Adsorption of Fluoride (F-) from aqueous solution by using Horse gram (*Macrotyloma uniflorum*) seed powder

N. Gandhi, D. Sirisha, K.B. Chandra Sekhar

Abstract— **Fluoride is an ionic form of the element fluorine and occurs naturally or used as an additive to municipal water supplies. Presence of fluoride beyond the permissible limit (>1.5 ppm) in drinking water is harmful and not suitable. Considering the range of health effects associated with high levels of fluoride in water, *Macrotyloma uniflorum* seed powder has been employed for its removal. The influence of various operational parameters i.e., effect of adsorbent dose, pH, temperature, initial concentration and contact time were studied by a series of batch adsorption experiments at room temperature (25±3∘C). The percentage removal was found to increase with adsorbent dose, pH of the medium and time for a given initial fluoride concentration (4 mg/L) while for increasing fluoride concentration, removal followed a decreasing trend. Although remarkable removal efficiency was observed in acidic range, removal at neutral pH is considered for adsorbent from drinking water viewpoint. At optimum conditions, the residual fluoride concentration was very less and percentage removal is above 80%, the concentration of fluoride after adsorption, which is below the prescribed limit and is thus able to meet the standard. The equilibrium adsorption data are modeled with different isotherm equations applicable to adsorption process. The dewatered *Macrotyloma uniflorum* seed powder better fitted with Freundlich isotherm having correlation coefficients (R^2) equal to 0.996, and 0.966, 0.644 for Langmuir isotherm, Temkin isotherm, respectively. FTIR analysis of dewatered *Macrotyloma uniflorum* seed powder showed that major peaks were pertaining to components like carbohydrates and other bio molecules that usually exist in the sludge.**

Index Terms— *Macrotyloma uniflorum* **seed powder, Adsorption, Fluoride, Isotherm Studies, Kinetic Models.**

I. INTRODUCTION

Fluoride occurs naturally in some ground water sources (linked to the presence of minerals like fluorspar, cryolite and fluorapatite) and in foods that have been grown or produced using water with high fluoride content. High amount of fluoride (>1.5 ppm) in drinking water is a serious issue in many parts of India. Fluorosis has been a serious issue in Andhra Pradesh & Telangana, as early as 1999 with maximum reported levels at 29 ppm. Ingestion of large amounts of fluoride can cause serious health problems for human, animals and plants [1-5].

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According to current world health organization permissible limit for the fluoride concentration of drinking water supplies is 1.5 mg/L. The fluoride level in ground water and surface water is increasing day by day due to fast growing population, industrialization and urbanization. Due to these domestic and industrial sources directly or indirectly causes the increasing level of fluoride in ground water and surface water. Several commercial methods are available to filter, degrade and remove fluoride from drinking and industrial wastewater. But adsorption method is very cheap and eco friendly why because it does not produce any waste dump at end. Taking all these factors into consideration the present study deals with the removal of fluoride from wastewater samples by using *Macrotyloma uniflorum* seed powder as bio adsorbent [5-11].

II. MATERIALS & METHODS:

2.1 Selection of Adsorbent:

Macrotyloma uniflorum is commonly known as Horsegram, it belongs to the family Fabaceae polyphenols present in seed extract of *Macrotyloma uniflorum* were water soluble, heat stable, polar, non-tannin and non-protein in nature, which may favors the adsorption process. Taking these factors into consideration *Macrotyloma uniflorum* seed powder is selected as an adsorbent.

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 ($25 \pm 2^\circ$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 ($25 \pm 2^{\circ}C$) 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 $0^{\circ}C$, $30^{\circ}C$, $40^{\circ}C$, $50^{\circ}C$, at different initial (1, 2, 3 and 4 mg/L) concentrations of fluoride [12-15].

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 [16]. 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 [17 - 19]. The assumptions made by Temkin are

✓ Heat of adsorption decreases with surface coverage due to the interactions between adsorbent and adsorbate [20].

✓ 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 [21 – 22]

$$q_e = B_T \ln K_T\, C_e \quad ......(i)$$

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

$$q_e = B_T \ln K_T + B_T \ln C_e \quad ....(ii)$$

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 [23] 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:

$$\frac{C_e}{q_e} = \frac{1}{k_L\, q_m} + \frac{C_e}{q_m} \quad ....(iii)$$

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 [24]. This is commonly used to describe the adsorption characteristics for the heterogeneous surface [25]. The data often fit the empirical equation proposed by Freundlich.

$$q_e = k_f\, C_e^{\,1/n} \quad .....(iv)$$

The linear form of Freundlich equation is as follows [171]

$$\log q_e = \log k_f + 1/n\, (\log C_e) \quad .....(v)$$

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 [26].

(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 [27]. A simple kinetic analysis of adsorption is the pseudo-first-order equation in the form [28 - 29].

$$dq_t/dt = k_1\,(q_e - q_t) \quad .....(vi)$$

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

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}\, X\, t \quad .....(vii)$$

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 [30].

(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, [31]. The pseudo second order kinetic order equation expressed as

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

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) [32]. 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 [33].

(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 [34-35]. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation [36]. The Elovich or Roginsky–Zeldovich equation is generally expressed as follows [37 - 39]

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

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 $(\alpha\beta)$.

(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 [40].

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

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 passing 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 [187]. 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.

$$K_c = \frac{q_e}{c_e}\ \ldots\ldots(xi)$$

K (L/g) values were obtained using the Khan and Sing method [41] by plotting ln (q/C) versus q 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 [42].

$$\Delta G^\circ = - RT\, \ln K_c\ \ldots.(xii)$$

The changes in enthalpy (ΔH) 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 [189].

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}\ \ldots.. (xiii)$$

Where ΔS^o is change in entropy, ΔH^o is change in enthalpy ΔG^o is change in free energy. Plotting ln K versus $1/T$ shows straight lines. From their slope and intercept, ΔH and ΔS are determined. The negative values of ΔG indicate a favourable and spontaneous process [43].

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 [16, 44].

$$R_L = \frac{1}{1+ bC_o}\ \ldots.(xiv)$$

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.

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.

III.   RESULTS & DISCUSSION:

3.1 Effect of Contact Time between Fluoride and *Macrotyloma uniflorum* Seed Powder:

The optimum contact time for the removal of fluoride is in between 20-30 minutes depending upon the concentration of fluoride. It is observed from figure-1 that the adsorption capacity of fluoride is increases with increase in contact time. The graph showing a smooth curve the initial steep rise in the curve is due existence of free valencies on the surface of horse gram seed powder. After the establishment of equilibrium the lines in the figure become parallel to the time axis, this can be explained on the basis of reaching saturation point [45]. The percentage removal of fluoride with contact time follows a smooth curve which indicates the mono layer coverage and it is also indicates the adsorption between horse gram seed powder and fluoride may follows pseudo first order kinetics.
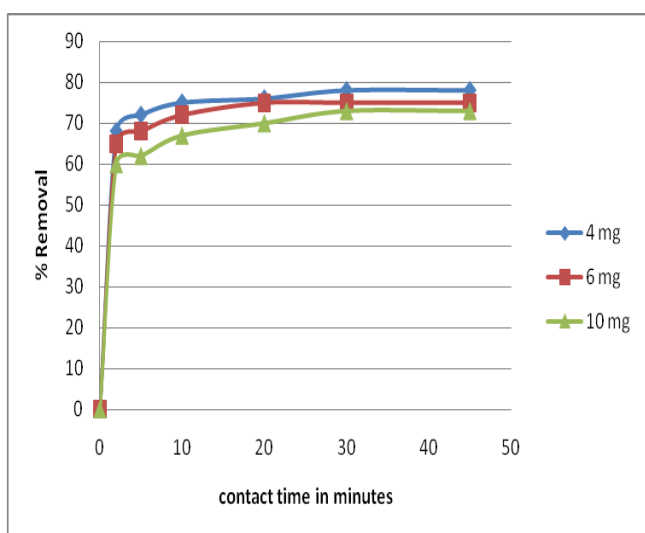

Figure-1: Effect of contact time between fluoride and horse gram seed powder

3.2. Effect of Initial Fluoride Concentration:

The mechanism of the adsorption is certainly dependent on the available surface area but it is dependent on the concentration. In the present study the particle size of *Macrotyloma uniflorum* seed powder size is 250 mic. Various concentrations of fluoride ranging from 1 mg to 4 mg have taken and performed batch adsorption experiments by keeping adsorbent dosage constant 1 gm/L. The percentage removal of fluoride is decreased with increase in fluoride concentration. The results are represented in graph mode (Figure-.2) by taking initial fluoride concentration on X- axis and % removal on Y- axis. The figure-2, indicating that maximum percentage removal of fluoride is observed at lower concentration. The absolute amount of adsorbed substance is more at higher concentrations than at the lower concentrations. This is due to greater mobility of the molecules at the lower concentration [46]. The mobility of the molecules decreases with increase in the concentration of fluoride.
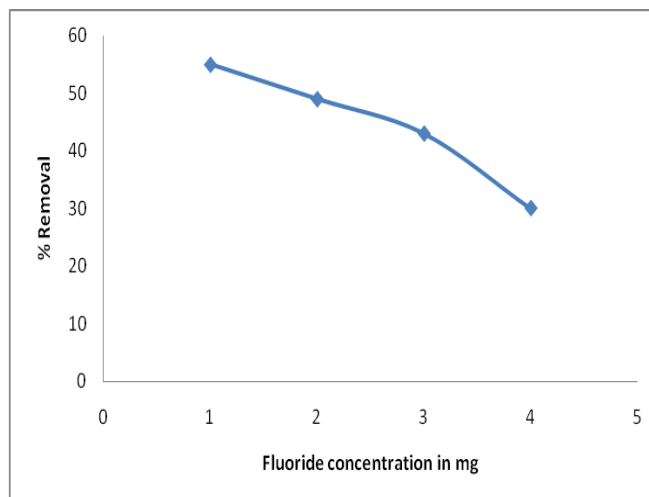

Figure- 2: Effect of fluoride concentration on adsorbent

3.3.   Effect of Adsorbent Dosage:

To study the *Macrotyloma uniflorum* seed powder dosage on adsorption of fluoride removal, various amounts of adsorbent was taken ranging from 0.2 gm to 1.0 gm. The concentration of fluoride solution is 2 mg/L and it was constant. The batch adsorption studies are carried out at room temperature. After 60 minutes of equilibrium period the samples were checked for percentage removal. The percentage removal is increase with increase in adsorbent dosage and it is shown in figure-3. This figure revels that the percentage removal of fluoride follows the smooth curve, which indicates the presence of equilibrium between fluoride and *Macrotyloma uniflorum* seed powder [47].
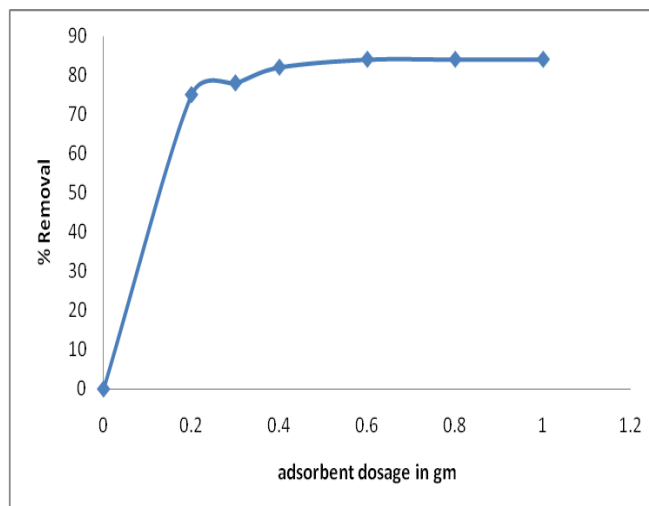

Figure-3: Effect of adsorbent dosage

3.4. Effect of pH on adsorption of fluoride:

The results of defluoridation using *Macrotyloma uniflorum* seed powder at different pH were shown in figure-4. The removal efficiency at pH 5.8 to 6.5 showed 80-82%, which was higher than pH 2. The removal efficiency increased with increase in pH and became optimum at pH 6. There is gradual decrease in adsorption was observed at basic pH
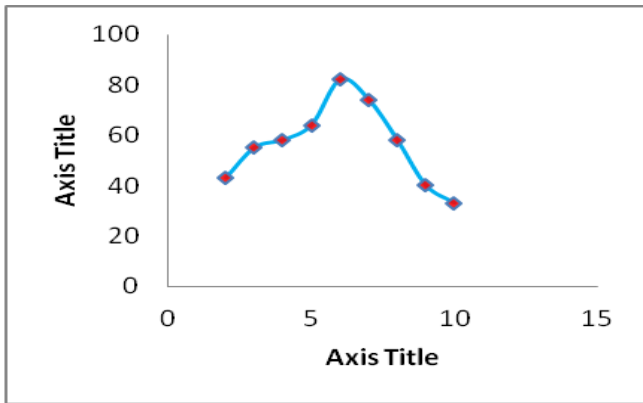
Figure-4: Effect of pH of the aqueous solution on fluoride removal by horse gram seed powder

3.5. Effect of Temperature on Adsorption of Fluoride:

The effect of temperature on fluoride adsorption capacity of *Macrotyloma uniflorum* seed powder is displayed in figure-5. The adsorption capacity was observed more at lower temperature indicating that process is physical adsorption. At 30ºC the adsorption capacity is more. These results concluding that removal of fluoride by *Macrotyloma uniflorum* seed powder will be more at room temperature i.e. 25 – 30°C.
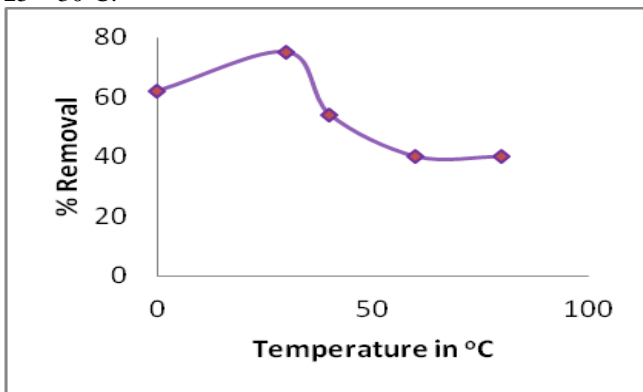

Figure-5: adsorption capacity of horse gram seed powder at different temperature

Adsorption Isotherm Studies:

Equilibrium study on adsorption provides information on the capacity 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 different adsorbate. 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 experiment.

Temkin adsorption isotherm:

A graph is plotted between x/m on Y-axis, and initial concentration on X-axis at different temperatures, the graph shows a single straight curve indicates that the adsorption capacity of fluoride by *Macrotyloma uniflorum* seed powder is increases with increase in temperature. The sorption data were analyzed according to the linear form of the Temkin isotherm and the linear plots are shown in Figure-6.

Examination of experimental data with the statistical or calculated data which reveals that the Temkin isotherm provides a close fit to the fluoride sorption data.
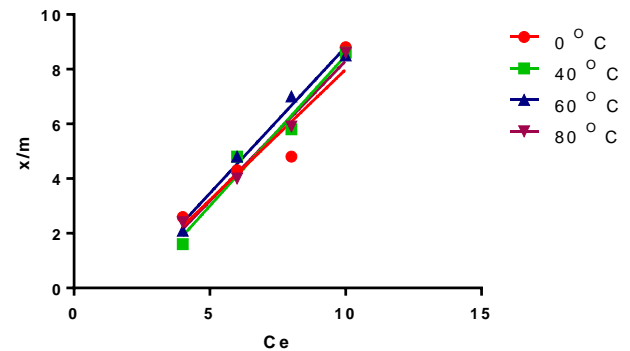

Figure-6: Temkin isotherm plots for removal of fluoride by horse gram seed powder

Freundlich Isotherm:

For the present investigation the experimental results were shown in figure-7. The highest value of *n* at 60°C indicates that it has highest intensity of adsorption and log k value indicates that higher temperature is favourable for the reaction. The Freundlich constant log k and 1/n values (table-1) increase with increase in temperature suggesting that adsorption capacity and intensity of adsorption are enhanced up to 60°C. From the figure-7 and table-1, it is concluded that the R^2 values are comparatively higher than the other isotherm models. This report is resulting that adsorptive removal of fluoride by *Macrotyloma uniflorum* seed powder perfectly fitted into Freundlich adsorption isotherm and fluoride removal by *Macrotyloma uniflorum* seed powder can perfectly described by Freundlich adsorption isotherm studies.
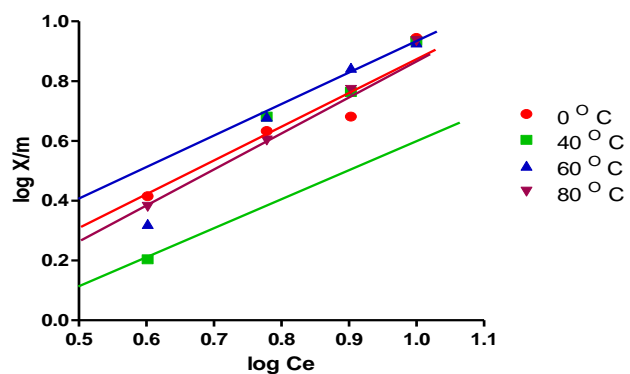

Figure- 7: Frendulich Adsorption Isotherms plots for removal of fluoride by horse gram seed powder

Langmuir isotherm:

According to Langmuir adsorption isotherm the Ce/qe versus C_e should give a linear relation. For the present investigation the same graph was plotted and shown in figure-8. From the figure-8, it was observed that the adsorption capacity is increases with increase in temperature and it is concluding that adsorptive removal of fluoride by *Macrotyloma uniflorum* seed powder can also described by Langmuirs adsorption isotherms.
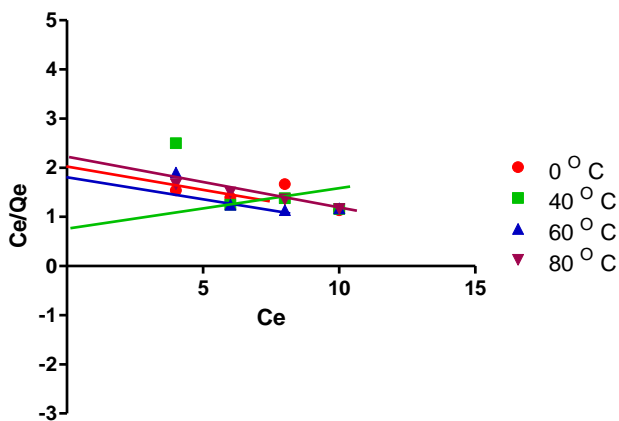
Figure-8: Langmuir Adsorption Isotherms plots for removal of fluoride by horse gram seed powder

Kinetic Models:

The adsorption data were tested with pseudo first order kinetic model. The results shown in figure-9. The lagergren pseudo first order mechanism shows good linear plots and follows pseudo first order kinetic reaction. The same data were tested with pseudo second order kinetic mechanism, and results are shown in figure-10. The plots have better linearity and the adsorption of fluoride by using *Macrotyloma uniflorum* seed powder is follows pseudo second order kinetic model. The results of sorption of fluoride by using *Macrotyloma uniflorum* seed powder has been represented in the form of Elovich equation in Figure-11, at various initial concentration of fluoride. From the plot a linear relationship between the amount of fluoride adsorbed, q_t and In (t) was established. These plots showed different distinct linear regions within individual sets of data and follows pseudo second order kinetics.

The experimental data tested with intraparticle diffusion model to find out the involvement of intraparticle diffusion model. The plot qt versus $t^{1/2}$ for different fluoride concentration at room temperature shown in figure-12. The rate constant of intraparticle diffusion model K_I were found from the slope of the plots. From the figure it is observed that multi kinetic models were involving in rate limiting step of adsorption of fluoride by concrete powder. The initial linear region is attributed to film diffusion, governed by boundary layer effect. The second parallel line describes the intraparticle diffusion stage and the final gradual uptake is governed by the pore diffusion mechanism.
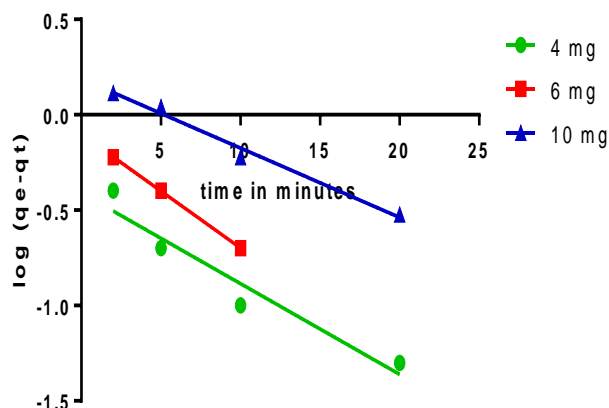

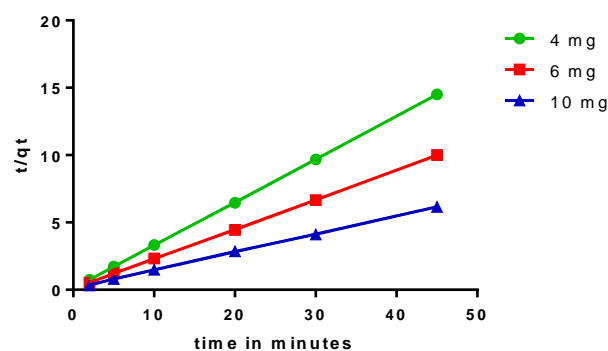**Figure-9: Lagergren model (Pseudo first order kinetic model)**

Figure – 10: Pseudo Second order kinetic model
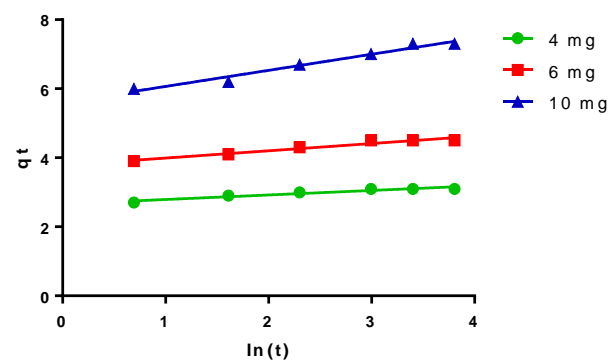
Figure – 11: Elovich kinetic model.
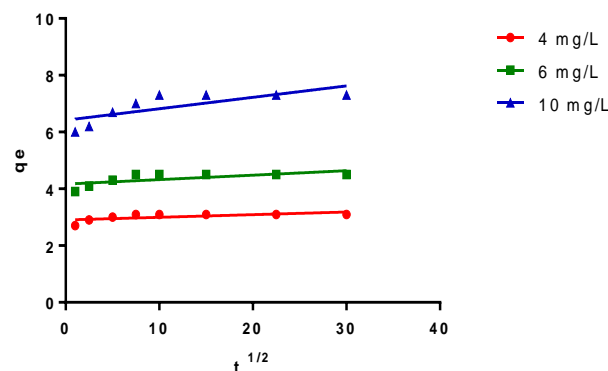
Figure-12: Intraparticle Diffusion Model

Calculation of Thermodynamic Parameters:

Thermodynamic parameters were calculated from the variation of thermodynamic equilibrium constant Kc with temperature. A graph was plotted between In Kc and 1/T. It was found to be linear (Figure-13). ΔH^o and ΔS^o were determined from the slope and intercept of the plot.

Figure 13: Relationship between Kc and 1/T Values:

Equilibrium parameter:

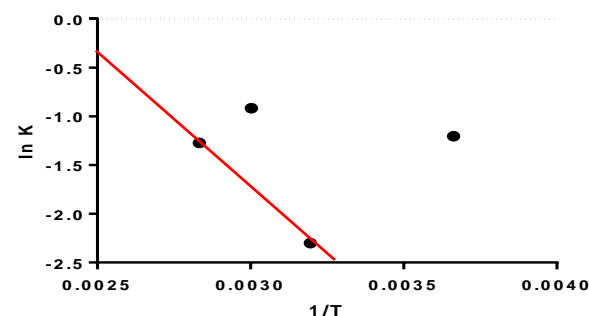Values of the dimensionless equilibrium parameter, R_L, of different temperatures are calculated for the initial concentrations of Fluoride are given in table-4. The parameters explain the differences in the shapes of the isotherm. The observed R_L values for Fluoride are between 0 to 1 and it indicative of the favourable adsorption.

Fourier Transform Infrared Spectroscopy:

The FTIR spectra of *Macrotyloma uniflorum* seed powder before adsorption and after adsorption were shown in figure-14 and figure-15. From the figures it is observed that IR spectrum of horse gram seed powder is very complex and contains different functional groups i.e. proteins, sugars, complex carbohydrates and etc. a high intensity broad peaks were observed at 3429.43 cm^{-1}, 2927.94 cm^{-1} caused by the hydroxyl groups contained in lignin, cellulose, hemi cellulose, pectin and sugars.

There is a lot of change was observed in this region after adsorption could be due to the fluoride bio sorption. Carboxyl group (C=O) were also observed at 1759.06 cm^{-1} before adsorption and is modified to 1757.15 cm^{-1} after adsorption process. This modification in peaks was confirming presence of carboxyl groups. These bands are associated with aldehydes, ketones, pectin, hemi cellulose and lignin. The peaks appeared in the region of 1400-1500 cm^{-1} might be attributed to the presence of quinine and OH groups. The peaks in the region of 1000-1100 cm^{-1}, before and after adsorption process indicating modification of C-O asymmetrical stretching of hydroxyl groups from primary alcohol related to the phenolic compounds present in lignin. The peaks appearing after bio sorption in the region of 900-1000 cm^{-1} indicated the presence of C-H, C-N and C-F stretch groups.
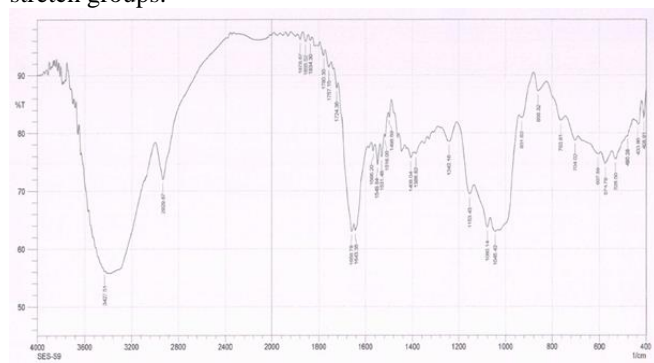

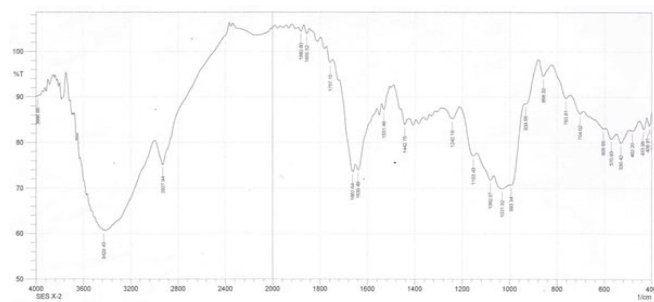**Figure-14: FTIR spectrum of *Macrotyloma uniflorum* seed powder before adsorption.**

Figure-15: FTIR spectrum of *Macrotyloma uniflorum* seed powder after adsorption.

IV. CONCLUSIONS:

Water containing more than 5 µg/ml of fluoride is not recommended for drinking. Most commonly used alumina has problems of low capacity leaching of aluminum. A non toxic *Macrotyloma uniflorum* seed powder used in present study removes fluoride without release of ion during remediation process. The process is cost effective and eco-friendly which can be used by the poor people.

The present bio adsorption study suggests as a potential alternative for detoxification of toxic fluoride present in the water. The percentage removal of fluoride was found to function of adsorbent dosage and contact time. Optimum dosage and optimum contact time for adsorption process is 0.8 gm and 20-30 min respectively. The percentage removal is more at lower concentration compared to high concentration. The statistical analysis reveals that the data follows Freundlich and Temkin Adsorption isotherms compared to that of Langmuir adsorption isotherm. The adsorption process follows Pseudo second order kinetics. Thermodynamic data indicates that process is exothermic and spontaneous.

Table-1: Adsorption isotherm constant and statistical comparison values of adsorption isotherm models for Fluoride adsorption by *Macrotyloma uniflorum* seed powder.

S.No	Parameters	Temperature ºC			
		0	40	60	80
Temkin Adsorption Isotherm					
01	R^2	0.882	0.966	0.984	0.985
	ASS	2.427	0.840	0.362	0.315
	SEE	1.101	0.648	0.425	0.396
	RSS	2.427	0.840	0.362	0.315
	a_T	-1.560	-2.500	-1.890	-1.950
	b_T	0.950	1.100	1.070	1.025
Langmuir Adsorption Isotherm					
02	R^2	0.282	0.644	0.674	0.996
	ASS	0.111	0.415	0.126	0.004
	SEE	0.235	0.455	0.251	1.449
	RSS	0.111	0.415	0.126	0.0004
	Q_0	1.761	2.933	2.170	2.001
	b_L	-0.046	-0.194	-0.114	-0.082
Freundlich Adsorption Isotherm					
03	R^2	0.919	0.942	0.971	0.996
	ASS	0.011	0.0168	0.006	0.000
	SEE	7.554	9.184	5.594	1.826
	RSS	0.011	0.016	0.006	0.0006
	Log k_f	-0.327	-0.804	-0.570	-0.458
	$1/n$	1.213	1.767	1.541	1.377

Adsorption of Fluoride (F-) from aqueous solution by using Horse gram (Macrotyloma uniflorum) seed powder

Table-2: Adsorption Kinetic constant and statistical comparison values of adsorption kinetic models for Fluoride adsorption by *Macrotyloma uniflorum* seed 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	0.932	0.999	0.985
	ASS	0.030	0.000	0.003
	SEE	0.124	2.272	4.262
	RSS	0.9850	5.16	0.0036
	K_1	0.047	0.059	0.036
	Pseudo Second order kinetic model			
02	R^2	0.999	0.999	0.999
	ASS	0.004	0.004	0.008
	SEE	3.390	3.520	4.55
	RSS	0.0045	0.0049	0.0083
	K_2	0.319	0.219	0.134
	Elovich model			
03	R^2	0.917	0.947	0.968
	ASS	0.010	0.016	0.047
	SEE	5.158	0.064	0.109
	RSS	0.010	0.016	0.047
	α	2.660	3.781	5.601
	β	7.633	0.004	2.150
	Intraparticle diffusion model			
04	R^2	0.425	0.472	0.592
	ASS	0.085	0.200	0.810
	k_{id}	0.009	0.015	0.040
	I	2.903	4.166	6.417

Table-3: Thermodynamic parameters of Fluoride adsorption by *Macrotyloma uniflorum* seed powder

S. No	Temperature	ΔG^o (KJ/mol)	ΔS^o (KJ/mol)	ΔH^o (KJ/mol)
01	273	9.494×10^{-6}	-1.019	-127.4
02	303	11.696×10^{-6}		
03	313	12.481×10^{-6}		
04	323	13.291×10^{-6}		
05	333	14.126×10^{-6}		
06	353	15.874×10^{-6}		

Table-4: Equilibrium parameter R_L 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	0.262	0.174	0.104
02	30	0.310	0.206	0.124
03	40	0.282	0.188	0.112
04	50	0.272	0.181	0.108

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