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KINETIC AND THERMODYNAMIC STUDIES ON FLUORIDE BIOSORPTION BY DEVDARU (*POLYALTHIA LONGIFOLIA*) LEAF POWDER

Ranjan K. Bharali^{a*} and Krishna G Bhattacharyya^b

a, b. Department of Chemistry, Gauhati University, Guwahati 781014, Assam, India

* Corresponding author's Email: rbharali84@gmail.com

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Abstract: Devdaru (*Polyalthia longifolia*) leaf powder, DLP, prepared from mature, dried *Polyalthia longifolia* (Devdaru) leaves was used as biosorbent for removal of fluoride from aqueous solutions using the batch adsorption process. The biosorbent was first characterized with respect to surface area, surface functional groups by FTIR, cation and anion exchange capacities, surface topography by SEM technique and then effects of pH, agitation time and fluoride concentration, adsorbent amount and temperature on adsorption of fluoride were investigated to determine optimum adsorption properties. The biosorbent was found to be effective around pH 7.0 and the maximum fluoride removal capacity of this adsorbent was about 77 % at 303 K. Kinetic study showed that the fluoride sorption on DLP was predominantly chemical in nature and its mechanism was a complex one involving both surface adsorption and intra-particle diffusion. Thermodynamic study showed that sorption process was exothermic in nature and was found to be favourable at lower temperature. The results showed that the biosorbent, DLP may be used as cost-effective adsorbent for treating fluoride bearing water.

Keywords: Fluoride biosorption, Kinetic study, Thermodynamic study.

Postal Address: Department of Chemistry, Gauhati University, Guwahati 781014.

INTRODUCTION

Fluoride in drinking water has been considered as an essential micro-nutrient for human body and as a micro-nutrient, a small amount of fluoride is essential for production and maintenance of healthy bond and teeth (Srimurali *et al.*, 1998; Rahmani Boldaji *et al.*, 2009). For optimal dental health, the World Health Organization recommends a level of fluoride from 0.5 to 1.5 mg/L as the permissible limit of fluoride concentration in drinking water (WHO, 1984). At high concentrations (above the permissible level), fluoride become toxic and can give rise to dental and skeletal fluorosis in human body (Kumar *et al.*, 2008; Karthikeyan *et al.*, 2011). Therefore, defluoridation of drinking water is now becoming an important practice through out the world. Several adsorbent materials including activated alumina (Wu and Nitya, 1979), bauxite (Sujana and Anand, 2011), zeolites (Mayadevi, 1996), charcoals (Bhargava and Killedar, 1991), magnesia-loaded fly ash cenospheres (Xu *et al.*, 2011), KMnO₄-modified activated carbon (Daifullah *et al.*, 2007), kanuma mud (Chen *et al.*, 2011.), fishbone charcoal (Bhargava and Killedar, 1993) and many more have been studied and reported for fluoride removal from water. In this work, Devdaru (*Polyalthia longifolia*) leaf powder (DLP) developed from the mature leaves of *Polyalthia longifolia* tree was used as biosorbent for removal of fluoride from water.

EXPERIMENTAL

Preparation of the biosorbent: The biosorbent, DLP was prepared from mature leaves of Devdaru (*Polyalthia longifolia*) tree by initial cleaning of dust particles with water, drying in the Sun for 4–5 days, grinding the dry leaves into a fine powder using a mechanical grinder, sieving and fractionating the powder into 74 – 105 μm particle fractions, again washing the powder with distilled water to remove all the coloured pigments and then re-drying in an air oven at room temperature as like Neem leaf powder (Bhattacharyya and Sharma, 2004).

Chemicals and reagents: Chemicals used in this work, including NaF, SPADNS, Zirconyloxy chloride, Copper (II) chloride, Ethylene diamine, NaOH, HCl were of analytical grade. A stock solution of adsorbate (NaF) was prepared by dissolving 0.221 g of NaF in 1.0 L of distilled water (F concentration, 100 mg/L), which was further diluted to required concentration during the experiments.

Adsorption experiments with DLP: In the present work, fluoride adsorption experiment was carried out in 100 mL polypropylene conical flasks by mixing a pre-weighed amount of the DLP with 50 mL of the aqueous NaF solution of particular concentration and then agitating the mixture for a pre-determined time interval in a thermo-stated water bath shaker at a constant speed. After adsorption was over, the mixture was filtered off and the fluoride remaining unadsorbed was estimated spectrophotometrically by SPADNS method (APHA, 1998), using a spectrophotometer (Shimadzu Spectrophotometer, UV-1800) with SPADNS reagent at $\lambda_{\text{max}} = 570 \text{ nm}$. Effects of pH on fluoride sorption was studied in the pH range of 2.0 to 11.0 with a biosorbent amount of 3.0 g/L, fluoride concentration, 3.0 mg/L and contact time of 180 min at 303 K. The pH of the fluoride solutions were adjusted by adding 0.1 M ($\text{M} = \text{mol/dm}^3$) HCl and 0.1 M NaOH solutions and was measured using a pH meter (Systronics, Digital pH meter 335). Effect of contact time (min) and the sorption kinetics were determined by analyzing uptake of the fluoride by constant amount of adsorbent (3 g/L) at 303 K at different time intervals of 5, 10, 20, 30, 45, 60, 90, 120, 180 and 240 min. The amount adsorbed per unit mass of the adsorbent (q_t) at time t was calculated using the following mass-balance equations:

$$q_t (\text{mg/g}) = (C_o - C_t)/m \quad (1)$$

$$\text{Extent of adsorption (\%)} = [(C_o - C_t)/C_o] \times 100 \quad (2)$$

Where, C_o and C_t were initial ($t = 0$) and final ($t = t$) fluoride concentrations in mg/L when the adsorption was carried out for a time interval of t min. with an adsorbent amount of m g/L.

RESULTS AND DISCUSSION

Characterization of the biosorbent

The specific surface area of DLP was determined by Methylene blue adsorption method (Pham and Brindley, 1970) and was found to be $24.4 \text{ m}^2\text{g}^{-1}$, which was higher than that of a number of plant-based adsorbents (Boonamnuyvitaya et al., 2004), e.g. coffee residue ($2.57 \text{ m}^2\text{g}^{-1}$), pyrolyzed coffee residue ($3.91 \text{ m}^2\text{g}^{-1}$), coffee residue bound on clay ($6.48 \text{ m}^2\text{g}^{-1}$). FTIR spectra DLP before (A) and after (B) fluoride sorption are presented in Figure 1 and the functional groups identified from the spectrum are -OH (3437.2 cm^{-1}), -CH₃ (2927.9 & 2862.4 cm^{-1}), -C≡N (2364.7 cm^{-1}), -C≡C- (2337.7 cm^{-1}), C-C, C-N<, C-O- ($1064 - 1257.6 \text{ cm}^{-1}$), >C=O (1647.2 cm^{-1}), >C=C< (1735.9 cm^{-1}), C-C, C-N< & C-O- ($1060.8 - 1257.6 \text{ cm}^{-1}$), >C=S (1114.8 cm^{-1}), C-X (675.1 cm^{-1}). Comparison of FTIR spectra of DLP (Figure 1) before (A) and after fluoride adsorption (B) showed that the -OH band shifted from 3437.2 to 3452.6 cm^{-1} and the -C≡N band shifted from 2357 to 2372.4 cm^{-1} after fluoride adsorption. The peak at 1064.7 cm^{-1} , due to stretching vibration of C-OH group of carboxylic acid also shifted to 1037.7 cm^{-1} due to interaction with fluoride (Mondal et al., 2012).

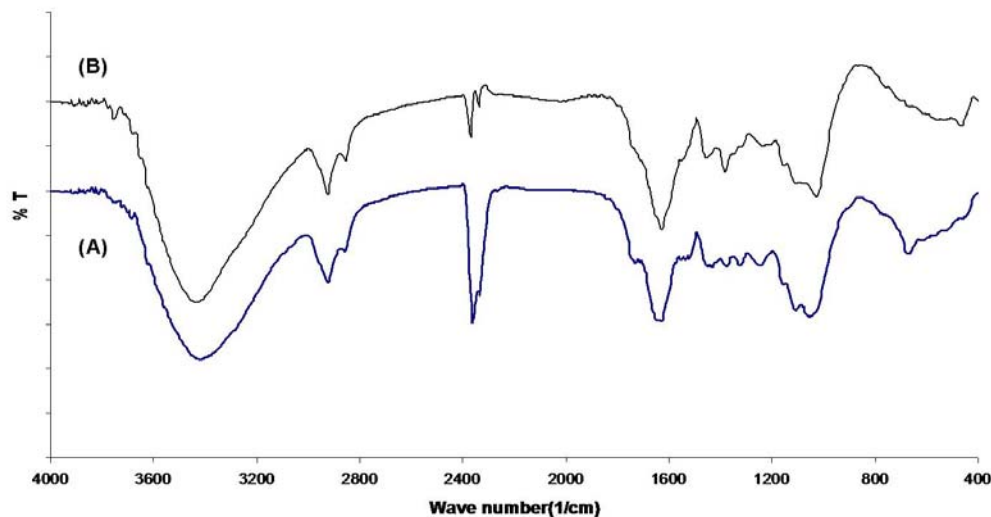


Figure 1. FTIR spectrum of Devdaru leaf powder before (A) and after (B) fluoride sorption

The presence of polar groups on the DLP surface is likely to give considerable cation and anion exchange capacity (CEC and AEC) to DLP. The CEC values for DLP was determined by Cu (II) bisethylene-diamine complex method (Bergaya and Vayer, 1997) and was found to be 0.736 meq/100 g, whereas, the anion exchange capacity (AEC) of DLP was found to be 1.5 meq/g, which was determined by using conductometric method (Anirudhan and Jalajamony, 2010). The SEM micrographs of DLP particles before (DLP-1) and after fluoride sorption (DLP-2) are shown in Figure 2. The SEM images (Model, JEOL JSM-6360) before adsorption show that the DLP consists of particles of different shapes and sizes. The surfaces of the particles are irregular and contain a number of heterogeneous holes and small openings with wavy and highly broken edges. These may have resulted in higher surface area and consequently, higher adsorption capacity. After fluoride adsorption, a change in surface morphologies of these two DLP samples is observed, probably due to fluoride sorption. During fluoride adsorption, the DLP surface is somewhat swollen and size of the pores become somewhat larger. The change in the surface morphologies further revealed that the process of fluoride sorption on DLP was predominantly a surface phenomenon.

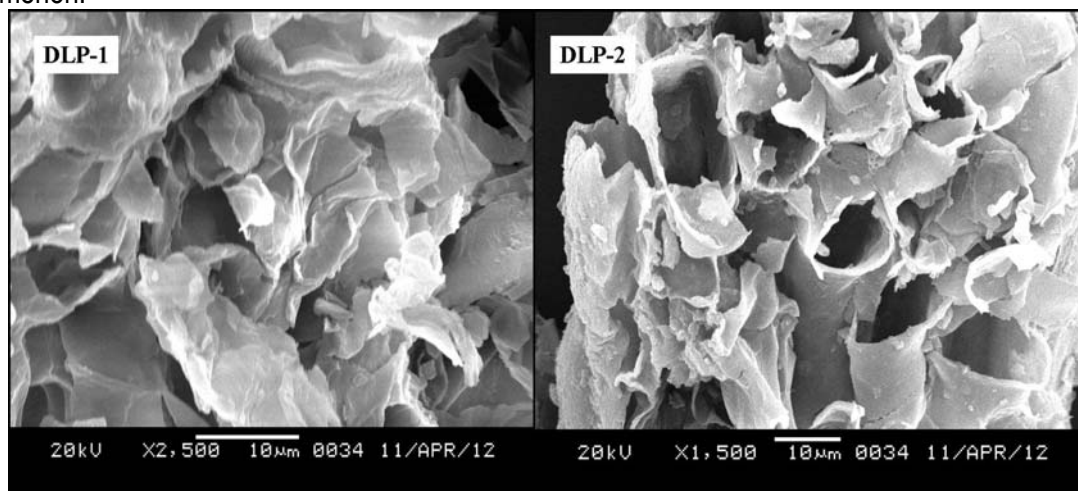


Figure 2. SEM images of the surface of a single big DLP particle before (DLP-1) and after fluoride adsorption (DLP-2)

Effects of pH

The effect of pH on adsorption of fluoride by DLP is presented in Figure 3.

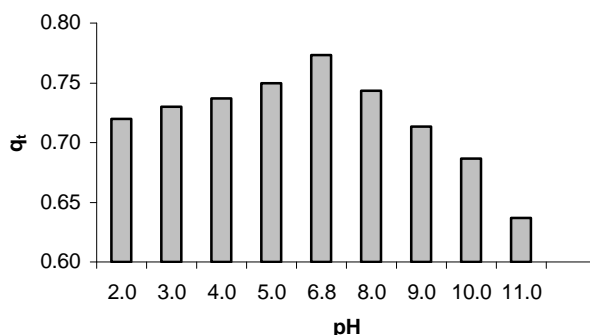


Figure 3. Effects of pH on fluoride sorption by DLP at 303 K (fluoride 3 mg/L, contact time 180 min, DLP 3 g/L)

It was observed that the amount of fluoride adsorption (q_t) gradually increased with pH up to 6.8 (maximum adsorption was found to be 77.3 %), then decreased gradually above pH 7. The decrease in adsorption of fluoride in the acidic pH range may be due to the formation of weak hydrofluoric acid, whereas in the alkaline pH range, the decrease in adsorption may be attributed to the competition of the hydroxyl ions with the fluoride ions for adsorption (Karthikeyan et al., 2011). Since, above 77 % adsorption was achieved at the natural pH of 6.8 of aqueous NaF solution, therefore, subsequent experiments were carried out without pH adjustment.

Effect of contact time and initial fluoride concentration

Effect of contact time on adsorption of fluoride on DLP at 303 K (Figure 4) showed that the fluoride adsorption process was fast, up to 60 min, and then it became slow with attainment of equilibrium at 180 min (for all the five concentrations). The first rapid stage in which 60 – 75 % adsorption was achieved in 60 min, may be due to the initial accumulation of fluoride at the DLP surface, as the relatively large surface area was utilized at the initial stage (Alagumuthu et al., 2011).

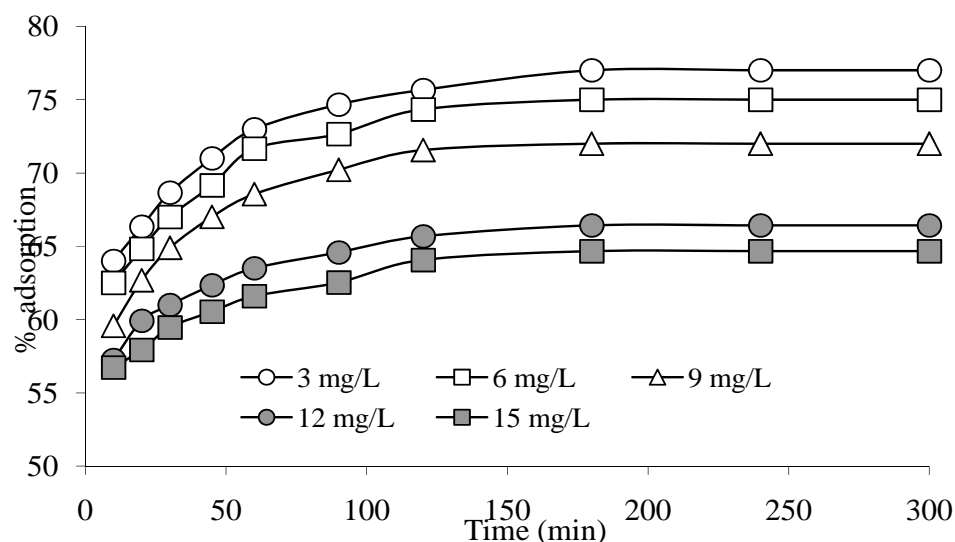


Figure 4. Effect of contact time on fluoride adsorption by DLP at 303 K (DLP 3 g/L)

With the increasing occupation of surface binding sites by fluoride ions, the adsorption process slowed down. The second stage was due to the penetration of fluoride ions to the inner active sites of the

adsorbent. Similar observation was reported earlier for adsorption of fluoride on Kunuma mud (Chen et al., 2011). Since equilibrium time for fluoride adsorption on DLP was found to be 180 minutes, therefore this time interval was maintained constant for all the other sets of studies. From Figure 4, it was also observed that the extent of adsorption (%) gradually decreased with increasing initial fluoride concentrations from 3 mg/l to 15 mg/l for a fixed adsorbent dose of 3 g/l at 303 K. This might be due to the fact that for a constant adsorbent dose, total available adsorption sites were limited and hence, there would be stiff competition among the fluoride ions for the adsorption sites resulting in decrease in fluoride adsorption (Bhargava and Killedar, 1993).

Effect of adsorbent dose: For a fixed fluoride concentration of 3 mg/L, a gradual increase in adsorption was observed (Figure 5) with increasing adsorbent amount from 1.0 to 5.0 g/L for a constant agitation time of 180 minutes at 303 K. This may be due to increased surface area of the adsorbent with increasing amount of the adsorbent (Srimurali et al., 1998).

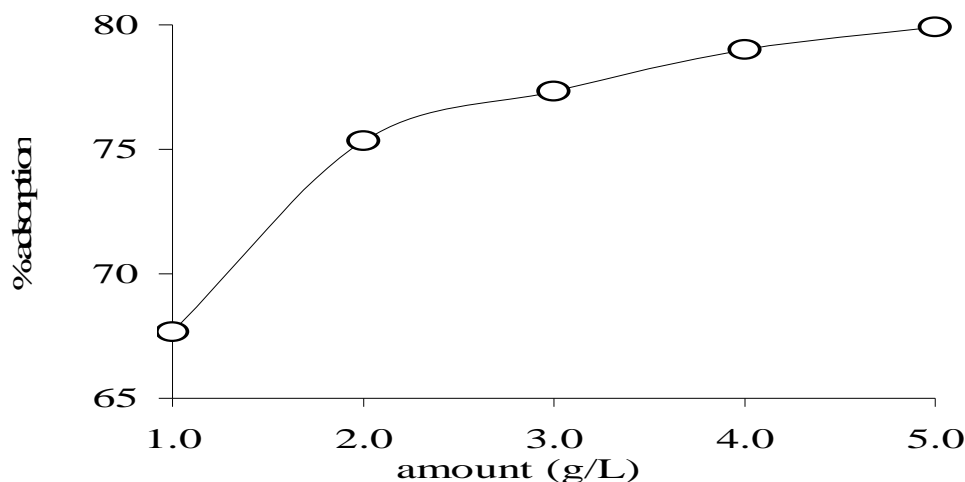


Figure 5. Effects of adsorbent amounts on fluoride adsorption by DLP at 303 K

It was further observed that the fluoride adsorption was rapid and significant up to adsorbent amount of 3.0 g/L, and then became somewhat slow. Therefore, the amount 3.0 g/L was considered as the optimum adsorbent amount for the studied DLP-fluoride sorption.

Kinetic Study

Kinetic study on sorption process is significant as it provides valuable information about the reaction pathways and the mechanism of sorption interactions. Besides, it describes the solute uptake rate which controls the residence time of sorbates at the solid–solution interface. Several kinetic models may be used to explain the mechanism of the adsorption processes, which are mainly of two types, namely reaction-based (e.g. Pseudo first and second order models) and diffusion- based models (e.g. intraparticle diffusion model) (Ho et al., 2000). In the present work, to under stand the mechanism of fluoride sorption process on DLP, the intraparticle diffusion model and the Elovich model were used. When the intra-particle diffusion process controls the rate of adsorption or when adsorption takes place inside the pores by a diffusion mechanism, the intra particle diffusion model is applied and the intra-particle diffusion rate constant (k_i) is given by the equation (Weber and Morris, 1963):

$$q_t = k_i t^{0.5} \quad (3)$$

Where, k_i is the intra-particle diffusion rate coefficient.

The Weber–Morris plots, obtained by plotting q_t versus the square root of time ($t^{0.5}$) for DLP-fluoride sorption system are given in Figure 6. The plots in the present case yield a reasonably high mean rate

coefficient, k_i of $2.09 \times 10^{-2} \text{ mg/g/min}^{1/2}$ and also good linearity (mean regression coefficient = 0.91). However, if the intra particle diffusion is the sole rate determining step, the plots should not only be linear, they should also pass through the origin (Ozcan and Ozcan, 2005). Although, the plots in the present case have good linearity, the plots do not have zero intercept as required by the theoretical considerations. Instead, the intercepts are quite large, ranging from 0.64 to 2.81 (Table 1). This indicated that the mechanism for fluoride adsorption by DLP powder was a complex one. The results further indicated that and the rate of fluoride adsorption on DLP, was not solely controlled by pore diffusion and both surface adsorption as well as intra-particle diffusion could have contributed to the rate determining step (Mahramanlioglu et al., 2002). The increase in the pore diffusion rate constant, k_i , with increasing fluoride concentration further indicated a higher pore sorption possibility of fluoride onto the adsorbent at room temperature (Alagumuthu et al., 2011). The kinetic parameters, obtained from the plots are given in Table 1. Similar results have been reported for adsorption of fluoride on thermally activated Neem and Kikar leaves carbon (Kumar et al., 2008) and Moringa Indica based activated carbon (Karthikeyan and Ilango, 2007).

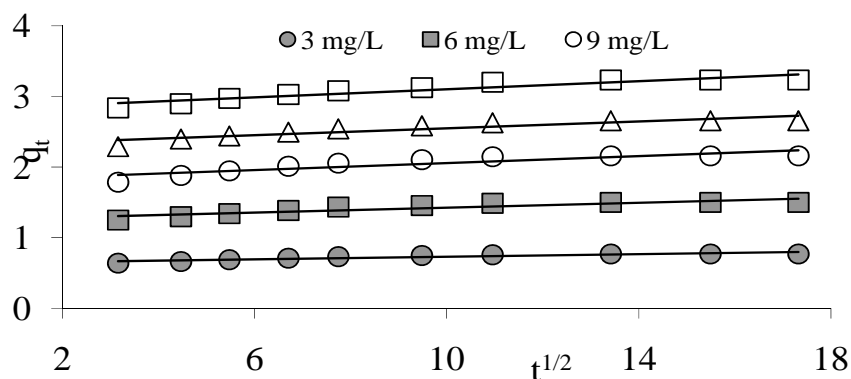


Figure 6. Intra-particle diffusion plots for adsorption of fluoride on DLP at 303 K (DLP, 3 g/L, fluoride 3.0-15.0 mg/L)

The adsorption data may also be analyzed using the Elovich equation. The simplified form of Elovich equation has the form (Ho and McKay, 2002),

$$q_t = \beta \ln(\alpha\beta) + \beta \ln(t) \quad (4)$$

Where, α is the initial sorption rate constant and β is the desorption rate constant. The constants can be obtained from the slope and the intercept of the plot of q_t versus $\ln(t)$. A plot of q_t against $\ln(t)$ is linear when the Elovich equation is obeyed.

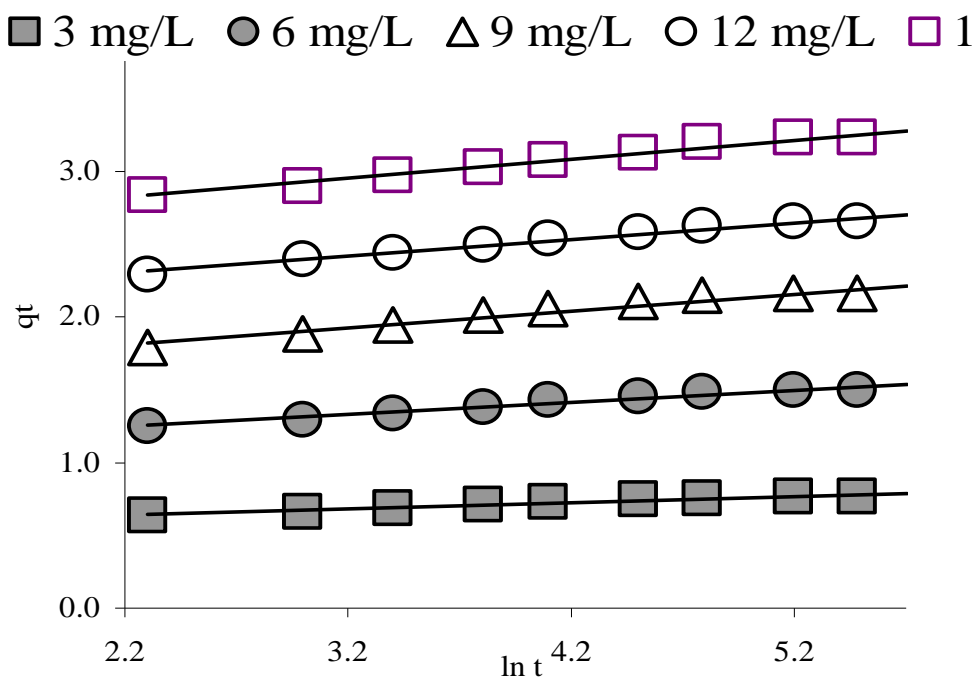


Figure 7. Elovich plots for fluoride adsorption on DLP at 303 K (DLP 3g/L, fluoride 3.0-15.0 mg/L)

Table 1. Kinetic parameters for sorption of Fluoride on DLP at 303 K

Kinetics	Parameters	Fluoride (mg/L)					Mean
		3	6	9	12	15	
Intra-particle diffusion	$k_i \times 10^{-2} \text{ mg/g/min}^{0.5}$	0.91	1.74	2.48	2.43	2.87	2.09
	R	0.92	0.91	0.89	0.92	0.94	0.91
	Intercept	0.64	1.25	1.81	2.31	2.81	1.76
Elovich Model	R	0.98	0.97	0.97	0.98	0.99	0.98
	$\beta \text{ (mg g}^{-1} \text{ min}^{-1})$	0.04	0.08	0.12	0.11	0.13	0.10
	$\alpha \times 10^7 \text{ (g mg}^{-1} \text{ min}^2)$	1.2	0.7	0.6	86.9	221.2	62.1

In the present work, kinetics of adsorption of fluoride on DLP was also found to be followed the Elovich equation with the linear plots (mean r of 0.98) of q_t versus $\ln t$ (Figure 7). The Elovich equation does not predict any definite mechanism, but it is useful in describing adsorption on highly heterogeneous adsorbents similar to the DLP. Applicability of the Elovich equation shows the fluoride adsorption on DLP to be predominantly chemical in nature (Bhattacharyya and Sharma, 2004). The success of the Elovich model further supports the application of second order kinetics to adsorption of fluoride on DLP surface. The Elovich constants computed from the plots are given in Table 1.

Effects of temperature and thermodynamic study

The temperature has a significant influence in the sorption process and hence, in the present study, the sorption of fluoride on DLP was monitored at five different temperatures, viz., 298, 303, 308, 313 and 318 K. It was found that the extent of adsorption of fluoride on DLP decreased with increase of temperature from 298 K to 318 K (Figure 8) which might be attributed to the weakening of adsorptive forces between fluoride ions and the DLP surface (Murugan and Subramanian, 2006).

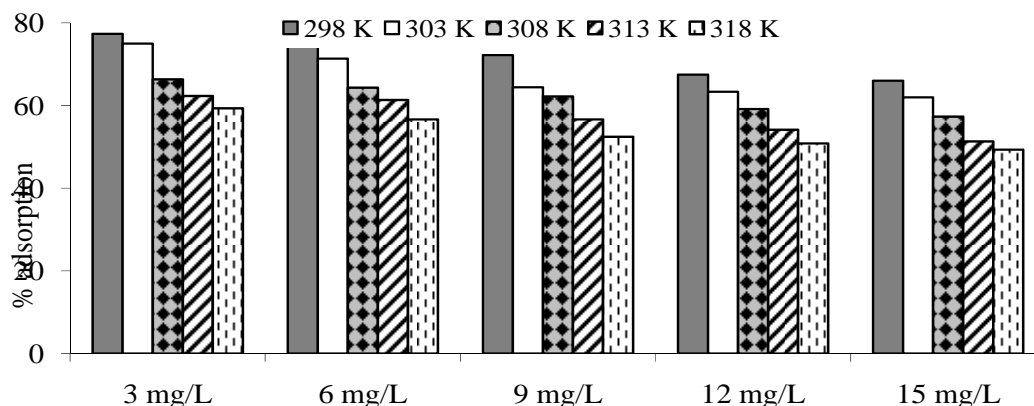


Figure 8. Effects of temperature on fluoride sorption by DLP (DLP 3.0 g/L, fluoride 3.0-15.0 mg/L, time 180 min)

The important thermodynamic parameters viz., entropy (S), enthalpy (H) and Gibbs energy (G) for the adsorption process can be obtained from the following two fundamental relationships:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

$$\Delta G^0 = -2.303 RT \log K \quad (6)$$

Where, ΔG^0 , ΔH^0 and ΔS^0 represent standard Gibbs energy change, standard enthalpy change and standard entropy change for the adsorption process respectively, and K is the equilibrium constant for the adsorbate-adsorbent equilibrium. The classic van't Hoff equation is given by,

$$\log (q_e/C_e) = \Delta S / (2.303R) - \Delta H / (2.303 RT) \quad (7)$$

Where the ratio q_e/C_e is called the adsorption affinity.

The van't Hoff plots of $\log (q_e/C_e)$ versus $1/T$ (Figure 9) were used to compute the thermodynamic parameters, viz., the enthalpy change, ΔH , entropy change, ΔS and Gibbs energy change, ΔG and the values are presented in Table 2.

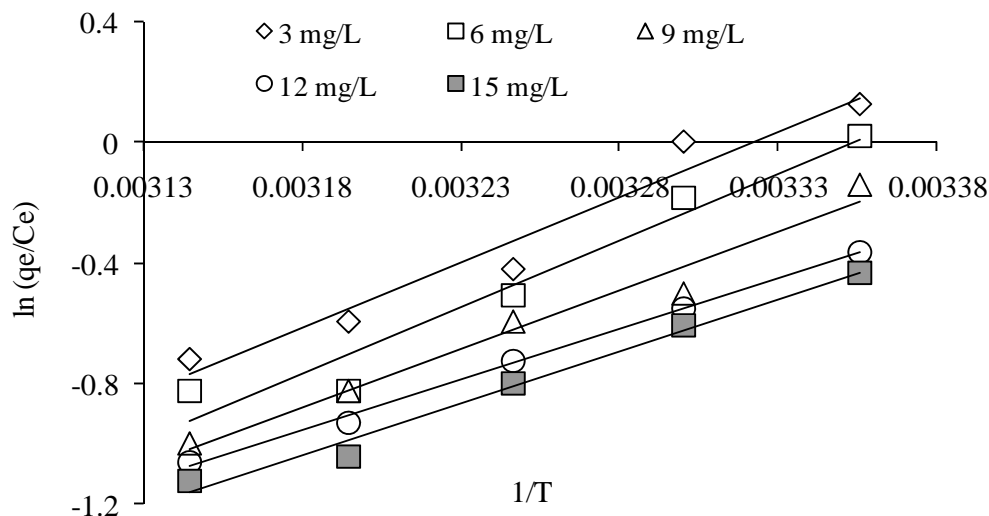


Figure 9. The van't Hoff plots for fluoride sorption on DLP (DLP 3.0 g/L, fluoride 3.0-15.0 mg/L, time 180 min)

It was found that ΔH varied from -83.4 to -64.4 kJ mol $^{-1}$ while the entropy change, ΔS , varied from -0.28 to -0.23 J K $^{-1}$ mol $^{-1}$ in the temperature range of 298 – 318 K at fluoride concentrations of 3.0 – 15.0 mg/L. These negative values of enthalpy are in conformity with the exothermic nature of the adsorption process, while the negative value of entropy suggested a higher degree of ordering of the fluoride ions on the solid phase compared to their ordering in the solution phase (Murugan and Subramanian, 2006). The ΔG values were both negative and positive. Xu et al., 2011 reported similar results with negative and positive values of ΔG for adsorption of fluoride on magnesia-loaded fly ash cenospheres.

Table 2. Values of thermodynamic parameters for adsorption of fluoride on DLP

C ₀ (mg/L)	ΔH (kJ/mol)	ΔS (J/K/mol)	ΔG (kJ/mol)				
			298 K	303 K	308 K	313 K	318 K
3	-83.4	-0.28	-0.83	0.55	1.94	3.04	4.71
6	-85.1	-0.29	-0.05	1.38	2.80	4.23	5.66
9	-74.2	-0.25	1.14	2.40	3.67	4.93	6.19
12	-64.4	-0.22	2.10	3.21	4.33	5.44	6.56
15	-66.0	-0.23	2.48	3.62	4.77	5.92	7.07

It was further observed that the negative values of ΔG were found only for the lower temperatures and lower fluoride concentrations. However, the ΔG values became positive with increasing temperature and fluoride concentration. This indicated that the adsorption process was favorable and feasible at lower temperature or normal temperature (298 - 303 K) and at lower fluoride concentration (3.0 – 6.0 mg/L). Thus, DLP may suitably be used in practical situation (at room temperature) to reduce water pollution caused by fluoride.

CONCLUSION

From the above experimental investigations, it was observed that fluoride can be removed from aqueous solutions effectively by adsorption process using Devdaru (*Polyalthia longifolia*) leaf powder (DLP). In the present work, about 77.0 % of fluoride was removed from water using DLP at the natural pH of the aqueous solution. Kinetic study showed that fluoride adsorption process on DLP was a chemisorption process and intraparticle diffusion was also involved in the process although it was not the sole rate limiting step. Thermodynamic study had shown that fluoride sorption by DLP was exothermic and the process was found to be favourable at lower temperature. Therefore, Devdaru leaf powder (DLP) may suitably be used as cost effective biosorbent to treat fluoride bearing water especially in rural areas.

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CONFLICT OF INTEREST : Nothing