



BIOSORPTION OF FLUORIDE FROM AQUEOUS SOLUTIONS BY *TINOSPORA CORDIFOLIA* LEAVES

Dasaiah Srinivasulu^{1*}, Yakkala Kalyan¹, Battala Gangadhar¹, Pavan Kumar Pindi² and Gurijala Ramakrishna Naidu^{1*}

¹Department of Environmental Sciences, Sri Venkateswara University, Tirupati-517 502, Andhra Pradesh, India

²Department of Microbiology, Palamuru University, Mahabubnagar-509001, Telangana State, India

*Corresponding Author

Abstract

The leaf biomass of *Tinospora cordifolia* was used for fluoride removal from aqueous solutions. Batch biosorption technique was applied to examine effects of pH, contact time, biosorbent dose and initial fluoride concentration. Scanning Electron Microscopy (SEM) and Fourier Transform Infra red (FTIR) techniques were used to study the surface characteristics and presence of chemical functional groups on the biosorbent. Biosorption isotherm models and kinetic models were applied to understand sorption mechanism. Results revealed that pH, contact time, biosorbent dose and initial fluoride concentration played significant effect on fluoride removal from aqueous solutions. The biosorbent developed from *Tinospora* leaf biomass was found to be a low cost and could be used for the effective removal of fluoride from synthetic as well as real water samples.

Key words: Biosorption, Contact time, fluoride, isotherms, *Tinospora cordifolia*

INTRODUCTION

Water contamination by fluoride is a major concern in many places of India as well as the world. When its concentration in drinking water is more than 1.5 mg/L, which is the maximum allowable concentration of fluoride by the World Health Organization (WHO), it can become harmful to public health causing dental or skeletal fluorosis (Fan et al. 2003, Srimurali et al. 2001). In many states of India, the problem of excessive fluoride in drinking water is particularly serious and therefore, it is most urgent to develop advanced and cost-effective technique for fluoride removal from potable water.

Various methods for defluoridation reported in literature are; adsorption (Raichur et al. 2001), chemical treatment (Reardon et al. 2000), ion exchange (Singh et al. 1999), membrane separation (Amer et al. 2001), and electrolytic defluoridation (Mameri et al. 2001), etc. Among these processes, adsorption has been reported to be an effective and economical method for removal of fluoride ions (Mohan et al. 2002). Recently, more focus has been given by the scientists in using various naturally occurring biosorbents in pollutants removal. Biosorption utilizes the ability of biological materials to accumulate pollutant ions from water by either metabolically mediated or physico-chemical pathways of uptake. Biosorption offers advantages of low cost, minimization of the quantity of chemical or biological sludge to be disposed, high efficacy in

dilute effluents, environmental friendly properties, regeneration of biosorbent, and possibility of pollutant recovery (Ahalya et al. 2003).

MATERIALS AND METHODS

Adsorbate

Fluoride stock solution was prepared by dissolving 2.21g of sodium fluoride in 1000mL distilled water in standard flask. By diluting the stock solution with distilled water, required standard solutions were prepared.

Plant Collection and Preparation of Biosorbent

Tinospora leaves were collected from Sri Venkateswara University campus, Tirupati, Andhra Pradesh state, India. These were washed several times with deionised water to remove dirt and other particulate matter then cut into small pieces, sun dried for 7 days and then kept in a hot air oven at 60° till dryness. It was then powdered and sieved for getting uniform size biosorbent as shown in the Fig.1.

Analytical Instruments

pH meter (Hanna instruments) was used to determine the pH during the experiment which was previously calibrated with standard buffer solutions. Fluoride ion selective electrode (Extech fl-700, USA) was employed for the measurement of fluoride ion concentration. The method of direct potentiometry was used, where the concentration of fluoride can be measured

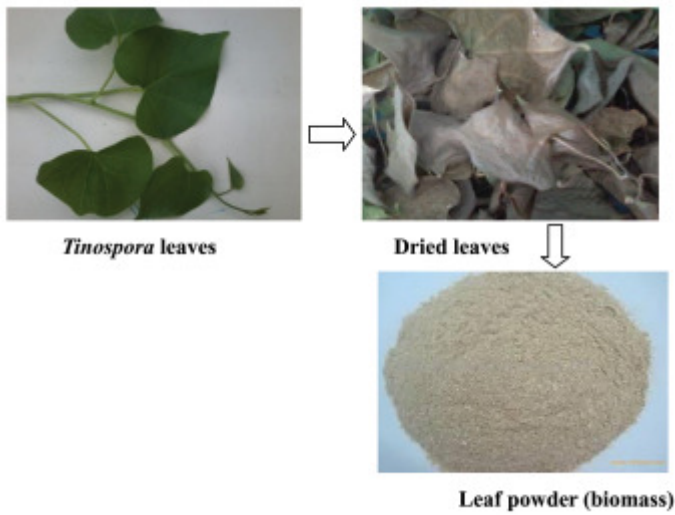


Fig. 1. Preparation of biosorbent from leaf biomass

directly. Before measurement of fluoride concentration the instrument was calibrated with freshly prepared Total Ionic Strength Adjustment Buffer (TISAB) solution.

Batch biosorption experiment

Batch experiments were carried out to determine the biosorption capacity of fluoride ions onto the leaf biosorbent in 100mL conical flask with fixed volume of fluoride solution (50mL). The flasks were kept in mini rotary shaker at a constant speed (150rpm) allowing sufficient time for biosorption equilibrium. It was assumed that the applied shaking speed allows all the surface area to come in contact with fluoride ions during the course of experiments. The study was performed at room temperature to be representative of environmentally relevant condition. The pH of the solution was measured with pH meter. The flasks were plugged and kept closed to avoid the fluctuation of pH due to the exchange of gases during the experiment. The effects of various parameters on the rate of biosorption process were observed by varying contact time, adsorbent concentration, temperature, and pH of the solution. The solution volume was kept constant. The amount of fluoride biosorbed was calculated by using following equation:

$$Q_e = \frac{(C_i - C_e)}{m} \times V \dots\dots\dots(1)$$

Where,
 Q_e is the fluoride ion concentration biosorbed at equilibrium,
 C_i and C_e are the initial and equilibrium concentrations (mg/L) of fluoride,
 m is the mass of the biosorbent (mg) and
 V is the volume of the solution (mL).
 Percentage fluoride ion removal (%) was calculated by using the following equation:

$$\text{Fluoride ion removal (\%)} = \frac{(C_i - C_e)}{C_i} \times 100$$

Where C_i and C_e are the initial and equilibrium concentrations (mg/L) of fluoride.

Biosorption Isotherm Models

Biosorption is a quantitative relationship describing the equilibrium between the concentrations of sorbate in solution (mass/volume) and its concentration (mass sorbate/mass sorbent). Biosorption isotherm relates the concentration of solute on the surface of the adsorbent to the concentration of the solute in the fluid with the sorbent in contact. These values are usually determined experimentally. In order to describe the equilibrium isotherm of biosorption process, Langmuir and Freundlich isotherm models are discussed in the present study.

Langmuir Isotherm Model

Langmuir isotherm model is based on the following assumptions:

- Each active site interacts with only one adsorbate molecule,
- Sorbate molecules are adsorbed on well localized sites,
- There is no interaction between adjacent adsorbed molecules and
- The adsorption sites are all energetically equivalent.

Langmuir isotherm is given by the following equation:

$$Q_e = \frac{KLQ_{max} C_e}{1 + KL C_e} \dots\dots\dots(3)$$

Where, Q_e is the equilibrium fluoride ion concentration on the adsorbent (mg/g), C_e is the equilibrium fluoride ion concentration in the solution (mg/g), Q_{max} is the maximum biosorption capacity of adsorbent (mg/g) and K_L is the Langmuir biosorption constant (L/mg). The equation (3) can be represented by the following linear form;

$$Q_e = \frac{KL Q_{max} C_e}{1 + KL C_e} \dots\dots\dots(4)$$

The values of Langmuir constant Q_{max} and K_L were calculated from the slope and intercept of the linear plot C_e/Q_e versus C_e . The essential features of Langmuir isotherm model can be expressed by means of a separation factor of equilibrium parameter (R_L), which is calculated according to the following equation;

$$R_L = \frac{1}{1 + KL C_i} \dots\dots\dots(5)$$

The values of R_L indicate the type of biosorption isotherm to be:

- Linear ($R_L = 1$),
- Favorable ($0 < R_L < 1$),
- Unfavourable ($R_L > 1$) and
- Irreversible ($R_L = 0$).

Freundlich Isotherm Model

Freundlich isotherm model is derived from Gibbs adsorption combined with a mathematical description of the free energy of the surface. Freundlich proposed an empirical isotherm equation assuming a heterogeneous adsorption surface and active sites with different energy.

Freundlich equation is as follows:

$$Q_e = \frac{1/n}{K_f C_e} \dots\dots\dots(6)$$

Freundlich isotherm can be derived from Langmuir isotherm by assuming that there exists a distribution of sites on the adsorbent that have different affinities for different adsorbents with each site behaving according to Langmuir isotherm. Here K_f is a measure of the capacity of the adsorbent and n is a measure of how affinity for the adsorbate changes with changes in adsorption density. When $n = 1$, the Freundlich isotherm becomes linear isotherm and indicates that all sites on the adsorbent have equal affinity for the adsorbates. Values of $n > 1$ indicate the affinities decreases with increasing adsorption density.

The linear form of Freundlich isotherm equation can be as $\log Q_e = \log K_f + 1/n \log C_e \dots\dots\dots(7)$

Freundlich isotherm constants $1/n$ and K_f are calculated from the slopes and intercepts of the linear plot of $\log Q_e$ versus $\log C_e$.

RESULTS & DISCUSSION

Characterization of Biosorbent

Scanning Electron Microscopy: To understand morphology of biomass, particles were observed in Scanning Electron Microscopy with coupled Energy Dispersive Spectroscopy (EDS). The major morphological aspects of the *Tinospora* leaf biomass are shown in Fig. 2. The examination of the SEM micrographs revealed dark and grey areas indicating pores and carbon matrix respectively and showed rough surface of the adsorbent that provided large surface area for adsorption. Overall, a well-developed porous surface was observed at higher magnification, and further, randomly distributed pore size was observed in all micrographs. The grey surface area in every micrograph contained smaller microparticles (nm to μ m) which might be due to the surface functional groups of the carbon. The adsorption of fluoride might be due to the presence of pores and functional groups on the surface. SEM micrographs proved fluoride adsorption (Fig.2 a, b).

EDX elemental analysis highlighted presence of Calcium, Magnesium, and Carbon ions in pure biosorbent samples (Fig. 2 c, d). Nitrogen is also present but in lesser mass compared

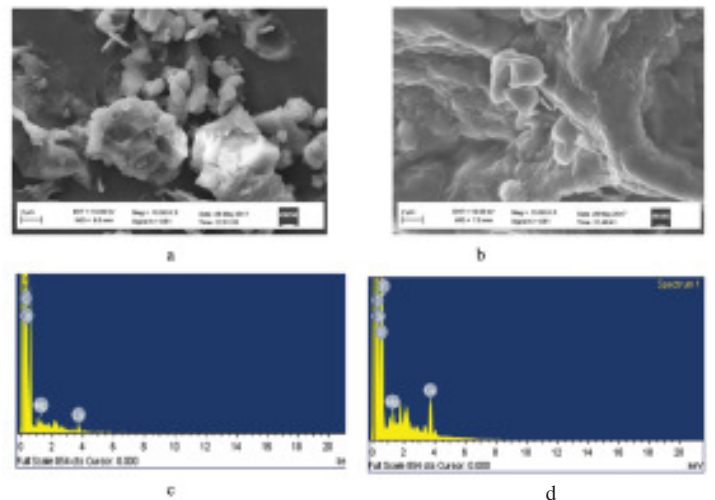


Fig. 2. SEM image of *Tinospora* leaf biomass: (a) pure (b) fluoride loaded EDX images: (c) pure and (d) fluoride loaded

to carbon and oxygen. The intensity of fluoride signals was higher in samples treated with fluoride which can clearly conclude that the oxygen element concentration has been reduced after adsorption process, but simultaneously fluoride concentration increased in the adsorbent and hence the fluoride ion may replace ion-containing oxygen atom (OH) on the surface of adsorbent.

FTIR (Fourier transform infrared) Spectroscopy

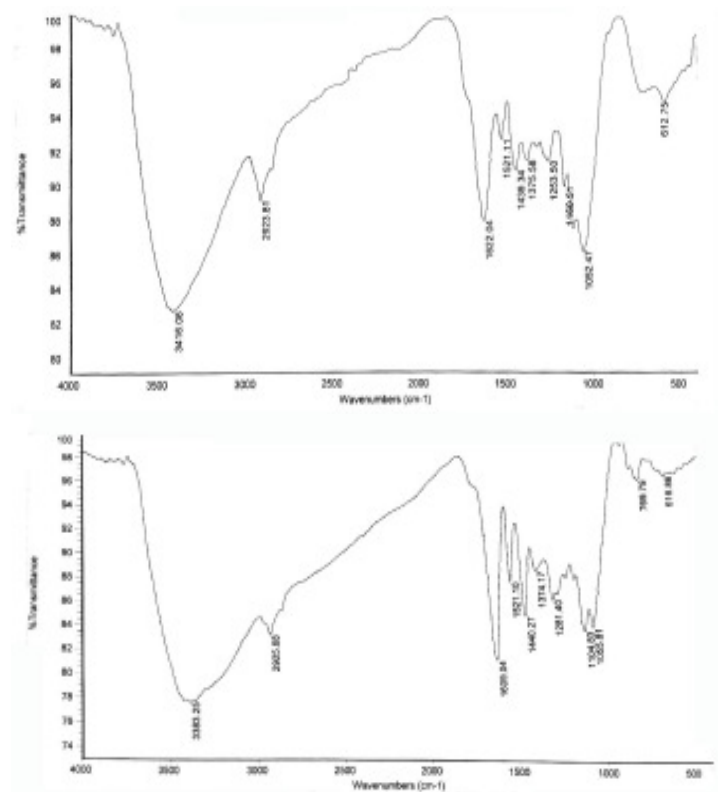


Fig. 3. FTIR Spectrum of *Tinospora* leaf biomass before and after fluoride biosorption

FT-IR analysis was used to identify the characteristic functional groups on the surface of biosorbent and the spectra of biosorbent is shown in Fig.3. In order to determine the characteristic functional groups responsible for biosorption of fluoride ions by leaf biomass, FTIR spectroscopy was utilized as a powerful tool. Biosorption of fluoride has resulted in several changes such as the disappearance of some bands, shifts and decrease in the percentage of transmittance in the IR spectra of the solid surface in the range 4000–500 cm^{-1} . Interpretations of the spectra were based on the information acquired from literature.

Very strong broad band at the region of 3416 cm^{-1} is the overlapping peak of NH group stretching vibration. The peak at 2923.81 cm^{-1} may be due to presence of alkane group. The strong band at 1622.04 cm^{-1} may be due to C=C and 1521.11 cm^{-1} stretching indicates nitro group. 1439.34 cm^{-1} peak is due to involvement of double bond structures such as C=C or C=O groups and peak at 1253.50 cm^{-1} is attributed to carbonyl group. The band observed at 1160.51 cm^{-1} was assigned to C-F and 612.75 cm^{-1} peak may indicate presence of alkyl halide. Thus, leaf biomass contains carboxyl, aliphatic ether and amine groups on its surface as important sorption sites. The peaks were shifted from 3416.06 cm^{-1} to 3707 cm^{-1} indicated NH group replaced with OH group. 2923.81 shifted to 3030.27 indicated alkane group replaced with alcoholic compounds. 1253.50 peak reduced to 1247.99 indicated carbonyl group replaced with amines. Shift of peak from 612.75 to 659 cm^{-1} indicated replacement of halides. Consequently, new bands appear at 3707.0, and 3890 cm^{-1} after fluoride biosorption may indicate the presence of alcohol stretching modes.

EXPERIMENTAL RESULTS

Effect of pH

As pH of the system controls biosorption capacity through its influence on the surface properties of the adsorbent and species of sorbate in solution, the effect of pH on adsorption of fluoride was studied in the pH range of 2.5–10.5 and results are depicted in Table 1.

Table.1 Effect of pH on fluoride removal

pH	Removal efficiency %
2.5	40
4.5	62
6.5	86
8.5	64
10.5	60

The best sorption and fluoride uptake capacity both occurred at pH 6.5 and biosorption capacities declined at both acidic and alkaline conditions, particularly in the former. The reduction in acidic conditions may be attributed to the formation of weak hydrofluoric acid whereas it may be due to the competition of excess hydroxyl ions with fluoride ions under alkaline conditions (Jagtap et al. 2009).

Effect of biosorbent dose

Biosorption efficiency of fluoride ion was studied by varying the amount of biosorbent dosages from 50 to 350mg while keeping other parameters (pH and contact time) constant. The influences of adsorbent dose on fluoride adsorption are shown in Table 2.

Table 2. Effect of biosorbent dose on fluoride removal

Biosorbent dose	Removal efficiency %
50	22
100	36
150	42
200	56
250	66
300	80
350	72

The fluoride removal increases with an increase in the dosage of *Tinospora* leaf biomass, which is obvious because of the increase in the number of active sites. With the increase dose from 50 to 300mg, fluoride removal increased from 22% to 80% but decreased (72%) at 350 mg. Hence, in all the subsequent experiments, 300 mg was fixed as the optimum dose for reasonably good removal of fluoride.

Effect of Contact Time

Fluoride removal increased with an increase in contact time from 15 to 75 minutes keeping other parameters such as dose of adsorbent and pH of solution constant. The results indicated that removal efficiency of fluoride increased from 16 to 88 per cent and thereafter, fluoride removal remained almost constant which indicates equilibrium (Table 3). The nature of biosorbent and available biosorption sites affect rate of fluoride biosorption. The mechanism of solute transfer to the solid includes diffusion through the fluid film around the biosorbent particle and diffusion through the pores to the internal biosorption sites. In the initial stages of fluoride biosorption, the concentration gradient between the film and the available pore sites was large, and hence the rate of fluoride biosorption was faster. The rate of fluoride biosorption decreased in the later stages probably due to the slow pore

diffusion of the solute ion into the bulk of the biosorbent (Huang et al. 2012). Thus the results illustrated that the optimum contact time for maximum removal of fluoride (88%) was 60 minutes.

Table 3. Effect of contact time on fluoride removal

Contact time	Removal efficiency %
15	16
30	44
45	66
60	88
75	84
90	82

3.2.4. Effect of initial fluoride ion concentration

The effect of initial fluoride concentration on adsorption rate was studied in the range (1-6 mg/L) at constant pH, and contact time. The percentage removal improved with increase in initial fluoride concentration (Table 4). The increasing concentration gradient acts as driving force to overcome all mass transfer resistances of the fluoride between the aqueous and solid phase, leading to an increasing uptake capacity until sorbent saturation achieved. Similar trend has been reported for fluoride removal by geomaterials (Sujana et al. 2010) and activated charcoal (Saha et al. 2010). Therefore it was evident from the results that fluoride adsorption was dependent on the initial ions concentration.

Table 4. Effect of initial fluoride ion concentration on fluoride removal

Initial fluoride concentration	Removal efficiency %
1	20
2	30
3	56.6
4	70
5	86
6	81.6

Biosorption Isotherm Models

Biosorption isotherms describe equilibrium relationships between biosorbent and sorbate and also indicate how sorbate particles are distributed between liquid and solid phases when biosorption process reaches the equilibrium (Athar et al. 2014). Equilibrium biosorption isotherms are used to describe capacity of a biomass which is characterized by certain constants whose values express the surface properties and affinity of the biomass. They describe equilibrium correlation between the sorbate concentration, mass loading, biosorbent dose and

equilibrium concentration of the sorbate. Moreover, equilibrium modeling offers useful information about studied sorption system. Sorption equilibrium isotherms the Langmuir and Freundlich isotherm models were used to describe the biosorption equilibrium of biomass. It is also helpful in comparing different biomaterials under different operating conditions.

The values of the Langmuir constants (K_L , Q_{max}) and Freundlich constants (K , n) for fluoride sorption by leaf biomass are shown below in the Table 5.

The regression coefficient for fluoride biosorption in Langmuir isotherm model (0.6737) was lesser than regression coefficient (0.6934) in Freundlich isotherm. Freundlich equation therefore, better represents experiment isotherm data (Fig. 3). The maximum adsorption capacity (Q_{max}) = 0.52 for complete monolayer coverage, and $K_L=1.91$ indicated that particle radius

Table 5. Langmuir and Freundlich parameters of fluoride removal by leaf biomass.

Bio-sorbent	Pollutant	Langmuir values			Freundlich values		
		Q_{max}	K_L	R^2	$n=1/m$	K_f	R^2
Leaf Biomass	Fluoride	0.52	1.91	0.6737	0.6048	1	0.6934

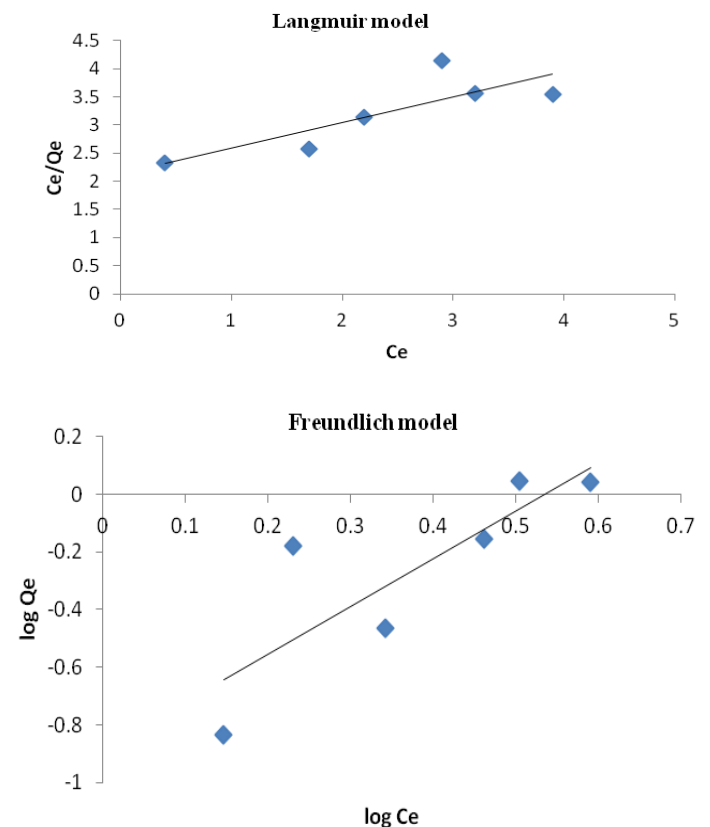


Fig. 3. Langmuir and Freundlich models for leaf biomass

of adsorbent was somewhat large towards adsorption. Overall Langmuir parameters revealed that fluoride adsorption on leaf biomass was unfavorable whereas Freundlich isotherm parameters revealed multilayer biosorption on heterogeneous surface and interactions between the sorbate ions. The adsorption capacity and other parameters were calculated from Freundlich equation and presented in Table 5. K_f is the Freundlich constant that shows adsorption capacity on heterogeneous sites with non-uniform distribution of energy level and n value shows intensity between sorbate and biosorbent. The calculated values of n (shown in Table 5) prove that the adsorption of fluoride ions using leaf biomass was showing little bit favourable as the value lies between 1 and 10.

3.4. Kinetic Study of Biosorption

In the present work, pseudo-first-order model and pseudo second-order model were discussed to study the rate and kinetics of biosorption of the fluoride ion onto the *Tinospora* leaf biomass. The kinetics of biosorption describe solute uptake rate, which in turn governs residence time of biosorption reaction.

3.4.1. Pseudo-First-Order Model

For biosorption of the fluoride ion on the leaf biomass, linear plot of $\log(q_e - qt)$ vs. t at different contact times for the extent of removal of the fluoride ion from water is applied to confirm the applicability of pseudo-first-order model.

The pseudo-first order equation is $\log(q_e - qt) = \log q_e - k_1 t$ 2.303.

It was found that the plot of $\log(q_e - qt)$ vs. t obtained a linear relationship from which values of the k_1 and q_e could be determined from the slope and intercept of the plot, respectively (Fig. 4).

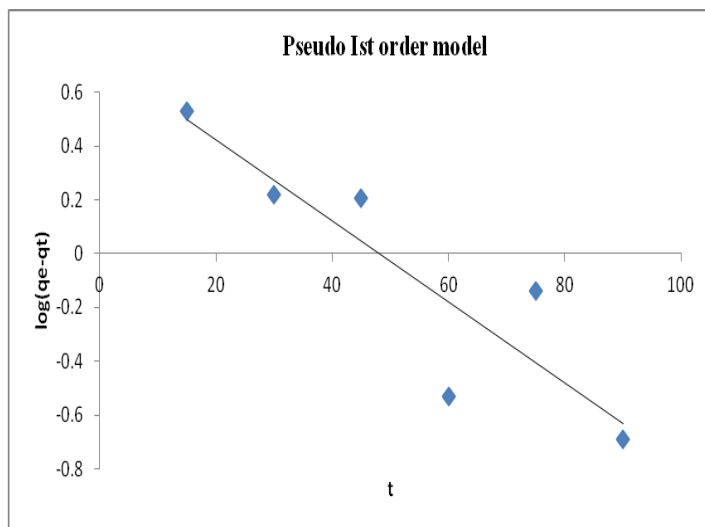


Fig.4. Pseudo first order model for *Tinospora* leaf biomass

3.4.2. Pseudo-second-order model

For biosorption of fluoride ion on the leaf biomass, linear plot of (t/qt) vs. t at different contact times for the extent of removal of the fluoride ion from water is applied to confirm the applicability of pseudo second order model.

The pseudo-first-order equation is $t/qt = 1/k_2 q_e^2 - (1/q_e)t$

The plot of (t/qt) vs. t obtained a linear relationship from which the values of the k_2 and q_e could be determined from the intercept and slope of the plot respectively (Fig. 5).

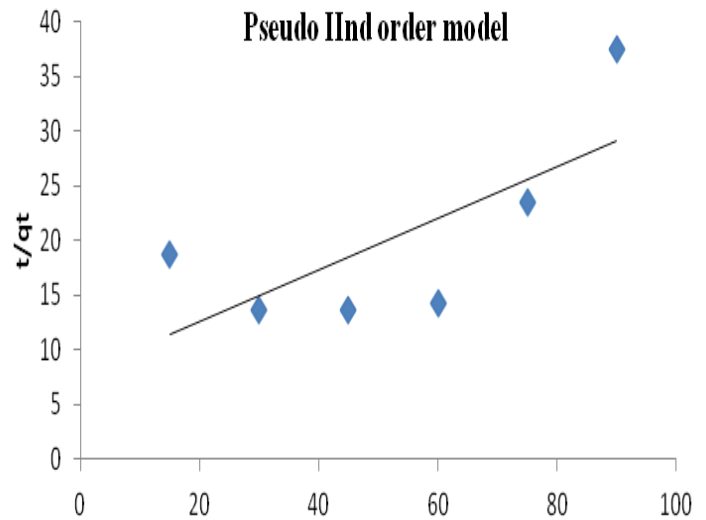


Fig. 5. Pseudo second order model for *Tinospora* leaf biomass

Table 6. Pseudo first and second order kinetic parameters.

Pseudo-first order model			Pseudo-second order model		
k_1 (min- 1)	q_e , cal. (mg g- 1)	R^2	k_2 (gmg- 1 min- 1)	q_e , cal. (mg g- 1)	R^2
0.307	0.8	0.799	0.04	0.54	0.5057

From Table 6, it was found that there is an agreement between experimental and calculated q_e values for the pseudo first-order model. Hence, the pseudo first-order model better represents the sorption kinetics.

Application to Real Water Samples: The developed procedure was used to remove the fluoride ions from real field water samples (Table 7). Groundwater samples were collected from the fluoride affected villages of Mahabubnagar district of Telangana state where the groundwater crossed fluoride limit as prescribed by World Health Organisation (WHO). To the volume of 50mL of groundwater samples, which were previously analysed for fluoride concentration,

Table 7. Application of developed biosorbent in real field water samples.

Sampling Station	Fluoride	Bio-sorbent	Residual	Bio-sorbed	Removal efficiency
Zamisthapur	1.91	300 mg	0.92	0.98	51.5
R R Gudem	1.65	300 mg	0.85	0.80	48.4
Oblaipally	1.63	300 mg	0.80	0.83	50.9
Narsapur	1.81	300 mg	1.23	0.58	32.0
Oblaipally Thanda	1.7	300 mg	1.03	0.67	39.4

300mg of leaf biomass was added and after adjusting pH to 6.5, mixture was kept in mini orbital shaker at 150rpm for 60 minutes. Estimated fluoride removal efficiency of biosorbent ranged between 32-51%.

CONCLUSION

In this study, a novel biosorbent was prepared using *Tinospora* leaf biomass was examined for its potential in removing fluoride from drinking water. The maximum biosorption of fluoride was achieved at pH 6.5. Experimental equilibrium data well fitted to the Langmuir isotherm indicating monolayer biosorption on a homogenous surface. Thermodynamic parameters reveal that sorption of fluoride is spontaneous and endothermic in nature. Modeling of biosorption kinetics showed agreement of experimental data with the pseudo-second order kinetic model. *Tinospora* biomass has also shown encouraging results with groundwater samples collected from endemic fluoride areas of Mahabubnagar district, Telangana state. It was found that *Tinosopra* leaf biomass could be an alternative biosorbent for defluoridation of water from real water samples to below the WHO recommended value.

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