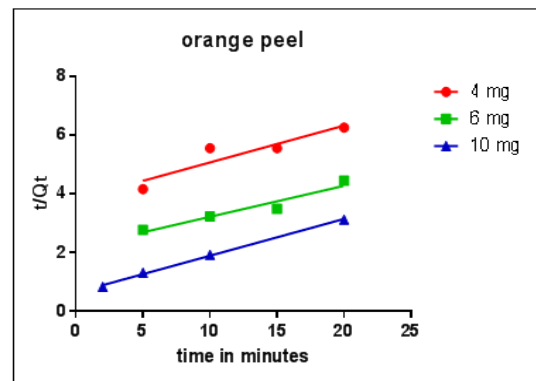
Figure 15 (b). Pseudo Second Order Model for removal of fluoride orange peel powder

3.9. Intraparticle Diffusion Model

To check the involvement of intraparticle diffusion, the experimental data tested with intraparticle diffusion model proposed by weber. The plot qt versus $t^{1/2}$ shown different behavior with involvement of various diffusions for both adsorbents. The said figure explains us: The initial linear region is attributed to film diffusion, governed by boundary layer effect.

The second parallel line describes the intraparticle diffusion stage. The final gradual uptake and stable line is governed by the pore diffusion mechanism. The correlation coefficient (R^2) values, obtained values of K_{id} and *I* from the slope and intercept were listed in table for both adsorbents. From the figure and table it is concluded that the adsorption of fluoride by pineapple peel and orange peel powders, cannot describe by using intraparticle diffusion model.

3.10. Equilibrium Parameter

Values of the dimensionless equilibrium parameter, R_L, of different temperatures are calculated for the initial concentrations of Fluoride are given in Table 5. The parameters explain the differences in the shapes of the isotherm. The observed R_L values for Fluoride are between 0 to 1 and it indicative of the favourable adsorption.
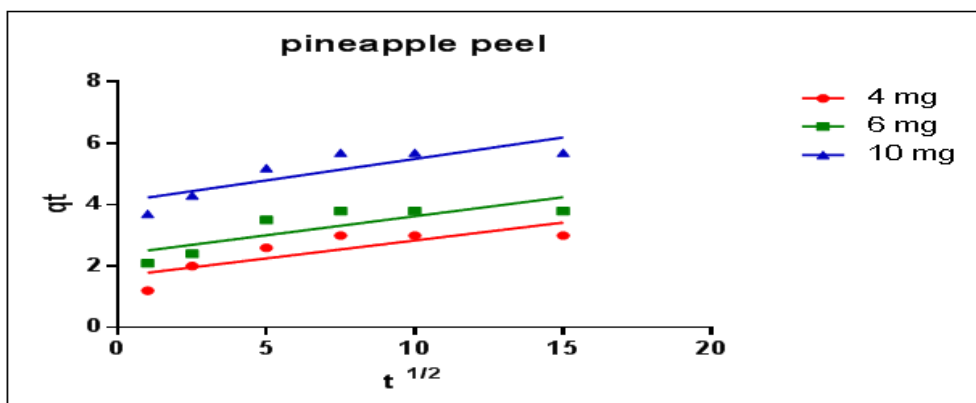
Figure 16 (a). Intraparticle diffusion model for adsorption of fluoride by pineapple peel powder
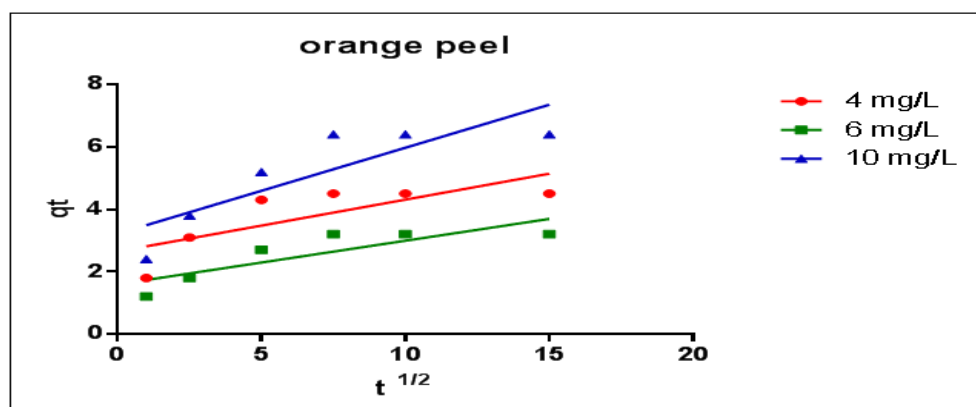
Figure 16 (b). Intraparticle diffusion model for adsorption of fluoride by orange peel powder

4. Mechanism of Biosorption of Fluoride

The pineapple peel consists functional groups such as OH, COOH, NH-O and C=O. There are hetero atoms i.e. O and H, which undergo protonation and they release a lone pairs of electrons. These lone pair electrons develop a positive charge and they participate in the adsorption of fluoride.
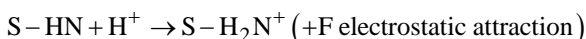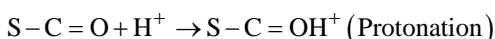
$$S-OH+H^+ \rightarrow S-OH_2^+ \left(+F \text{ electrostatic attraction}\right)$$

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

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

Electrostatic physisorption between ions and dipoles took place. Electrostatic attraction between positive poles of partial bonds of OH, NH and CO groups of adsorbents and fluoride took place.

$$S-O^{-s}-H^{+s}+F \rightarrow S-O^-$$

$$-H^{+s}-\ldots\ldots F \rightarrow S-N^{-s}-H^{+s}$$
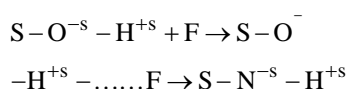
5. Conclusion

In the present study, two adsorbents are studied for the defluoridation process. The results indicate the pineapple peel is efficient and potential adsorbent for defluoridation process. The adsorptions of fluoride are affected by contact time, concentration, adsorbent dosages and temperature. From the results it can be concluded the percentage removal increases with increase in contact time and adsorbent dosage till the surface has reached its optimum capacities. The negative value of ΔG^o indicates the spontaneous process.

Table 2. Adsorption isotherm constant and statistical comparison values of adsorption isotherm models for Fluoride adsorption by orange peel powder

S.No	Parameters	Temperature °C			
		0	40	60	80
	Temkin Adsorption Isotherm				
01	R^2	0.932	0.171	0.637	0.999
	ASS	0.163	0.348	4.167	0.000
	a_T	-0.270	5.320	2.190	8.800
	b_T	0.335	-0.060	0.605	0.050
	Langmuir Adsorption Isotherm				
02	R^2	0.002	0.620	0.771	0.681
	ASS	0.920	0.361	0.107	0.004
	Q_0	1.406	2.722	2.273	1.369
	b_L	0.011	-0.171	-0.134	-0.032
	Freundlich Adsorption Isotherm				
03	R^2	0.564	0.941	0.977	0.992
	ASS	0.065	0.016	0.005	0.000
	$\log k_f$	-0.133	-0.751	-0.637	-0.158
	$1/n$	0.978	1.717	1.644	1.115

Table 3. Kinetic parameters for adsorption of Fluoride by orange peel powder

S.No	Parameters	Fluoride concentration (4mg/L)	Fluoride concentration (6 mg/L)	Fluoride concentration (10 mg/L)
		Pseudo first order kinetic model		
01	R^2	0.508	0.229	0.847
	ASS	34.50	15.96	11.88
	K_1	0.533	0.194	0.595
		Pseudo Second order kinetic model		
02	R^2	0.853	0.929	0.997
	ASS	0.337	0.104	0.006
	K_2	0.125	0.105	0.125
		Elovich model		
03	R^2	0.979	0.955	0.997
	ASS	0.095	0.108	0.026
	α	-1.511	-1.275	1.111
	β	0.486	0.686	0.569
		Intraparticle diffusion model		
04	R^2	0.594	0.709	0.722
	ASS	2.518	1.066	3.903
	k_{id}	0.166	0.139	0.276
	I	2.646	1.594	3.214

Table 4. Thermodynamic parameters of Fluoride adsorption by orange peel powder

S. No	Temperature	ΔG^o (KJ/ mol)	ΔS^o (KJ/ mol)	ΔH^o (KJ/ mol)
01	273	5.902×10^{-9}	-0.012	79.15
02	303	7.270×10^{-9}		
03	313	7.758×10^{-9}		
04	323	8.261×10^{-9}		
05	333	8.780×10^{-9}		
06	353	9.867×10^{-9}		

Table 5. Equilibrium parameter RL values at different concentration and different temperatures

S.No	Temperature (ºC)	Concentration of Fluoride (mg/L) and R_L values		
		4 mg/L	6 mg/L	10 mg/L
01	0	0.247	0.164	0.098
02	30	0.301	0.201	0.120
03	40	0.288	0.192	0.115
04	50	0.258	0.172	0.103

Table 6. Adsorption isotherm constant and statistical comparison values of adsorption isotherm models for Fluoride adsorption by pineapple peel seed powder

S.No	Parameters	Temperature °C			
		0	40	60	80
		Temkin Adsorption Isotherm			
01	R^2	0.992	0.998	0.995	0.988
	ASS	0.147	0.035	0.082	0.081
	a_T	-1.310	-1.750	-0.090	-0.016
	b_T	1.005	1.125	0.920	0.925
		Langmuir Adsorption Isotherm			
02	R^2	0.670	0.843	0.059	0.609
	ASS	0.043	0.017	0.025	0.155
	Q_0	1.753	1.687	1.225	0.493
	b_L	-0.066	-0.068	-0.008	0.110
		Freundlich Adsorption Isotherm			
03	R^2	0.983	0.996	0.999	0.231
	ASS	0.002	0.000	0.000	0.036
	Log k_f	-0.387	-0.381	-0.045	0.418
	1/n	1.344	1.368	1.000	0.353

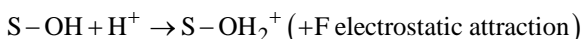**Table 7. Kinetic parameters for adsorption of Fluoride by pineapple peel powder**

S.No	Parameters	Fluoride concentration (4mg/L)	Fluoride concentration (6 mg/L)	Fluoride concentration (10 mg/L)
		Pseudo first order kinetic model		
01	R^2	0.979	0.975	0.927
	ASS	0.401	0.877	0.185
	K_1	0.322	0.420	0.112
		Pseudo Second order kinetic model		
02	R^2	0.999	0.988	0.998
	ASS	0.001	0.113	0.009
	K_2	0.277	0.230	0.162
		Elovich model		
03	R^2	0.992	0.918	0.982
	ASS	0.014	0.166	0.043
	α	0.693	1.420	3.010
	β	1.261	1.242	1.108
		Intraparticle diffusion model		
04	R^2	0.674	0.680	0.709
	ASS	0.875	0.963	1.066
	k_{id}	0.116	0.124	0.139
	I	1.669	2.386	4.094

Table 8. Thermodynamic parameters of Fluoride adsorption by pineapple peel powder

S. No	Temperature	ΔG° (KJ/ mol)	ΔS^{o} (KJ/ mol)	ΔH^{o} (KJ/ mol)
01	273	5.435×10^{-7}	-1.732	729.3
02	303	6.695×10^{-7}		
03	313	7.144×10^{-7}		
04	323	7.608×10^{-7}		
05	333	8.087×10^{-7}		
06	353	9.087×10^{-7}		

Table 9. Equilibrium parameter R_L values at different concentration and different temperatures

S.No	Temperature (^{o}C)	Concentration of Fluoride (mg/L) and R_L values		
		4 mg/L	6 mg/L	10 mg/L
01	0	0.251	0.178	0.107
02	40	0.268	0.178	0.107
03	60	0.252	0.168	0.100
04	80	0.225	0.150	0.090

References

[1] Bhargava, D.S., and Killedar, D.J., Defluoridation and Empirical Models in Column Studies using Fishbonme Charcoal. *Indian Journal of Engineering & Materials Sciences* 1997. (in press).

[2] Nawalakhe, W.G., Kulkarni, D.N., Pathak, B.N., and Bulusu, K.R., Defluoridation of water with alum, *Ind. J. Environ. Health* 16 (1) 202-210, 1974.

[3] Brindha, K., Rajesh, R., Murugan, R., and Elango, L., Fluoride contamination in groundwater in parts of Nalgonda District, Andhra Pradesh, India. *Environ Monit Assess,* 172(1-4) 481-492, 2011.

[4] Subba Rao, N., Fluoride in groundwater, Varaha river basin, Vsakhapatnam district, Aandhra Pradesh, India. *Environmental Monitoring Assessment,* 152, 47-60, 2008.

[5] Muralidharan, D., Nair, A. P., and Sathyanarayana, U., Fluoride in shallow aquifers in Rajgarh tehsil of Churu district Rajasthan—An arid environment. *Current Science*, 83, 699-702, 2002.

[6] CDC. "Water Fluoridation – Surgeon General's Statement on Community Water Fluoridation" http://www.atsdr.cdc.gov/tfacts11.html, Dec.14, 1995.

[7] Code of Federal Regulations, Title 40, part 143, section 5, 560-584, July 1, 1999.

[8] Faust, S.D., and Osman, M.A., "Chemistry of Water Treatment", Ann Arbor Press., 2nd Ed., 417-450, 1998.

[9] John, D.J., Water treatment, Handbook of Drinking Water Quality Standards and Controls, Van Nostrand Reinhold, New York, pp. 407-490, 2000.

[10] Li, Z., Hong, H., Liao, L., Ackley, C.J., Schulz, L.A., Macdonald, R.A., Mihelich, A.L., and Emard, S.M., A Mechanistic Study of Ciprofloxacin removal by Kaolinite. *Collo. Sur. –B,* 8, 339-344, 2011.

[11] Bhise, R.M., Patil, A.A., Raskar, A.R., Pati, P.J., and Desh Pande, D.P., Removal of Colour of Spent Wash by Activated Charcoal Adsorption and Electro coagulation, *Res. J. Recent Sci.* 1, 66-69, 2012.

[12] Temkin, M.I., and Pyzhev, V., Kinetic of Ammonia Synthesis on Promoted Iron Catalyst, *Acta Phy. Chem,* URSS 12, 327-356, 1940.

[13] Ho, Y.S., Porter, J.F., and Mckay, G., Equilibrium Isotherm Studies for Sorption of Divalent Metal ions onto Peat, Copper, Nickel and Lead single Component Systems, *Water, Air. Soil, Pollu.* 141, 1-33, 2002.

[14] Chen, Z., Ma, W., and Han, M., Biosorption of Nickel and Copper onto Treated Alga (*Undriapinnarlifida*). Application of Isotherm and Kinetic Models, *J. Hazar. Mater.* 155, 327-333, 2008.

[15] Brow, P., Jetcoat, I., Parrisha, D., Gilla, S., and Grahams, E., Evaluation of the Adsorptive Capacity of Peanut hull Pellets for Heavy Metals in Solution, *Advanc. Envir. Res.* 4, 19-29, 2008.

[16] Cossich, E.S., Tavares, C.R.G., and Ravagnani, T.M.K., Biosorption of Chromium (III) by *Sargassun* Sp. Biomass, *Elctro. J. Biotech.* 5, 133-140, 2002.

[17] Langmuir, I., The Adsorption of Gases on Plane Surfaces of Glass Mic and Platinum. *J. American Chem. Soci.* 40, 1361-1403, 1918.

[18] Tembhurkar, A.R., and Shipa, D., Studies on Fluoride Removal using Adsorption Process, *J. Envir. Sci. Eng.* 48, 151-156, 2006.

[19] Dakiky, M., Khamis, M., Manassra, A., and Mereb, M., Selective Adsorption of Chromium (VI) in Industrial Wastewater using Low – Cost Abundantly Available Adsorbents, *Advanc. Envir. Res.* 6, 533-543, 2002.

[20] Freundlich, H.M.F., Over the Adsorption in Solution, *J. Phy. Chem.* 57, 385-470, 1906.

[21] Demirbas, E., Kobya, M., Sentark, E., and Ozkan, T., Adsorption Kinetics for the Removal of Chromium (VI) from Aqueous Solution on the Activated Carbons Prepared from Agricultural Waste, *Water SA,* 30, 533-539, 2004.

[22] Lagergren, S., About the Theory of so Called Adsorption of Soluble Substances, Kungliga Svenska Vetenskapsakademiens Handlingar, 24, 1-39, 1898.

[23] Deng, L., Su, Y., Su, H., Wang, X., and Zhu, X., Sorption and Desorption of Lead (II) from Wastewater by Green Algae (*Cladophora fascicularis*), *J. Hazar. Mater.* 143, 220-225, 2007.

[24] Doyurum, S., and Celik, A., Pb (II) and Cd (II) Removal from Aqueous Solution by Olive Cakes, *J. Hazar. Mater. B.* 138, 22-28, 2006.

[25] Suresh, G., and Babu, B.V., Removal of Toxic Metal Cr (VI) from Aqueous Solutions using Saw Dust as Adsorbent. Equilibrium, Kinetics and Regeneration Studies. *Chem. Eng. J.* 150, 352-365, 2009.

[26] Ho, Y.S., Adsorption of Heavy Metals from Waste Streams by Peat, Ph.D. Thesis, University of Birmingham, Birmingham UK, 1995.

[27] Elifantz, H., and Telor, E., Heavy Metal Biosorption by Plant Biomass of the Macrophyte (*Ludwigia stolonifera*), *Water Air and Soil Pollution,* 141, 207-218, 2002.

[28] Ho, Y.S., and Mcay, G., Study of the Sorption of Divalent Metal ions to Peat. *Adsorption Sci. Technol.* 18, 639-650, 2008.

[29] Yakout, S.M., and Elsherif, E., Batch Kinetics, Isotherm and Thermodynamic Studies of Adsorption of Strontium from Aqueous Solutions onto Low –Cost rice Straw Based Carbons. *Carbon Sci. Technol-* 1, 144-153, 2010.

[30] Sparks, D.L., Kinetics of Soil Chemical Process, Academic Press, New York, (1989).

[31] Zhang, J., and Stan forth, R., Slow Adsorption Reaction between Arsenic Species and Geothite. Diffusion or Heterogeneous Surface Reaction Control, *Langmuir* 21, 2895-2901, 2005.

[32] Low, M.J.D., Kinetics of Chemisorption of Gases on Solids, *Chem. Rev.* 60, 267-312, 1960.

[33] Chien, S.H., and Clayton, W.R., Application of Elovich Equation to the Kinetics of Phosphate Release and Sorption on Soils, *Soil Sci. Soci. American J.* 44, 265-268, 1980.

[34] Sparks, D.L., Kinetics of Reaction in Pure and Mixed Systems in Soil Physical Chemistry, CRC Press, Boca Raton, 1986.

[35] Weber, W.J., and Morris, J.C., Kinetics of Adsorption on Carbon from Solution, *J. Sanitary Eng. Div. American Soci. Chem. Eng.* 89, 31-39, 1963.

[36] Wu, F., Tseng, R., and Juang, R., Initial behaviour of Intraparticle Diffusion Model used in the Description of Adsorption Kinetics, *Chem. Eng. J.* 153, 1-8, 2009.

[37] Khan, A.A., and Singh, R.P., Adsorption Thermodynamics of Carbofuran on Sn (IV) Arseno silicate in H^+, Na^+ and Ca^{+2} forms, Colloids. Surface. 24, 33-42, 1987.

[38] Uslu, H., and Inci, I., Adsorption Equilibria of L – (+) – Tartaric Acid onto Alumina. *J. Chem. Eng. Data,* 54, 1997-2001, 2009.

[39] Palanisamy, P.N., and Sivakumar, P., Adsorption Studies of Basic red 29 by a Non _Conventional Activated Carbon Prepared from Euphorbia Antiguorum L. *Inter. J. Chemtech. Res.* 1, 502-506, 2009.

[40] Karthikeyan, M., and Elongo, K.P., Removal of Fluoride from Aqueous Solution using Graphite. A Kinetic and thermodynamic Study, *Indian J. Chem. Technol.* 15, 525-532, 2008.

[41] Gandhi, N., Sirisha, D., Chandra Shekar, K.B., and Smita Asthana., Removal of fluoride from water and waste water by using low cost adsorbents. *International Journal of Chem Tech Research,* Vol. 4(4); pp 1646-1653, 2012.

[42] Gandhi, N., Sirisha, D., Smita Asthana., and Manjusha, A., Adsorption studies of fluoride on multani matti and red soil. *Research Journal of Chemical Sciences*, Vol. 2(10); pp 1-4, 2012.

[43] Manjusha, A., Gandhi, N., and Sirisha, D., Removal of Chromium (VI) from paint manufacturing industry waste water by using papaya peel powder. *International Journal of Pharma world Research,* Vol. 3(2); mar-jun, 2012.

[44] Manjusha, A., Gandhi, N., and Sirisha, D., Adsorption of Chromium (VI) from aqueous solution by using *mangifera indica* bark dust. *Universal Journal of Environmental Research and Technology.* Vol. 2(1); 2012.

[45] Gandhi, N., Sirisha, D., Mary Priyanka, V., and Arthisree, S.R., Adsorption Studies on Mixed algae to control SO_2 and NO_2 pollution. *International Journal of Pharma and Bio sciences,* Vol. 3(4) B; pp 304-310, 2012.

[46] Marry priyanka, V., Sirisha, D., and Gandhi, N., Sulphur dioxide adsorption using *Macrtyloma uniflorum* Lam. Seed powder. *Proceedings of the International Academy of Ecology and Environmental Sciences,* vol. 2(4); pp 251-254, 2012.

[47] Sirisha, D., Mukkanti, K., and Gandhi, N., Adsorption Studies on Alum Sludge. *Advances in Applied Science Research,* vol. 3(5); pp 3362-3366, 2012.

[48] Marry priyanka, V., Sirisha, D., and Gandhi, N., Adsorption studies on *Mangifera indica* controlling of SO_2 pollution. *Journal of Chemical and Pharmaceutical Research,* Vol. 4(3); pp 1768-1771, 2012.

[49] Sirisha, D., Mukkanti, K., and Gandhi, N., Adsorption of SO_2 by Marble chips. *International Journal of Chemical Sciences, Vol. 10(2); pp 847-854, 2012.*

[50] Mamatha, K., Gandhi, N., and Sirisha, D., Adsorption of aqueous solution of NO_2 by certain waste materials. *Asian Journal of Research in Chemistry,* Vol. 5(1); pp 143-145, 2012.

[51] Arthisree, S.R., Sirisha, D., and Gandhi, N., Adsorptions of aqueous solution of NO_2 by Neem bark dust. *International Journal of Chem Tech Research,* Vol. 5(1);pp 450-455, 2013.

[52] Sirisha, D., Mukkanti, K., and Gandhi, N., Adsorptive Removal of SO_2 by using Magnesium Carbonate ($MgCO_3$). *International Journal of Green and Herbal Chemistry.* Vol. 2(3), 576-580, 2013.

[53] Gandhi, N., Sirisha, D., and Chandra Shekar, K.B., Adsorption of Fluoride from aqueous solution by using chalk powder. *World Journal of Pharmacy and Pharmaceutical Sciences,* Vol. 2(5), 3897-3914, 2013.

[54] Gandhi, N., Sirisha, D., and Chandra Shekar, K.B., Adsorption of Chromium (VI) from aqueous solution by using brick powder. *Asian Academic Research Journal of Multidisciplinary,* Vol. 1(15), 112-137, 2013.

[55] Gandhi, N., Sirisha, D., and Vikas Chandra Sharma., Microwave-Mediated Green Synthesis of Silver Nanoparticles Using *Ficus Elastica* Leaf Extract and Application in Air pollution Controlling Studies. *International Journal of Engineering Research and Applications.* Vol. 4(1), 01-12, 2014.

[56] Gandhi, N., Sirisha, D., and Chandra Shekar, K.B., Adsorption of Chromium (VI) from aqueous solution by using Multani miti. *International Journal of Research in Pharmacy and Chemistry,* Vol. 4(1), 168-180, 2014.

[57] Gandhi, N., Sirisha, D., and Chandra Shekar, K.B., Removal of Chromium (VI) from Industrial Wastewater by Coagulation Process using Pithecellobium Ducle Seeds as Natural Coagulant. *Continental Journal of Water, Air and Soil Pollution,* Vol. 4(1), 32-39, 2013.

[58] Gandhi, N., Sirisha, D., and Chandra Shekar, K.B., Bioremediation of Wastewater by using *Strychnos Potatorum* Seeds (Clearing nuts) as Bio Adsorbent and Natural Coagulant for Removal of Fluoride and Chromium. *Journal of International Academic Research for Multidisciplinary. Vol. 3(1), 253-272, 2014.*

[59] Gandhi, N., Sirisha, D., Hasheena, M., and Smita Asthana., Eco-friendly Method for Synthesis of Copper Nanoparticles and Application for removal of Aqueous Sulphur Dioxide (SO_2) and Nitrogen Dioxide (NO_2). *International Journal of Engineering Research and Technology.* Vol. 3(11), 1253-1262, 2014.

[60] Gandhi, N., Sirisha, D., and Smita Asthana., Bio adsorption of Alizarin red dye using immobilized *Saccharomyces cerevisiae. International Research Journal of Natural and Applied Sciences. Vol. 2(3), 1-17, 2015.*

[61] Sirisha, D., Smita Asthana, Gandhi, N., and Hasheena, M., Adsorptive removal of aqueous SO_2 by using Orange Peel Powder. *Indian Journal of Science-Discovery. Vol. 12(34), 39-51, 2015.*